Development of Newer Catalytic Systems and Protocols for a few Important Catalysts and Inorganic Reagents based on Cobalt(II and III), Copper(II), Chromium(VI), Vanadium(IV and V) and Tribromide(Br_3^-)

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by

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Dedicated

to my

Grandfather

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CH 610	Organometallics
CH 621	Newer Reagents in Organic Chemistry
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It is certified that the work contained in the thesis entitled "**Development of Newer Catalytic Systems and Protocols for a few Important Catalysts and Inorganic Reagents based on Cobalt(II and III), Copper(II), Chromium(VI), Vanadium(IV and V) and Tribromide (Br_3^-)**" by Sanjay K. Dehury, a student in the Department of Chemistry, Indian Institute of Technology, Guwahati for the award of degree of Doctor of Philosophy has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

… November, 2004. **Mihir K. Chaudhuri**

CONTENTS

Abstract

The present thesis is based on the results of investigations of a few chosen aspects of metal acetylacetonates, oxofluorochromates(VI), organic ammonium tribromides and peroxovanadates(V). It constitutes, in part, an interpretative account of solvent-less and peroxometal-mediated synthesis of metal acetetylacetonates and development of metal acetylacetonate based heterogeneous catalysts and catalytic systems to work in water. In the next part of the thesis the importance of synthesis and versatility of some chromium(VI) reagents and catalysts have been highlighted. Another part of the thesis focuses on solvent-less synthesis of quaternary ammonium tribromides and solid-phase experiments for bromine-less brominations. The concluding section presents our work on synthesis, isolation, and structural assessment of a few vanadium-peroxo-citrate complexes. The subject matter of the thesis is distributed over six chapters.

Chapter 1. Introduction and Scope of the Work

This chapter presents an overview of different aspects of metal acetylacetonate, oxofluorochromium(VI) and peroxovanadium(V) chemistries. It focuses on multifarious applications of metal acetylacetonates both in basic research as well as in industries, and brings out the importance of their economic synthesis. In addition, the importance of homogeneous catalysis in water is emphasized. However, heterogenization of catalysts has been preferred in many instances owing to several advantages, such as ease of product separation, isolation and the possibility of reuse of catalysts. Some of the documented ways of heterogenization of catalysts by immobilization employing different techniques, e.g. microencapsulation, solid support and ionic liquid, have been highlighted. Further described is the literature precedence for some of the important organic transformations, viz., Barbier allylation, aziridination, sulfimidation and sulfide oxidations, as relevant to the present Ph.D. research. The results of such studies constitute a good part of the thesis.

While continuing with inorganic catalysts, one would like to confess that there appears to be no parallel to chromium(VI) oxidants owing to their versatility, selectivity, capability of working very well under mild conditions and cost effectivity. In particular, because of some important advantages of a chromium(VI) oxidant, namely, pyridinium fluorochromate(VI) (**PFC**), it drew a renewed attention especially in terms of its economic synthesis and use in solid-phase as well as in catalytic oxidation of organic substrates. In addition, this section while presenting an account of a companion reagent, 3,5-dimethylpyrazolium fluorochromate(VI) (**DmpzHFC**)**,** also emphasizes the need for better performing oxidizing reagents, and may be more so for catalysts.

Pertinently, bromination of organic molecules though constitutes a rather small area of activity yet considered to be important for some chemical processes to provide important intermediates. Traditional bromination processes are often environmentally unacceptable because of the use of toxic Br_2, HBr or a combination of the two, hazardous solvents and auxiliaries. It is in view of these problems that one would like to develop rather clean and safer brominating agents which could as well be obtained economically. It would be necessary also to work out benign bromination protocols which would be operated easily. A rational choice would be to look into the cleaner synthesis of **organicammonium tribromides**, a 'store house' of bromine, and investigate their efficacy in solid phase bromination of organics. It is significant to mention that solid-phase reactions appear to be very promising alternatives to reactions in solution especially if they are more selective, efficient to afford products that are rather difficult, complicated and at times impossible to obtain in solution.

Quite apart from the kind of activity profile highlighted above, studies on various aspects of peroxo-vanadium chemistry has been enjoying a great relevance in contemporary chemistry research because of some definite and important chemical and biochemical reasons including catalysis, bio-mimetic modeling and medications. Accordingly, there has been a continuous endeavor for newer synthesis of peroxovanadates(V) with heteroligands of biochemical relevance, structural evaluation and investigation of reactivity profiles. It is pertinent to mention that the chemistry of monoperoxovanadates(V) having appropriate heteroligands needs attention in terms of synthesis and reactivity studies. Investigation of reaction chemistry of peroxovanadium(V) compounds appear to be always very rewarding.

Contemporary importance of the chosen aspects of chemistry that have been addressed in the present thesis provides stimulating inspiration to look into these areas more closely thereby providing enough scope for further work.

Chapter 2. Method of Preparation of Starting Materials, Elemental Analyses and the Details of Equipment used for Characterization and Structural Assessment of the Compounds

The sources of chemicals and solvents, methods for quantitative determination of elements, and the details of all the equipment used for physico-chemical studies are provided in **Chapter 2**.

Chapter 3. Newer Preparation of Metal Acetylacetonates and a few Heterogeneously and Homogeneously Catalyzed Reactions by Metal Acetylacetonates

As a matter of convenience the subject matter of this chapter is divided into four sections. **Section 3.1** describes solvent-less and peroxometal(inter)mediated synthesis of

selected metal acetylacetonates. The main focus of **Section 3.2** is on $SnCl_2$ mediated and $Co(acac)_2.2H_2O$ catalyzed Barbier coupling of carbonyls with allyl halide. The efficacy of immobilized copper(II) acetylacetonate catalyst for heterogeneous nitrene transfer reactions has been described in **Section 3.3**, while **Section 3.4** contains $VO(acac)_2$ supported titania catalyzed sulfide oxidations.

Section 3.1 Solvent-less and Peroxometal(inter)mediated Synthesis of Selected Metal Acetylacetonates

Two newer protocols, one each based on solvent-less and peroxo-metal(inter)mediated reactions, have been developed for the preparation of metal acetylacetonates. The solvent-less method provides an improved, economical and environmentally benign process for metal acetylacetonates having the general formula $M(acac)_n$ wherein M is a metal cation selected from the group consisting of Fe, Co, and Cu, n is an integer which corresponds to the oxidation state of M. The compounds have been obtained from the reaction of the corresponding metal hydroxide, or metal hydrated oxide with a stoichiometric amount of acetylacetone (acacH, $C_5H_8O_2$) (**Scheme 1)**.

Scheme 1

$$M(OH)_n + n\ acacH \longrightarrow M(acac)_n.xH_2O$$

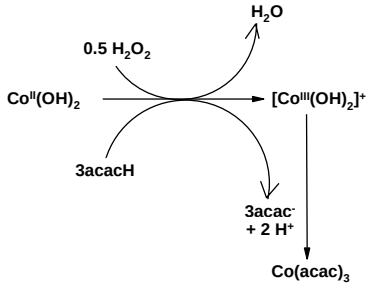
Where M = Fe, n = 3 and x = 0

M = Cu, n = 2 and x = 0

M = Co, n = 2 and x = 2

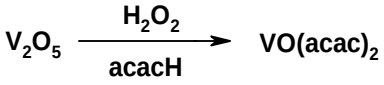
The peroxo-metal(inter)mediated protocols provide routes to afford either metal acetylacetonates in higher or lower oxidation states depending upon the reaction conditions. As a typical example, the hydrated metal oxide of cobalt(II) is directly reacted with acetylacetone in the presence of hydrogen peroxide to obtain $Co(acac)_3$ as the product with cobalt being in higher oxidation state (**Scheme 2)** as evident. The reaction is very facile rendering the product with high crystallinity and in almost quantitative yield.

Scheme 2



In yet another example, vanadyl acetylacetonate has been synthesised by dissolving vanadium pentoxide in an excess of H_2O_2 in ice cold condition to get a dark red solution of a peroxo-vanadium intermediate, which on subsequent treatment with acetylacetone rendered $VO(acac)_2$ (**Scheme 3)** in very high yield.

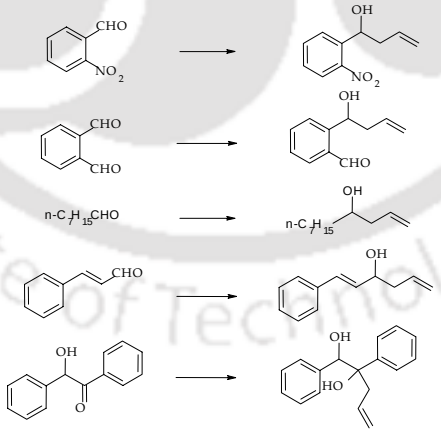
Scheme 3



Section 3.2 Barbier Coupling in Water: $SnCl_2$-Mediated and $Co(acac)_2$-Catalyzed Allylation of Carbonyls

The Barbier reaction is a century old C-C bond forming reaction that works as the kingpin of synthetic organic chemistry. More specifically this is a coupling reaction between a carbonyl function and an organic halide mediated by a metal to afford the corresponding alcohol. In so far as the Barbier reaction in water is concerned, a large number of reagents and reaction protocols have been developed for the synthesis of homoallylic alcohols, however, there are some limitations in terms of versatility, efficacy and selectivity, for instance. In a successful endeavor, we have demonstrated that $Co(acac)_2.2H_2O$ efficiently catalyzes the $SnCl_2$-mediated Barbier coupling in water between carbonyls, including aromatic, aliphatic and α, β-unsaturated aldehydes, ketones, sugars, and allyl halide to afford the corresponding homoallylic alcohols in high yields (**Panel 1)**.

Panel 1



The catalyst was reused for several cycles with nearly consistent activity

Section 3.3 Immobilized Copper(II) Acetylacetonate Catalyst for Heterogeneous Nitrene Transfer Reactions

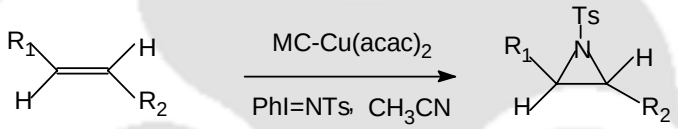
Section 3.3 comprises of two subsections, a comprehensive account of the results of aziridination of olefins using MC-$Cu(acac)_2$ catalyst and PhI=NTs as the nitrene source

constitute the text of **Subsection 3.3.1**. Once it was realized that $Cu(acac)_2$ microencaspulated in polystyrene efficiently catalyzed aziridination reactions, it appeared quite logical to explore the possibility of synthesis of sulfimide by nitrene transfer to a sulfide using MC-$Cu(acac)_2$ catalyst and PhI=NTs as the nitrene source. In addition, these results prompted us to apply $Cu(acac)_2$ catalyst immobilized in ionic liquid to the synthesis of sulfimides from sulfides and compare the results with those of MC-$Cu(acac)_2$. **Subsection 3.3.2** discusses the results of this investigation.

Subsection 3.3.1 Microencapsulated $Cu(acac)_2$: A Recoverable and Reusable Polymer- Supported Copper Catalyst for Aziridination

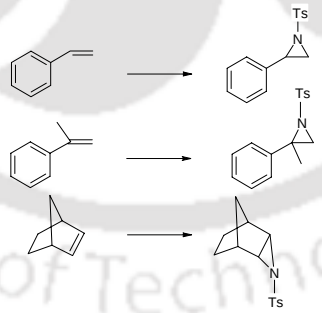
In this subsection, we have described the preparation of microencapsulated copper(II) acetylacetonate, [MC-$Cu(acac)_2$], by immobilization of $Cu(acac)_2$ onto polystyrene accomplished by physical envelopment by the polymer. This was followed by the results of our studies on aziridination of alkenes using [MC-$Cu(acac)_2$] as the catalyst and [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrogen source **(Scheme 4)**.

Scheme 4



The chosen examples of aziridination of alkenes catalyzed by microencapsulated copper(II) acetylacetonate, [MC-$Cu(acac)_2$], are shown below **(Panel 2)**:

Panel 2



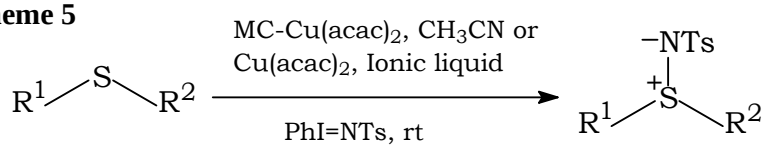
It is important to note that in these reactions MC-$Cu(acac)_2$ catalyst was reused for several cycles with consistent activity.

Subsection 3.3.2 Heterogeneous Catalytic Sulfimidation using Immobilized $Cu(acac)_2$

In a successful endeavor, heterogeneous catalytic sulfimidation of a variety of sulfides with PhI=NTs by microencapsulated copper(II) acetylacetonate, [MC-$Cu(acac)_2$], has been demonstrated for the first time. The products have been obtained in good to excellent yields.

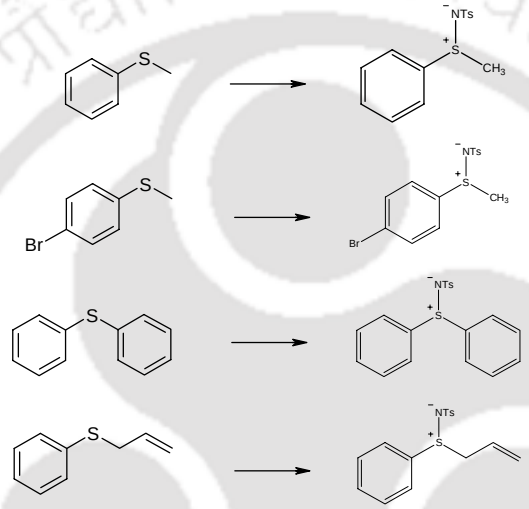
Further, $Cu(acac)_2$ has been immobilized in ionic liquids viz., $BmimBF_4$ and $BmimPF_6$, and the immobilized copper catalyst has been used for sulfimidation of sulfides **(Scheme 5)**.

Scheme 5



Selected examples of sulfimidation catalyzed by immobilized copper(II) acetylacetonate are shown below **(Panel 3)**:

Panel 3



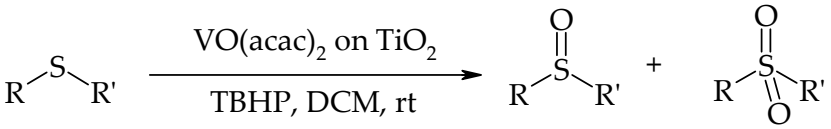
MC-$Cu(acac)_2$ and $Cu(acac)_2$ immobilised in ionic liquids were recycled with consistent activity.

We have also demonstrated that ionic liquids can act as powerful media not only for facilitating the catalyst recycling but also for accelerating the reaction rate in $Cu(acac)_2$ catalyzed sulfimidation reactions.

Section 3.4 $VO(acac)_2$ Supported Titania: A Heterogeneous Catalyst for Oxidation of Sulfides using TBHP

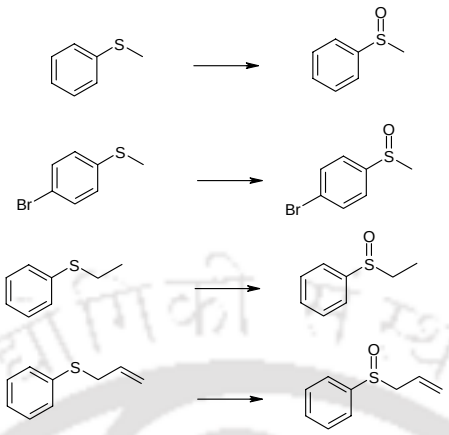
We, in this section, describe a heterogeneous catalytic system comprising of vanadyl acetylacetonate, $VO(acac)_2$, supported on titania for facile catalytic oxidation of sulfides to sulfoxides and/or sulfones using *tert*-butylhydroperoxide (TBHP) as an oxidant in methylene chloride in nearly quantitative yields at room-temperature. In most cases sulfoxide is obtained as the major product (*ca*. >90 %) (**Scheme 6**).

Scheme 6



Selected examples of sulfide oxidation are shown below (**Panel 4)**:

Panel 4



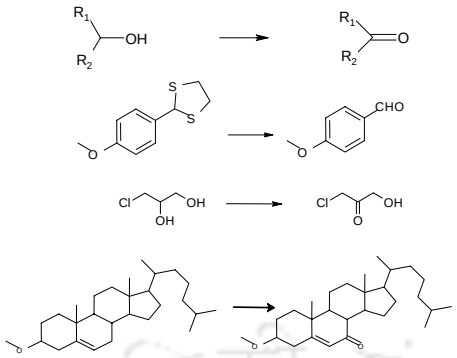
The catalyst is reusable and tested for five cycles without significant loss of activity and selectivity.

Chapter 4. Solvent-free and Catalytic Oxidations with Chromium(VI) Based Reagents and Catalysts

This chapter presents the economic synthesis of pyridinium fluorochromate(VI), $C_5H_5NH[CrO_3F]$ (**PFC**), and solvent-free oxidation of organic substrates with PFC. Also its application as a catalyst for oxidation of benzylic bromide to benzaldehyde has been brought into attention. In addition, solvent-free as well as catalytic oxidation of organic substrates by 3,5-dimethylpyrazolium fluorochromate(VI), $C_5H_8N_2H[CrO_3F]$ (**DmpzHFC**), has been reported herein.

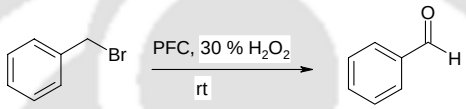
A 1: 1: 1 stoichiometric reaction among CrO_3, aqueous HF and pyridine afforded orange crystalline pyridinium fluorochromate(VI), $C_5H_5NH[CrO_3F]$ (**PFC**), in 99.2% isolated yield demonstrating 100 % of atom economy. PFC under solvent-free conditions readily converted primary, secondary and allylic alcohols to the corresponding carbonyls, and selectively oxidized secondary alcohols in the presence of primary alcoholic functions, polycyclic hydrocarbons to cyclic ketones, benzoin to benzil, PPh_3 to $O{=}PPh_3$, methylphenyl sulfide to sulfoxide, cyclohexanone oxime to cyclohexanone, an allylic Δ^5-steroid to the corresponding α, β-unsaturated ketone and deprotected dioxolanes and dithiolanes to aldehydes (**Panel 5)**.

Panel 5



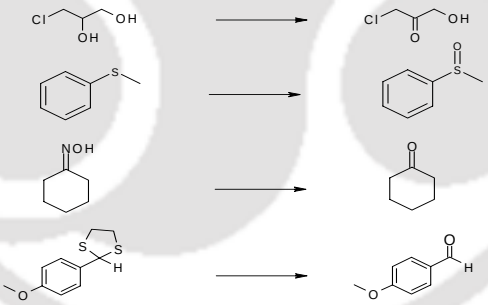
PFC efficiently catalyzed oxidation of benzyl bromide to benzaldehyde with H_2O_2 being the oxidizing agent (**Scheme 7)**.

Scheme 7



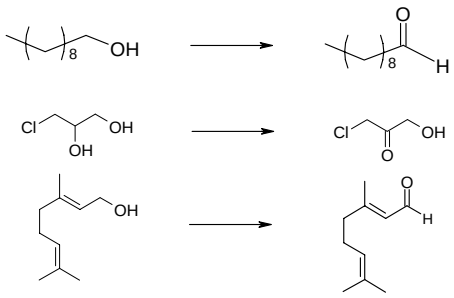
3,5-Dimethylpyrazolium fluorochromate(VI), $C_5H_8N_2H[CrO_3F]$, (**DmpzHFC**), serves as an efficient reagent for oxidation of primary, secondary, allylic and benzylic alcohols, oxo-transfer to sulfides and triphenylphosphene, deoximation and deprotection (**Panel 6**).

Panel 6



DmpzHFC has been used to activate H_2O_2 and accordingly oxidations of a few chosen alcohols with H_2O_2 and catalytic amount of **DmpzHFC** have been carried out under solvent free conditions (**Panel 7)**.

Panel 7



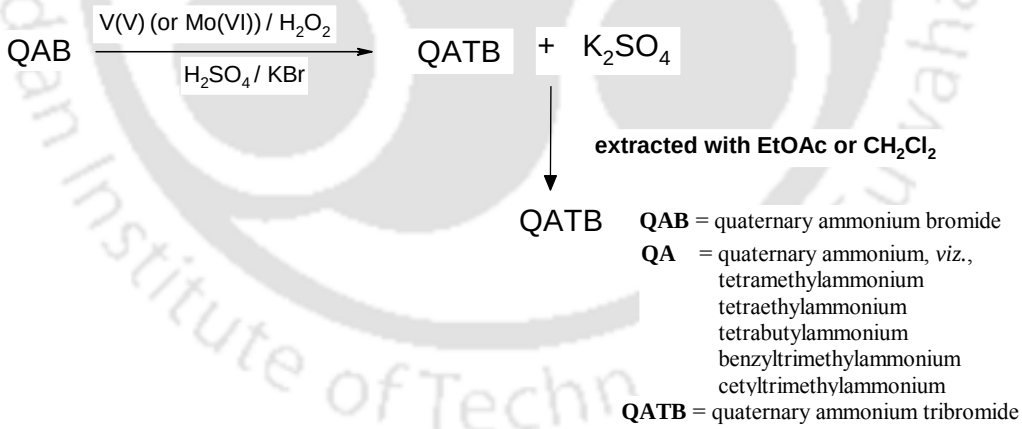
A comparison of the results of **DmpzHFC** catalyzed oxidations with those obtained under solvent-free conditions evidences that the reactions are equally facile in both the cases affording the products in similar yields.

Chapter 5. Economic and Solid-Phase Synthetic Protocols for Quaternary Ammonium Tribromides and Solvent-free Bromine-less Bromination of Organic Substrates

This chapter focuses on the economic as well as solid-phase synthesis of quaternary ammonium tribromides, **QATB**s. In addition, the versatility of quaternary ammonium tribromides, **QATB**s, as brominating agents for solvent-free bromine-less bromination of chosen organic substrates is described.

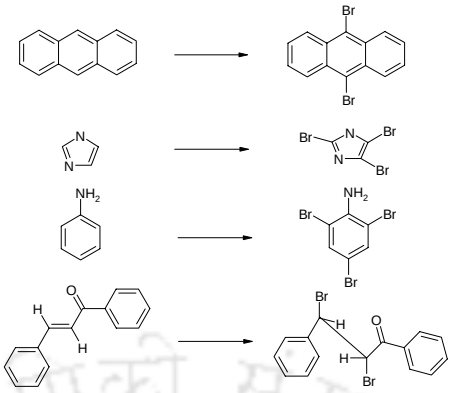
Peroxo-metal complexes are known to oxidize bromide under a weak acidic condition. Using this knowledge, Br_3^- was obtained in solution and then isolated in the solid state as a quaternary ammonium salt of tribromide. In order to make the method economic and the reactions faster, a solid-phase prtotocol has been developed rendering the products with high to very high yields (**Scheme 8)**. The products have been obtained in highly crystalline form with a very long shelf life.

Scheme 8



Bromination of a few selected substrates, viz., anthracene, phenanthrene, phenol, aniline, imidazole and chalcone have been carried out very successfully using cetyltrimethylammonium tribromide, **CTMATB**, under solvent-free conditions **(Panel 8)**. The reactions have been found to be selective for monobromination at room temperature, however, on carrying out the reactions at a higher temperature further bromination takes place. A comparison of results of bromination using **CTMATB** with those of its companion reagents, e.g., **TMATB**, **TEATB**, **TBATB**, and **BTMAB** reveals that the reactions are much faster with **CTMATB**.

Panel 8



Chapter 6. Monoperoxo(citrato)vanadates(V) as Probable Catalysts: Synthesis, Structural Assessment and Studies of a few Reactions

The combination of citrato and peroxo ligands on vanadium, a bioessential metal ion of relatively less known biological function, is of great interest owing to biochemical relevance of vanadium for several reasons. For example, in the process of purification and characterization of vanadium enzymes, the bromoperoxidases, VBrPOs, two operations are directly related to the properties of the peroxo(citrate)vanadates(V), the first of which is the formation of a product with a λmax of 420 nm, which gradually converts in slightly acidic solution into a different species with increasing the absorption at 460 nm due to the formation of $VO(O_2)^+$ cation. Secondly, a citrate/phosphate buffer is used, and consequently bonding of some citrate to vanadium is likely.

As a part of the present Ph.D research, a few peroxo(hetroligand)vanadate(V) complexes have been synthesized with citrate ion as the heteroligand of choice and NH_4^+, Na^+, K^+, Rb^+ or Cs^+ as the counter-cation. The compounds thus synthesized are $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$, $Na[VO(O_2)(C_6H_6O_7)].H_2O$, $K[VO(O_2)(C_6H_6O_7)].H_2O$, $Rb[VO(O_2)(C_6H_6O_7)].H_2O$ and $Cs[VO(O_2)(C_6H_6O_7)].H_2O$ (**Scheme 9)**.

Scheme 9

$$V_2O_5 \xrightarrow[\text{MOH or } M_2(CO_3)]{C_6H_8O_7,\ 30\%\ H_2O_2} M[VO(O)_2(C_6H_6O_7)].H_2O$$

$$\text{pH} \sim 2\text{-}4$$

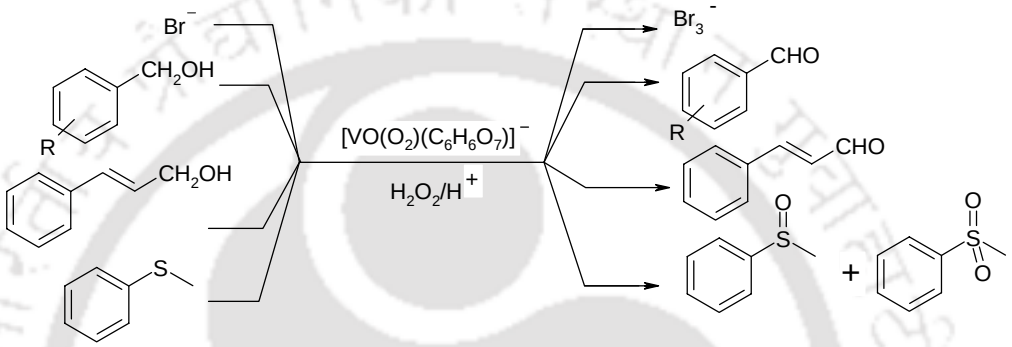
Where M = NH_4^+, K^+, Na^+,Rb^+ or Cs^+

Characterization of the complexes has been made on the basis of elemental analyses and a variety of spectroscopic studies. It may be mentioned that the compounds reported in this chapter exhibit a rather typical electronic spectral absorptions at around 450nm and 225nm

attesting the presence of peroxide coordinated to the vanadium(V) centre. It may provide an excellent scope for study of the peroxo-metal interactions in solution.

One of the main reasons for the synthesis of the title compounds was to investigate their reaction profile. It appears from the results obtained so far that the monoperoxo(citrato)vanadates(V) are like to be valuable additions to the tool kit efficient oxidation catalysts. The versatility of these compounds has been evaluated for oxidation of bromide, benzylic and α, β-unsaturated alcohols, and a organic sulfide (**Scheme 10**).

Scheme 10



Some parts of the work described in the thesis have been either published or accepted for publication, while the rest are yet to be published.

Chapter 3

US Patent Appl. Publ., Pub. No.:US 2004/0127690 A1, Pub. Date: Jul. 1, 2004.

Tetrahedron Letters **2003**, *44*, 9029.

C*atalysis Letters,* **2004**, *95*, 19.

Chapter 4

US Patent Appl. Publ., Pub. No.:US 2004/0133003 A1, Pub. Date: Jul. 8, 2004.

Synthetic Communications, **2004**, *22*, 4077.

Chapter 5

US Patent Appl. Publ., Pub. No.**:**US 2004/0126308 A1, Pub. Date: Jul. 1, 2004.

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF PANELS

Introduction and Scope of the Work

Chapter 1

The core inorganic chemistry research generally involves synthesis, structural evaluation and investigation of reactivity profiles of inorganic compounds with all these aspects being equally important. While these activities engage the attention of a vast majority of inorganic chemists, one is often encountered with a question as to what would be the end-use of all these endeavors. It is at this juncture that the applied inorganic chemistry probably finds its root. Emerge out here from are some of the sub-areas namely, materials chemistry and catalysts development, for instance. Development of newer catalysts and materials is an art based on strong science as they are meant to meet a specific end or a defined target.

As a part of an on going programme of the laboratory where the present Ph. D. research has been carried out, development of newer catalysts or catalytic formulations takes an important share. As well documented, catalysts or catalytic formulations, which are characterized by a much lower production volume and much higher added value, find wide applications in the domain of fine chemicals and pharmaceuticals. In addition, from the chemical point of view they encompass a wide diversity of chemical structures and compositions which may often be relatively complex.

Noncatalytic stoichiometric organic transformations using conventional reagents are still in use for numerous processes with stoichiometric reagents being used in the production of a wide variety of pharmaceuticals, fragrances and agrochemicals, etc. Despite the important role still played by stoichiometric reagents, the general trend is the development of catalytic processes to replace traditional stoichoimetric reagents. An obvious reason for this has been the global concern for making chemical processes more catalytic rather than stoichiometric thereby rendering the protocols more cost-effective, efficient and selective to reduce the burden on the environment.

Catalysis is crucial to chemical technology where the catalysts facilitate innumerable chemical reactions with chemical bonds broken and new chemical bonds formed during the process. These events occur repeatedly, usually without significant change of the catalyst. In the absence of catalysts, these chemical transformations would either not occur or take place with lower efficiencies and at slower rates. Catalyses were performed in a chosen organic solvent, which provided a homogeneous reaction medium for distribution of the reactant over a wide range of concentration. Though homogeneous catalysis in organic solvent is characterized by superior activity and selectivity but it usually involves a cumbersome process of separation of catalyst from reaction products and lowers activity of the recovered catalyst. Taking all these problems into account, one would like to opt for either or both the following alternatives: (i) *use of water as the solvent of choice in case of water soluble catalysts* and (ii) *heterogenization of*

the homogeneous catalysts by immobilization. In fact the potential advantages[1] of replacing organic solvents with water are the following (i) use of 'water as solvent' provides homogeneous medium for high catalytic efficiency, activity and selectivity, (ii) it allows for isolation of organic products and quantitative recovery and recycling of the water soluble catalyst through simple phase separation, and (iii) 'use of water' is cost-effective, safe and preferred in view of the global environmental norms.

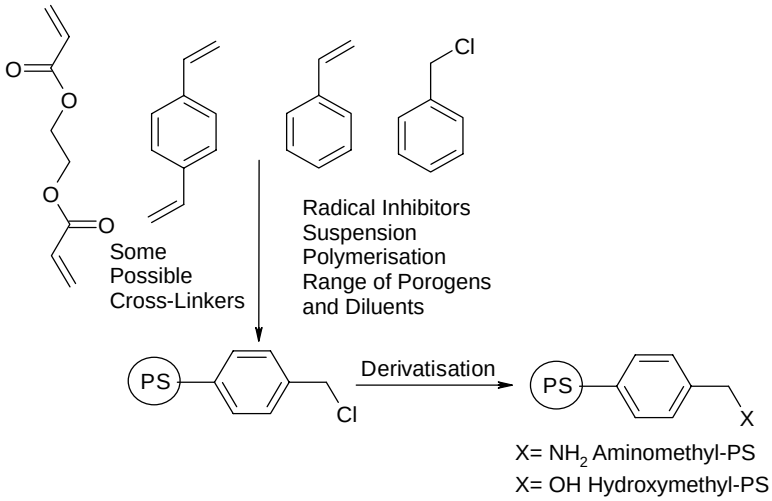
Chemists have already begun investigating the possibility of using water as the solvent[2,3] for organic reactions, with surprising and unforeseen results at times. Without overlooking some earlier contributions, the discoveries made in the laboratories of Breslow[4-6] and Grieco[7,8] in the early 1980s on the positive affect of water on rates and selectivities of Diels-Alder reactions triggered a more widespread interest in the field. Since then, significant progress has been made in the field of **organic chemistry in water/ aqueous media**, and new additions are continuously being made to the list of organic transformations that can be performed efficiently in water. Besides Diels-Alder reaction, other examples include Claisen-rearrangement,[9,10] aldol reactions,[11,12] and oxidations[13-15] and hydrogenations[16, 17] of alkenes to mention a few. In addition, 'organometallic' reactions in aqueous media[18-20] have also been of great interest for synthetic organic chemists. In a typical organometallic reaction a nucleophile of a organometallic reagent interacts with electrophilic center of the reactant leading to C-C bond formation. When the reactant nucleophile is a carbonyl compound, the transformation is frequently referred to as a Barbier-Grignard type reaction. The generation of the organometallic can be *in situ* (Barbier)[21] or stepwise (Grignard).[22] In general Barbier reaction is a coupling between a carbonyl function and an organic halide mediated by a metal to afford the corresponding alcohol. Incidentally, its synthetic utility was overtaken mainly by the Grignard and related organometallic reactions largely because the classical Barbier reactions suffered from the problems of interference from a host of side reactions especially reductions and couplings (*c.f.* pinacol coupling of carbonyl and Wurtz coupling of halide)[23] in organic solvents. On the other hand, a major requisite in these cases is the strict exclusion of moisture. Such a restriction can impose limitation on synthetic design in which various acidic hydrogens in the substrate have to be protected.[24] Hence, with the paradigm that water has an adverse effect on organometllic reactions, it may require a mind leap to think of water as a versatile solvent. Fortunately, Wolinsky *et al.*[25] observed that allylation of carbonyl compounds with allyl bromide mediated by zinc could be carried out in 95% ethanol and t-butyl alcohol. Significantly, the reaction sequence changes its course if it is carried out in an aqueous medium to provide the desired product almost quantitatively, if not exclusively.

Evidently, the realization started gaining momentum through the elegant contribution of Luche,[26-28] Nakami,[29-33] Benezra,[34,35] Li and Chan,[18,24,36-55] Whitesides,[56-59] Roy,[60-65] and Liu and Guo[66, 67] enriching our knowledge of Barbier type allylations of non-sugar aldehydes and ketones as well as carbohydrates both in terms of synthetic as well as mechanistic implications. An important incentive of this development is that water itself serves as the solvent of choice satisfying the demanding environment norms in keeping with the enhanced global interest in 'Green Chemistry.[68, 69] If one were to comprehend the current scenario in so far as 'the Barbier reaction in water' is concerned, the following would emerge as the main points: (i) owing to their importance in organic chemical technology and pharmaceutical industries a large number of reagents and reaction protocols have been developed, (ii) many metals viz. aluminium,[70] indium,[46, 71-74] antimony,[55] bismuth,[75] lead,[76] manganese,[53] magnesium,[54] zinc,[77,78] tin,[23,79-83] cadmium,[84] gallium,[85] and copper,[66] for instance, have been reported to be effective in mediating C-C coupling between allyl halides and carbonyls in aqueous medium, and (iii) metal-mediated reactions being heterogeneous in nature, often posses operational problems (*c.f.* stirring) with the result that the conversion of starting materials to the products are incomplete, presumably because of passivity of the catalyst due to oxo or hydroxo metal coating. Use of hydrobromic acid[29,30] or ultrasonication together with saturated aqueous NH_4Cl/THF,[26-28] however, improved the yield. In order to circumvent practical difficulties, an alternative protocol is desirable which would neither produce metal wastes nor require HBr thereby rendering it environmentally more benign. Also the protocol should be favorable to large scale preparations without the involvement of ultrasonication.

In so far as heterogeneization of catalysts[86-93] is concerned there has been a metamorphosis from the simplest strategy i.e., supporting the active sites on large surface area solids, to the more elaborate ones in which the active sites are part of the solid structure. Eventually, the massive increase in the use and the broadening range of applications for polymeric supports in chemistry illustrate the immense significance of the techniques to the chemists. The concept of performing traditional solution-phase reactions under "pseudo homogeneous" conditions has rapidly expanded into the domain of the medicinal, organic, organometalic, inorganic and polymer chemists, each exploiting the benefits, first realized by the peptide chemists, for their own advantages.[94]

The main benefits of immobilization of catalysts are due to the ease of physical separation of the polymer and its bound component from the reaction mixture and recycling (especially for expensive catalysts and ligands), and the simplification of handling a range of toxic or odorous materials. It also enables the use of high concentration of the reagent to drive

reactions to completion, as byproducts or excess reagent can be removed by filtration, often eradicating the need for time consuming, laborious purification steps such as chromatography, distillation, or crystallization. Another advantage is due to the unique microenvironment created for the reactants within the polymer support[94] that maintains high activity and selectivity.[95-97] Supported catalysts have also been used for rapid production of compound library.[98, 99]

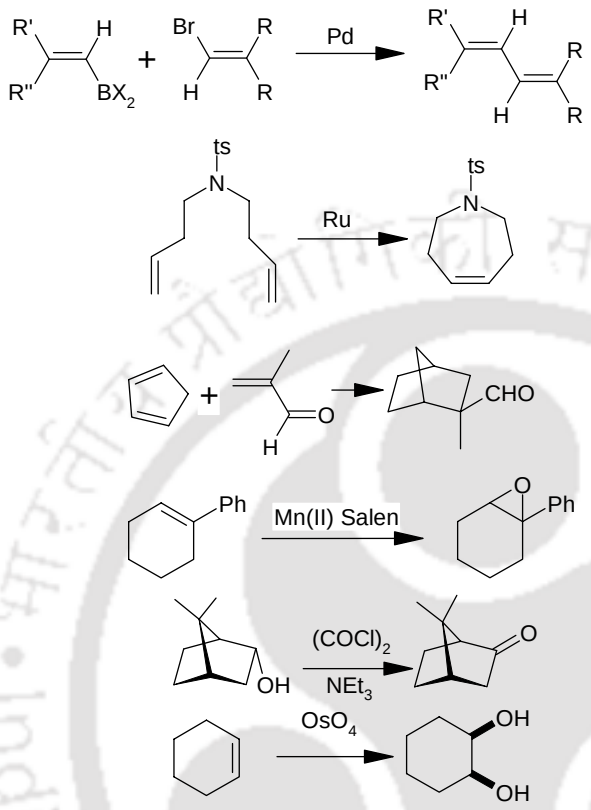


Scheme.1.1 Synthesis and Derivatisation of PS-Based Support

Polystyrene based recyclable catalysts[100] have been extensively used for crucial organic transformations like C-C bond formation reaction such as Suzuki coupling,[101] olefin metathesis,[102] asymmetric Diels-Alder cycloaddition,[103,104] asymmetric addition of diethylzinc to aldehyde,[105,106] asymmetric allylation of amine with allyltributylstannane.[107] Also several workers have addressed oxidations, such as alcohol,[108] alkene oxidations e.g. asymmetric epoxidation,[109] hydroformylation,[110] immobilizing various oxidizing agents upon a variety of supports, most being derived from common solution counterparts, while attempting to alleviate problems like poor selectivity and harsh reaction conditions. Various groups have reported asymmetric reduction processes, using immobilized reagents and catalysts, such as asymmetric reduction of ketones[111]and alkenes[112] (**Panel 1.1**).

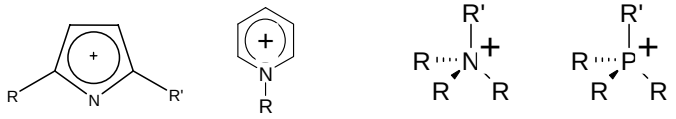
Immobilized catalysts are now well-recognized because of their ease of work up and separation of products and catalysts, economical considerations, and applications to industrial processes etc. In general, the catalysts can be immobilized on polymer via coordinate or covalent bonds. While the stability of polymer catalysts having co-ordinate bonds is often low,

preparation of polymer catalysts having covalent bonds can be troublesome and their activities are generally lower than those of the monomer catalysts.



Panel 1.1 Reactions Using PS-Supported Catalysts and Reagents

While immobilization of catalysts into polymer being regarded as one of the most effective way of heterogeneization, yet a potential technique e.g., use of ionic liquid[113-116] has emerged out. Ionic liquids are fused salts containing only ions;[115,117] nonetheless those which are liquids at or below room temperatures draw attention of synthetic organic chemists. Ionic liquids with weakly coordinated anion and suitable cation are highly justified as alternative "Green Solvent".[118] It provides an innocent solvent system for biphasic catalysis, heterogeneizing the catalyst and product into two separate and immiscible phases without loosing the selectivity and efficiency inherent in homogeneous catalysis. While the catalyst residing in solution in one of the two phases, the substrate resides in the other phase. During reaction, the catalyst and the substrate are allowed to interact by stirring the mixture vigorously. It has been well established that reactions can be accelerated in ionic liquids with improved selectivity. In fact an increased stability of the catalyst is observed in the ionic liquid, for instance. Finally, its nonvolatile nature enables significant advantage for distillative product separation, and the catalyst solution is available for immediate reuse. [119]

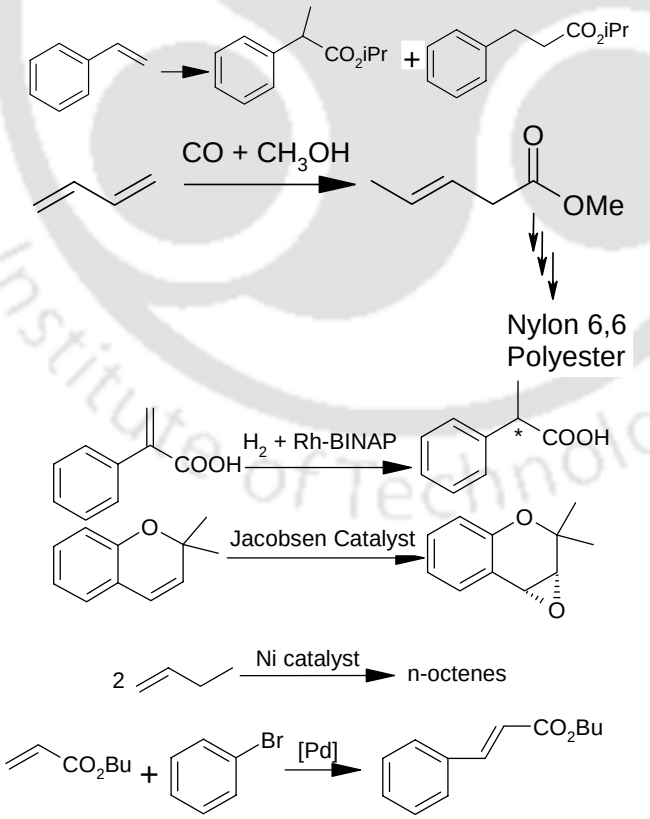


Scheme 1.2 Important Types of Cations in Ionic Liquid.

$AlCl_4^-$, $AlEtCl_3^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Al_2Et_2Cl_3^-$, BCl_4^-, $CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$, $SnCl_3^-$, BF_4^-, PF_6^-, SbF_6^-, $B(Et_3Hex)^-$

Scheme 1.3 Important Types of Anions in Ionic Liquid.

De souza *et al.*[120] addressed the Rh-catalyzed hydrogenation of cyclohexene in butylmethylimidazolium tretrafluoroborate. Chauvin *et al.*[121] dissolved the cationic Osborn complex $[Rh(nbd)(PPh_3)]PF_6$ in ionic liquids for biphasic hydrogenation of 1-pentene. Also, several groups have been investigating transition metal catalysis, such as oxidation,[122] hydroformylation,[123] alkoxycarbonylation,[124] Heck reactions, [125] and hydrodimerisation[126] immobilizing catalyst in suitable ionic liquids (**Panel 1.2)**.



Panel 1.2 Transition Metal Catalyzed Reactions in Ionic Liquid

Kobayashi et al. have reported a polystyrene supported lewis acid, *Microencapsulated Lewis Acid*, with the idea being to apply the *Microencapsulation* technique to immobilize catalyst onto polymer.[127-130] Adopting this technique *microencapsulated* $Sc(OTf)_3$, and [MC-$Sc(OTf)_3$], have been used for a variety of carbon-carbon bond-forming reactions such as, aza Diels-Alder, Strecker, cyanation and alkylation,[131] Mannich-type and aldol reactions,[127] silylation of alcohols.[132] Also microencapsulated osmium tetroxide [MC-OsO_4] was used for dihydroxylation of olefins[128, 133] and [MC-$Pd(PPh_3)$][130] for allylic substitution, Suzuki coupling and Mizoroki-Heck reactions.

In any case of immobilization, the support materials need to be thermally, chemically and mechanically stable during the course of the reaction. Moreover, the structure of the support needs to be such that the active sites are well disbursed on its surface and that these sites are easily accessible. Generally, this requires the support to have a high surface area (typically > 100 m^2g^{-1}) and appropriate pore size (i.e. > 20 Å) to allow easy diffusion of the reactants to the active sites.[134] Inorganic supports [135] such as silica, zeolite, alumina, zirconia, titania, ZnO, clay, etc., generally meet these requirements, although organic polymers[136,137] have been also extensively utilized. Literature precedence exists on the use of titania supported vanadia catalyst for benzylic C-H oxidation,[138] selective catalytic reduction,[139] oxidative destruction of hydrocarbon based volatile organic compounds,[140] oxidative dehydrogenation of propane,[141] oxidation of β-picoline to nicotinic acid,[142] oxidation of ethanol,[143] catalytic oxidation of chlorinated benzenes,[144, 145] catalytic oxidation of 2,4,6-trichlorophenol,[146] partial oxidation of methanol to formaldehyde.[147] Recent reports[148] show that vanadia (about 3 wt.%) supported on high-surface area TiO_2 (mostly anatase structure with 60–80m^2g^{-1}) are the most studied NH_3-SCR catalysts. The vanadia phase is a non-stoichiometric V_2O_5 oxide, which includes VO_3 and VO_2 surface monomer and polymer phases of higher activity relative to bulk V_2O_5. [149] Tungsta and molybdena, phases with moderate activity, act as chemical and structural promoters. However, they significantly decrease SO_2 oxidation activity; though improve the mechanical strength and extend the catalyst life. Moreover, MoO_3 extends the catalyst life in the presence of arsenic poisons from coal boilers.[150-153] Thus, the two promoters are usually employed in larger amounts (10 and 6 wt.% for WO_3 and MoO_3, respectively) than vanadia in the commercial catalysts. These increased loadings are necessary for the achievement of high active surface area. Therefore, what is now required is the identification of alternative metal complex of vanadium which on being supported on titania would be able to catalyze the desired reactions without using promoter like WO_3 or MoO_3.

It is also very important to note that stability of the immobilized catalysts is one of the key factors, for efficiency and reusability of the heterogeneous catalyst. The stability appears to depend on the nature of the metal complex to be immobilized and the nature of interaction i.e. coordinate, covalent or ionic. Hence, a metal complex satisfying the précised requirement needs to be chosen. In this context we, going by our experience in the development of catalytic systems,[154] believe that metal acetylacetonates could as well be the metal complexes of choice.

In line with this it is proposed to develop newer catalytic systems based on metal acetylacetonates, a class of compounds with which this group has a long association. It may not be out of place to mention that metal acetylacetonates find tremendous applications both in basic research as well as industrial processes. The compounds are used (i) in important chemical transformations such as oligomerization, polymerization, hydrogenation, isomerization of olefins, hydrosilylation of alkynes, coupling of organic halides and transesterification reactions,[155-176] (ii) in super critical fluid transport (SFT), CVD of thin films,[177] as contacts in microelectronic devices, in laser technology[178, 179] and as components in high temperature super conducting materials, (iii) in inorganic crystal engineering, as coordination polymer species,[180] (iv) in nanoparticle synthesis, $Co(acac)_3$, for example, has been used as a precursor for the production of nanoparticles of the transition metal[181] and size controlled synthesis of magnetite nanoparticles is possible using $Fe(acac)_3$ as the precursor,[182] (v) in diesel fuels as carbon scavengers, in rocket fuel, as combustion control catalysts, as components in functional fluids and as components of solid propellants,[183] (vi) as triplet quenchers[184] and as NMR shift reagents,[185] (vii) in the separation of enantiomers, for resin cross-linking, and for the synthesis of epoxy resins, (viii) in metal plating, for extraction and separation of metals, (ix) as source of metal oxides for controlled deposition, in glass coating (especially Mn, Co, Cr, Fe) and for surface coating. In addition, $VO(acac)_2$ is an example of a metal acetylacetonate that is important as a potent insulin mimic.[186]

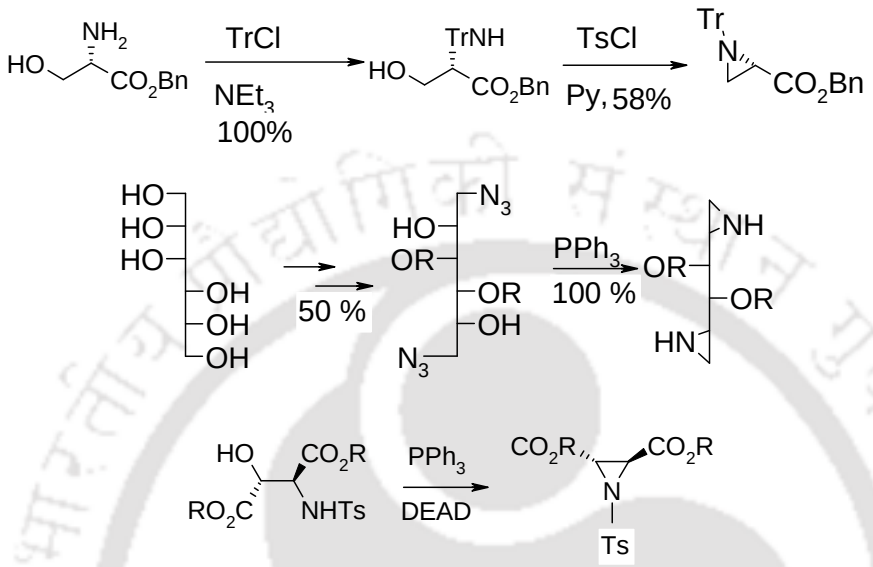
Thus, with metal acetylacetonates finding use in polymer industries, paint industries, rubber and leather technologies, it becomes more than apparent that it has mostly been a consequence of the applied needs that metal-acetylacetonates have always engaged the attention of researchers over the world. Since metal acetylacetonates constitute a the class of compounds of multifarious use and have also been selected for a good part of the present work, as a prerequisite to their use, it might be necessary to address a few issues related to the synthesis of metal acetylacetonates so as to enable us get the compounds of high purity rather easily. One may like to recollect that prior to the eighties,[187-189] the synthesis of such compounds had several limitations, such as the need for pH control, requirement of large excess of buffers, end-product

contamination, extra preparation steps for the starting materials and difficulties encountered in the handling of air-sensitive and toxic materials that were sometimes required for the preparation of the materials. In the early eighties, newer methods of syntheses were reported by our group,[190-199] by making use of not only the chelating ability of acetylacetone but also its potential as a reducing agent. However, these methods of synthesis are expensive and rather wasteful because of the use of an excess of acetylacetone. Hence, it **became a major concern to develop** a more economic synthesis of metal acetylacetonates and **then use them for newer catalytic reactions**.

The goal of catalyst development is to eventually produce and reproduce a commercially viable product which can be used as a stable, active and selective catalyst. Additionally, the requirement which are fundamental for catalyst performance generally require a compromise in order to produce a material which meets the contradictory demand imposed by industrial processes.[200] Catalytic materials becomes catalysts ultimately when they are used in industrial processes.[201] Current scenario of fine chemicals, pharmaceutical and petrochemical are characterized by a much lower production volume and much higher value with oxidative transformations[202] e.g. nitrene transfer and oxo transfer being some of the key areas of research.

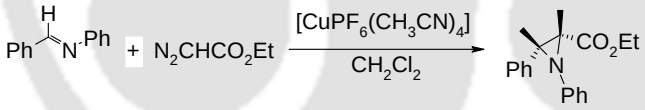
As far as nitrene transfer reactions are concerned one would like to encompass mostly on aziridination i.e. nitrene transfer to an olefin, and sulfimidation i.e. nitrene transfer to an organic sulfide. Aziridines[203] are saturated three-membered heterocycles containing one nitrogen atom. Like other three-membered rings such as cyclopropanes and epoxides, aziridines are highly strained.[204,205] The chemistry of aziridines is dominated by ring-opening reactions, driving force for which is relief of ring strain. These make them useful synthetic intermediates that fully deserve a prominent place in the domain of synthetic organic chemistry.[206] Also as expected, over the years, much emphasis is placed on the elaboration of naturally occurring starting materials. In this field, aziridines form an attractive class of compounds, since they are available in pure form by a variety of procedures and can be used for organic synthesis in a number of different ways. By suitable choice of substituents on the carbon and nitrogen atoms, excellent sterio- ragiocontrol can also be attained in ring-opening reactions with a wide variety of nucleophiles, including organometallic reagents;[207] this makes aziridines useful as **substrates**[208] for the synthesis of important biologically active species including alkaloids,[209] amino acids,[210] and β-lactum antibiotic.[211] Substrates-controlled diasterioselective synthesis is also possible by use of aziridines as removable **auxillaries**,[206, 212, 213] while in metalation a ring carbon atom allows aziridines to be used as **reagents**[214] for asymmetric synthesis. Bisaziridines can act as **ligands**[215-218] for transition metals having applications in catalysis.

Therefore, the synthesis of aziridines has been a subject of considerable research interest over the last few years. A critical review of literature delineates two general approaches[212] to aziridines, nonetheless the first is not only multistep route but also relies on the starting materials such as amino acids,[219,220]carbohydrates[221] or hydroxy acids[222] (**Panel 1.3**) ,

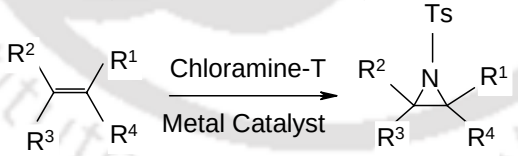


Panel 1.3 Synthesis of Aziridine from Amino Acid, Hydroxy acid and Carbohydrate

and the other is the shortest route; a single atom transfer to C-C[206] or C-N[223, 224] double bonds (**Scheme 1.4** and **1.5**)



Scheme 1.4 Synthesis of Aziridine by Carbene Transfer to Imine



Scheme 1.5 Synthesis of Aziridine by Nitrene Transfer to Alkene

The formation of aziridines from the addition of carbene moiety to an imine is a well known reaction; its utility is limited by low yield.[223, 224] Nevertheless a nitrogen atom transfer to olefin has emerged as interesting route to aziridines drawing attention of synthetic organic chemists. Several groups have reported Cu(I) and Cu(II) salts[225, 226] as homogeneous catalysts for aziridination of olefins using [*N*-(*p*-tolylsulfonyl)imino] phenyl iodinane (PhI=NTs) or chloramine-T as the nitrene donor. Later, heterogeneous copper-exchanged zeolite Y (CuHY) catalyst,[227,228] a polymer-supported Ru-porphyrin catalyst,[229] a silica-supported

polypyrazolylborate copper complex[230] and a polymer-supported manganese(II) complex[231] were also used for the aziridination of olefins by several other workers.

Akin to aziridination, one of the very valuable nitrene transfer reactions, is sulfimidation, however, there is limited development on its chemistry.[232] It may be partly because of lack of convenient synthetic method of obtaining optically active sulfimides. Optically active sulfimides were first prepared by conversion from the corresponding optically active sulfoxides[233] and then by kinetic resolution of racemic sulfimides using an optically active base.[234] Very recently, anion of sulfimides was demonstrated to be useful asymmetric methylidene transfer reagent to prochiral carbonyl groups in the presence of a base such as sodium hydride, the products being enantiomerically enriched epoxide.[235]

Recently, highly diastereoselective sulfimidations have also been reported by Gaggero *et al.*[336] and Uemura *et al.*[337] On the other hand, Uemera *et al.* reported catalytic asymmetric sulfimidation using the chiral Cu(I) bis(oxazoline) complex as a catalyst and also the racemic synthesis of sulfimides using $Cu(OTf)_3$ as a catalyst and PhI=NTs as a nitrene donor, albeit at moderate enantioselectivity and longer reaction times, respectively.[237-240] Katsuki *et. al.* have demonstrated that Mn(Salen)[241,242] and Ru(Salen)[243,244] complexes are efficient catalysts for asymmetric sulfimidation.

As discussed above nitrene transfer to sulfide to get the sulfimide has been an area of great interest for synthetic organic chemists. Similarly, oxo-transfer to sulfide to afford the corresponding sulfoxide or sulfone is a key step owing to the synthesis of many natural products and biologically active compounds.[245,246] Consequently, the oxidation of sulfides to chiral/achiral sulfoxides or sulfones has been the subject of extensive studies and a number of synthetic procedures are now available.[247-276] Various oxidising reagents are used for this purpose and unfortunately most of these reagents are not satisfactory for medium to large scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavourable by-products and high cost.

In recent years selective oxidation of sulfides to sulfoxides or sulfones has been carried out with heterogeneous catalysts e.g., titanium silicates (TS-1 and TS-2),[277] Ti-MCM-41[278] and $Ti(O^iPr)_4$ supported on silica.[279] But the drawbacks are small Ti active sites, loss of selectivity and the gradual leaching of titanium during the reaction. Recently, Choudary *et al.*[280] reported the catalytic oxidation of sulfides by tungstate-exchanged Mg-Al-LDH catalyst (LDH-WO_4) in quantitative yields in aqueous media with higher selectivities towards sulfoxides at lower conversions. However, the catalysts and catalytic systems are limited by tedious catalyst preparation, low yields of product, and low selectivity and long reaction times. Thus,

development of simple new heterogeneous catalyst and catalytic systems for nitrene transfer reaction like aziridination and sulfimidation, and oxo-transfer reactions like sulfide oxidation is most timely.

While continuing with inorganic catalysts one would like to confess that there seems to be no parallel to chromium(VI) oxidants in so far as oxidations on a commercial scale is concerned. In the realm of chemical technology, partial oxidations of organic substrates have an important role to play. The oxidized products of substrates like alcohols and hydrocarbons, for instance, are valuable as precursors for fine and speciality chemicals, pharmaceuticals and agrochemicals.[281] It is because of the importance of such oxidative transformations that a number of oxidants have been introduced over the years. However, no reagent other than those based on chromium(VI) have been as popular, useful and successful. This caused chromium(VI)-reagents to metamorphose over the decades from Collins' reagent,[282] CrO_3-3,5-dimethyl pyrazole complex,[283] pyridinium chlorochromate(VI) PCC,[284,285] pyridinium dichromate (PDC),[286] 2,2′-bipyridinium chlorochromate (BiPCC),[287]tetrabutylammonium fluorochromate(VI)[288] through pyridinium fluorochromate(VI) (PFC),[289-292] quinolinium fluorochromate(VI) (QFC)[293] and 3,5-dimethyl pyrazolium fluorochromate(VI) (DmpzHFC),[294] as reported in the literature. Also there are reports on a few other systems which work as reagents in combination with chromium(VI), e.g., chromium(VI)—*t*-butylhydroperoxide,[295-298] chromium(VI)—peroxocarbonate[299,300] and chromium(VI) — peroxoborate.[301] Among these PCC, PFC and DmpzHFC stand out to be highly potential, with PFC having additional advantages in terms of stability, versatility, controlled acidity, selectivity, operational simplicity and capability of functioning well under mild conditions, thereby assuming significant importance over the years. As of date there are at least hundred and fifty reports on the use of this reagent in the studies of oxidative transformations. Thus, it very efficiently oxidizes primary, secondary and allylic alcohols, fused ring hydrocarbons, benzylic systems, toluenes, sulfides, benzyl ethers, phosphorus compounds including triphenyl phosphine, arylalkanes, hydroxy acids, thio acids, benzaldehydes and aromatic anils, for instance.[302-306] **PFC**, owing to its controlled acidity (pk_a,2.7)[289-294] was successful in oxidizing acid sensitive substrates like 5-andostene-3β,17β-diol to the corresponding 17-keto-steroid,[302] and was used in the synthesis of biochemically important hydroxyethylene and ketomethylene dipeptide isosters,[307] S-(+)-4-formyl-4-butanolide, chiral synthon (R)-1-benzoyloxy-3-buten-2-ol, derivatives of dimethyl penam and dimethyl penam-S,S-dioxide[305] and 3β-acetoxy-lanost-8-en-24-one (24-ketolanosteryl acetate).[306] It also permits oxidative deprotection of oximes and desilylative

oxidations of alkyl trimethyl silyl ethers.[308] In order to understand the reaction dynamics, this reagent has been extensively used in studies being conducted on a variety of substrates.

As far as the Δ^5-steroidal oxidations are concerned, we have been particularly interested because Δ^5- steroids with keto functionality at the 7-position are much sought after owing to their medicinal values as reported in literature.[306,309-315] Accordingly, we developed a newer chromium(VI) reagent, 3,5-dimethylpyrazolium fluorochromate(VI), **DmpzHFC**, $C_5H_8N_2H[CrO_3F]$,[294] as a companion of **PFC** but with improved properties such as higher solubility in organic solvents, efficiency to perform very well under mild conditions, controlled acidity, shorter reaction time and high to very high yields of products. In addition, it has been demonstrated that **DmpzHFC** in acetonitrile efficiently oxidizes Δ^5- steroidal systems affording the desired products in good yields in a comparatively much shorter time.

It may be reiterated that chromium(VI) based reagents are never done away with owing to their selectivity, capability of working under mild conditions and cost effectivity and thus the interest in such oxidants does sustain. However, one must seek to improve upon the synthesis and reaction conditions in order to make an allowance for the bioincompatibility of hexavalent chromium. Economic synthesis of frequently used chemicals and solvent-free[316-320] chemical transformations have drawn significant attention in contemporary chemistry research due to the concerns for eco-benevolence.

While the economic synthesis produces zero waste, reactions in the absence of solvent are expected to have several advantages such as improved yield, selectivity, procedural simplicity and redundancy of detrimental organic solvents during reactions; such reactions are especially important in the context of 'Green Chemistry' and may have potential applications in combinatorial chemistry and high-technology industries.[321] What is surprising is that many of such organic transformations are reported to afford high conversions and yields after short reaction times, at moderate and even ambient temperatures through the interaction between two macroscopic solids.[322-324] Recently there has been substantial development on reactions carried out in the absence of solvent.[325-329]

The concept of a chemical reaction between two solids is a difficult one. Moreover, various name tags are frequently employed in this context. For the sake of clarity, one would distinguish here between *solid-phase synthesis* (the reaction of molecules from a fluid phase with a solid substrate, e.g., the polymer-supported peptide syntheses), *solvent-free synthesis* (any system in which neat reagents react together, in the absence of a solvent), and *solid-state synthesis* or *solid-solid reactions*, in which two macroscopic solids interact directly and form a

third, solid, product without intervention of a liquid or vapor phase. A cartoon of these three processes is shown in **Figure 1.1**.[328]

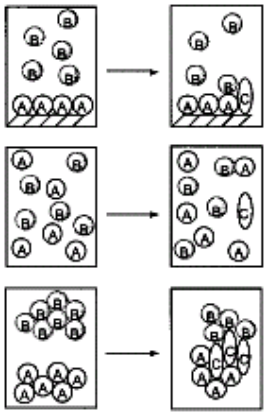


Figure 1.1 Cartoon of Solid-Phase Reaction (top), Solvent-Free Reaction (middle), and Solid-State reaction (bottom).

In several studies, it has been proposed that when two solid organic compounds capable of a chemical reaction are ground in the absence of a solvent (therefore, "solvent-free"), a chemical reaction occurs in the solid phase. Such solvent-free systems[326] have been recently reviewed and variously termed solid-solid[329, 330] or solid-state reactions.[331-336] In view of the advantages, several groups have addressed solvent-free reactions such as Baeyer-Villiger oxidations of ketones,[330] reduction of carbonyl compounds,[337] addition reactions e.g. halogenation,[338] hydrohalogenation,[339] Michael addition[340] and aldol addition,[341] C-C coupling reaction e.g. [2+2],[342] [4+2],[343, 344] and [6+2][345] cycloadditions, aldol condensation,[346] Dieckmann condensation,[347] Grignard,[348] Reformatsky,[349] and Luche[349] reactions, Wittig reaction,[350] Ylide reaction,[351] Pinacol coupling Reaction,[352] rearrangements e.g. Pinacol rearrangement,[353] benzilic acid rearrangement[354] and Beckmann rearrangement.[355] Also photoreaction[326] like photodimerization, photopolymerization, photocyclization, photorearrangement, photoisomerization, photosolvolysis and photodecarbonylation have been reported. When greater selectivity is required in the solid state reaction, host-guest chemistry techniques can be applied efficaciously. Although both thermal and photochemical reactions can be carried out selectively in inclusion crystals, the selectivity of the latter is usually higher than that of the former. However, solvent-free thermal reactions are important for practical synthetic processes in industry.

In continuation with the chemistry involving oxidation of inorganic as well as organic species, it is of worth looking into the chemistry of metal-dioxygen or more specifically peroxo-metallates owing to their immense use as industrial catalysts and importance in biological systems.[356] Nevertheless, the capability of molecular oxygen in acting as a reagent in

biochemical and industrial processes has attracted biochemists and industrial chemists alike in their pursuit in studying various aspects of oxygen transport and in the development of homogeneous analogues as well as heterogeneously catalyzed reactions. With the isolation, characterization and study of reaction of stable dioxygen complexes, information about bonding, structure, and reactivity of coordinated dioxygen have gained remarkable attention. It may not be totally out of place to have an overview of the bonding in molecular oxygen keeping in view the general interest in understanding the extent of activation of the O-O bond of coordinated dioxygen. While discussing metal-dioxygen chemistry, although the term molecular oxygen refers only to the free uncombined O_2 molecule with ground state $^3\Sigma_g$, the term dioxygen is used as a generic designation for the O_2 moiety in any of its several forms, and can refer to O_2 in either a free or combined state.[357] Dioxygen binding is subdivided into two main types, superoxide and peroxide and accordingly, the addition of one or two electrons to a neutral O_2 results in formation of the superoxide (O_2^-) and peroxide (O_2^{2-}) species, respectively, leaving the superoxide species with bond order of 1.5 and the peroxide with a bond order of 1; a situation that is best understood in terms of the molecular orbital theory.[358]

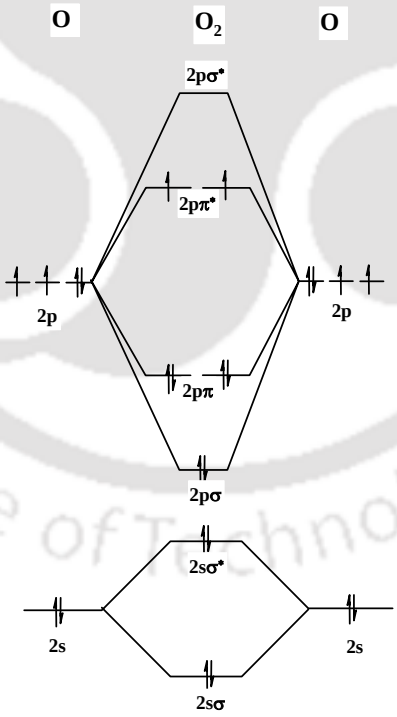


Figure 1.2. Molecular Orbital Diagram for O_2

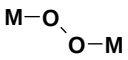
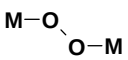
Molecular oxygen is a paramagnetic molecule having a triplet $^3\Sigma_g$ ground state as mentioned above and molecular orbital description of the $^3\Sigma_g$ level is

$$O_2\ KK(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\pi_g^*)^1(2p\pi_g^*)^1,$$

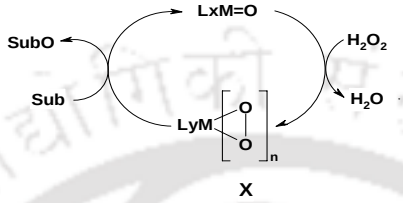
in which the KK term indicates that the K shells of the two oxygen atoms are filled. The two unpaired electrons in the $^3\Sigma_g$ ground state are found in the two degenerate antibonding $2p\pi_g^*$ orbitals, leaving O_2 with a formal bond order of two. The molecular orbital description of O_2 ($^3\Sigma_g$) shows a vacancy for the addition of a single electron each in both of the $2p\pi_g^*$ orbitals. (**Figure 1.2**) Addition of two electrons to these orbitals results in the formation of peroxide. Accordingly, a metal-peroxide complex is one in which the coordinated dioxygen resembles a peroxide (O_2^{2-}) anion.[359] The difference in the reactivity between peroxo and unreduced dioxygen complexes, whether binary or heteroligand, reveals that the chemistry of the two are very different owing to the presence of two extra electrons in the anti-bonding O- $p\pi^*$ orbital of the peroxide ion.

The modes of bonding of peroxide to metals are quite varied and interesting from the structural viewpoint. It can range from a symmetrical bidentate to a terminal monodentate position including all the possible angles in between. The bridging μ-peroxo could vary from cis-planar and trans-planar to trans-nonplanar configurations. Deviations from ideal symmetry are common and in the cases of heteroligand fields these deviations are, at times, due to the inherent symmetry of different donor atoms. **Table 1.1** shows the way in which a peroxo group is expected to coordinate to metals.[360]

Table 1.1 Structural Classification of Dioxygen Complexes

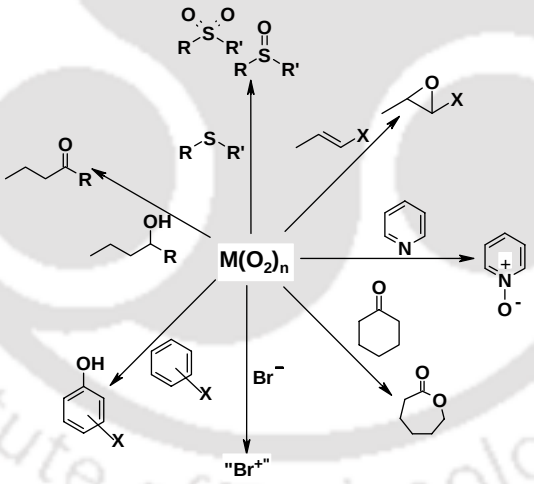
Structural type	Structural designation	Vaska classification
	η^1 dioxygen	Type a (superoxo)
	η^2 dioxygen	Type II a (peroxo)
	$\eta^1:\eta^1$ dioxygen	Type I b (superoxo)
	$\eta^1:\eta^1$ dioxygen	Type II b (peroxo)
	$\eta^2:\eta^2$ dioxygen	
	$\eta^1:\eta^2$ dioxygen	

While simple peroxometallates (*c.f.* binary peroxides and peroxo-metals) are often unstable, suitably ligated peroxometal complexes can be isolated and stored in many instances for prolonged periods.[360-362] By nature of reactivity they can be classified either as stoichiometric reagents or as catalytic agents. The general mechanism of catalysis, if the catalyst is not isolated, has been described graphically in **Scheme 1.6**, in which **'X'** is the real oxidant in solution. Its reduced form adds hydrogen peroxide again thus accounting for the catalysis.[363]



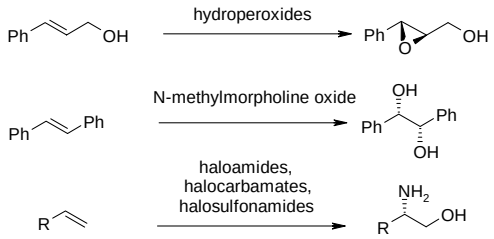
Scheme 1.6 A General Mechanism for Catalytic Oxidation by Peroxo-Transition Metal Complexes

Yet newer manifestations of their reactivity profiles are still under investigation.[364,365] Needless to mention that the peroxo-metal complexes referred to above are much stronger oxidants than H_2O_2 with their reactivity being many orders of magnitude higher than that of hydrogen peroxide.[365,366-369] A few examples in **Scheme 1.7** show the versatility of peroxometal oxidants.[363]



Scheme 1.7 Selected Oxidations of Organic Compounds by Peroxo-Metal Complexes (M = Ti, V, Mo, W)

Highly relevant and significantly important in this context are Sharpless's reagents[370] like hydroperoxides,[371,372] N-methylmorpholine oxide, $K_3[Fe(CN)_6]$,[373,374] haloamides, halocarbamates and halosulfonamides,[375,376] for instance, that are extremely important for catalytic assymmetric oxidations such as the asymmetric epoxidation of allylic alcohols (Katsuki-Sharpless epoxidation), [371,372] the asymmetric dihydroxylation of olefins[373,374] and the asymmetric aminohydroxylation of alkenes. [376,376] (**Panel 1.4**)



Panel 1.4 A Few Catalytic Asymmetric Oxidations

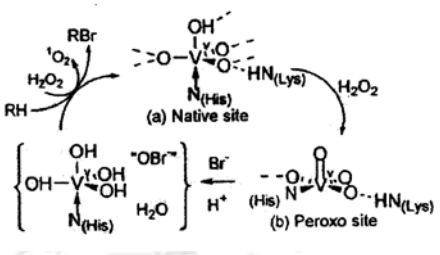
The chronology of developmental events reveals that from the early eighties on the importance of isolation in the solid state started gaining an enhanced importance, enabling further investigations involving them.[377-381]

Incidentally, the group with which the present Ph.D. research has been carried out has been involved in the synthesis and structural assessment of inorganic compounds, followed by looking into their reaction profiles with an intent to understand the underlying intricacies concerning their catalytic and biochemical activities. Peroxometal chemistry is one area that has received a lot of attention of our research group and the peroxometals have so far been drawn mainly from Ti,[382-385] V,[386-394] Mo, W, Zr,[395] Th[396] and UO_2^{2+}.[388, 397-403] Among these, it is vanadium that seems to have claimed the largest share and a good number of peroxo and heteroligand peroxovanadates(V) were synthesized in our laboratories. Subsequently (1985 on), the reaction chemistry of peroxovanadates(V) became one of the thrust areas of investigations.[404-413, 154] Interestingly, peroxovanadium chemistry is very flamboyant and by varying the pH values or in other words by changing the pH of the reaction solutions, different species of the type $[VO(O_2)]^+$, $[VO(O_2)_2]^-$, $[VO(O_2)_2(H_2O)]^-$, $[VO_2(O_2)_2]^{3-}$, $[VO(O_2)_3]^{3-}$, $[V(O_2)_3]^-$ and $[V(O_2)_4]^{3-}$,[414, 389] for example, are formed and the number of peroxo groups coordinated to a vanadium center generally increases with an increase in pH or alkalinity of the reaction solution. However, investigations on peroxovanadates outdate the physical isolation of $[V(O_2)_4]^{3-}$ species though it has been confirmed in independent experiments that an unstable blue–purple species is present in solutions at pH > 9.3 and at very high peroxide concentrations.[414b]

The involvement of peroxovanadates as catalysts in living systems was realized in 1983-84 when Vilter *et al.* reported the discovery of the vanadium bromoperoxidase (VBrPO)[415] enzyme from the marine algae *Ascophyllum nosodum*. The haloperoxidases (of which VBrPO is a member) are a group of enzymes which usually contain the FeHeme moiety or vanadium as an essential constituent at their active site, though a few haloperoxidases which lack a metal cofactor are also known.

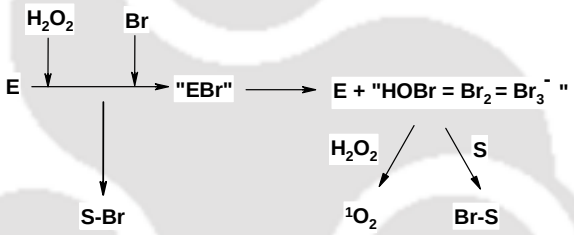
Vanadium haloperoxidases (VHPO) are found in marine algae, lichens and certain terrestrial fungi and are known to catalyze the halogenations, such as chlorination, bromination

and iodination, of organic substrates or the halide-assisted disproportionation of hydrogen peroxide (**Scheme1.8**)



Scheme 1.8 Proposed Catalytic Cycle for VHPO

Spectroscopic evidence reveals that it is the equivalent of hypobromous acid, bromine, tribromide, or an enzyme-bound bromonium ion-type species that can halogenate appropriate organic substrates (or react with another equivalent of hydrogen peroxide, forming dioxygen). This has been illustrated in **Scheme 1.9**.[416]



Scheme 1.9 Reaction Scheme Showing Substrate Binding to VBrPO

VO_2^+ is regarded as a functional mimic of VBrPO although, unlike VBrPO, it functions in acid and at much lower turnover rates.[417] *Cis*-dioxovanadium(V) in acidic solution coordinates 1 or 2 equiv of hydrogen peroxide forming the red monoperoxo, $VO(O_2)^+$, or the yellow diperoxo, $VO(O_2)_2^-$ species, as described by the following equations

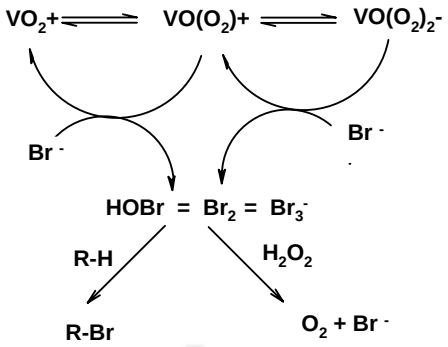
$$VO_2^+ + H_2O_2 \leftrightarrows \underset{\text{(red)}}{VO(O_2)^+} + H_2O$$

$$VO(O_2)^+ + H_2O_2 \leftrightarrows \underset{\text{(yellow)}}{VO(O_2)_2^-} + 2H^+$$

and it is believed[418] that under more acidic conditions (pH $\leq$ 2), dioxotriperoxodivanadium(V), $(VO)_2(O_2)_3$, forms from the dimerization of $VO(O_2)^+$ and $VO(O_2)_2^-$:

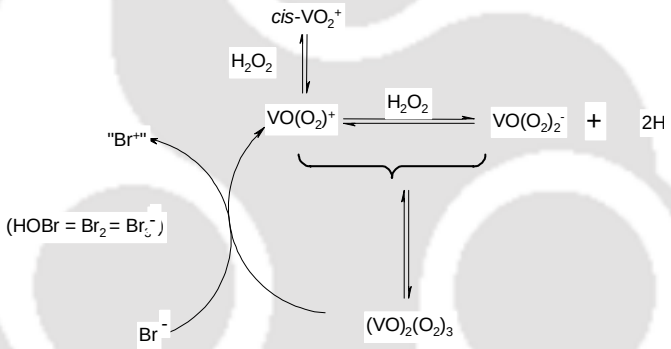
$$VO(O_2)^+ + VO(O_2)_2^- \leftrightarrows (VO)_2(O_2)_3$$

Though both monoperoxo and diperoxo vanadium(V) species are capable of bromide oxidation and hydrogen peroxide disproportionation (**Scheme 1.10**),[419]



Scheme 1.10 VO_2^+-Catalyzed Oxidation of Bromide by Hydrogen Peroxide

kinetic and spectroscopic evidences cause certain schools to believe that it is the triperoxovanadium(V) complex, $(VO)_2(O_2)_3$, that is actually involved in the oxidation of Br^-.[418,420] This has been explained schematically in **Scheme 1.11**, though this perception may be regarded as contentious.



Scheme 1.11 Proposed Mechanism of Bromide Oxidation involving a $(VO)_2(O_2)_3$ Intermediate

However, the aforementioned discussions are convincing enough to believe that the synthesis of mimics of the naturally occurring vanadium peroxidase enzymes is a very important area of research in itself. Importantly, an understanding of their reactivity profiles provide important cues to the development of bromoperoxidase mimics as greener alternatives to the environmentally noxious brominating agents. But a full appreciation of this relevance requires that the importance of bromination chemistry be fully appreciated.

Also naturally occurring organobromines, which range in structural intricacy from the simple but enormously abundant bromoform ($CHBr_3$) and bromomethane to the highly complex bryozoan bromine-containing indole alkaloids, are produced by marine and terrestrial plants, marine animals (sponges, tunicates, bryozoans, gorgonians, sea hares, nudibranchs), bacteria, fungi, some higher animals, and a few mammals including human. In the chemical industry bromo-compounds are widely used as intermediates in the manufacture of pharmaceuticals,

agrochemicals, flame retardants and other speciality chemical products[421] as some of the important activities of bromoorganic compounds include antifungal, antibacterial, antineoplastic, antiviral (e.g., anti-HIV) and anti-inflammatory actions.[421-423] The naturally occurring key bromoorganics provide a scope for studying bromination process adopted by the nature and thus adding value to the versatility of the brominating agents.

In the context of the present research it is necessary to mention that bromine (Br_2) is commonly used in most bromination reactions even though the reagent is extremely toxic and corrosive in both liquid and vapor forms. Moreover, the atom accountability in reactions involving bromine shows clear trends of inefficiency and waste. Therefore, what is now required is the identification of alternative reaction conditions and solvents for improved selectivity and energy minimization using less toxic and inherently safer chemicals, leading to the discovery and development of not only newer reagents but also newer synthetic pathways using environmentally benign chemistry.

Also the noxious and corrosive nature of Br_2 in both liquid and vapor form makes its transportation, storage and handling extremely difficult and risk proned.[424-426] Under the given situation, economically viable routes to bromination of organics with the adaptation of eco-friendly routes are necessarily going to be the protocols of choice.

Interestingly, marine natural chemicals contain bromometabolites that are important as they are responsible for providing defense mechanism to the marine lives.[423] What is equally interesting to note is that the metal, vanadium occurs in its pentavalent state in VBrPO and that it does not undergo any redox cycling in the catalytic bromination process.[422] Several groups of researchers [427-430] believe that an oxidized bromide exists in solution as:

$$OBr^- \leftrightarrows Br_2 \leftrightarrows Br_3^-$$

Knowledge obtained from such studies in conjunction with the existence of Br_3^- in solution (λ=267 nm)[431-433] in high concentration caused us to believe that Br_3^- could be not only generated in solution but also isolated in the solid state by providing an appropriate counter cation. This knowledge guided us[154,412,413] to develop an eco-friendly general route to the synthesis of quaternary ammonium tribromides (**QATBs**) with QA being tetramethylammonium (**TMA**), tetraethylammonium (**TEA**), tetrabutylammonium (**TBA**) or cetyltrimethylammonium (**CTMA**) followed by probing their efficacy as very effective brominating agents. However, the synthesis of quaternary ammonium tribromides were carried out in solution, which involved the formation of a peroxo-metal complex from the reaction of the catalyst (V_2O_5 or $H_2MoO_4.H_2O$) with H_2O_2 which in turn oxidized Br^- to Br_3^- in the presence of an acid. The aforementioned

method works quite well but is somewhat wasteful because it (i) uses excess amounts of H_2O_2 and H_2SO_4, and (ii) is rather time taking. In view of these it might be worthwhile to develop a rather economic protocol for the synthesis of quaternary ammonium tribromides.

While trying to bring the reaction chemistry of peroxovanadium complexes to the fore, the importance of synthesis of simple peroxo and heteroligand peroxovanadates cannot be underestimated. In view of the intrinsic interest in and contemporary importance of such compounds, as well as in a continuation of our endeavor in the field of peroxo-metal systems, it was thought relatively appropriate to synthesize types of compounds especially to study their reactivity. A knowledge of synthetic peroxo-metal chemistry entailing structural characterization is important for this purpose. Pertinently, in recent years there has been a remarkable advancement in the synthetic chemistry of peroxovanadium(V) through the endeavor of several groups of workers[378-381, 386-394,319, 434, 435-437] Yet there exists a good deal of continued interest in the synthesis of newer monoperoxovanadates(V)[438-441] in specific heteroligand environment owing to the biochemical significance, e.g. insulin mimic,[442, 443] and importance in the oxidation chemistry for the activation and oxygen transfer reactions. In any case isolation of such compounds in the solid state and characterization are the prerequisites.

Additionally, the wide occurrence of vanadium[444-449] in biological systems[450-452] has, over the recent years, aroused intense investigations, seeking to delineate its biochemical role and mode of action in, what appears to be, a diverse spectrum of biocatalytic processes. As an abundant transition element, vanadium is now known to exist in alternative nitrogenase metalloenzyme systems fixing nitrogen,[453] haloperoxidases oxidizing halides ultimately incorporated in organic substrates,[454-456] and others. Moreover, vanadium has been discovered to participate in biological processes exhibiting mitogenic behavior,[457, 458] enzyme inhibition[459-463] or activation of a plethora of metabolic functions.[464-468] In this capacity, vanadium has been involved in interactions with a number of enzymes such as phosphoglucomutases.[469,470] Among the properties of vanadium, however, its insulin mimetic action in the important symptomatic clinical condition of diabetes stands prominent.[471-477] The latter physiological aberration has, indeed, spurred considerable research activity, targeting the underlying (bio)chemistry of that element in biological fluids and its interactions with biological macromolecules, ultimately contributing to insulin mimetic action. To that effect, a number of ligands have been employed in the exploration of the chemistry of vanadium in various solvent systems and in biologically relevant oxidation states, such as V(IV) and V(V).[478]

Ligands can potentially be tailored to modulate systematically redox potential, electron-transfer rate, and magnetic moment of the bound metal ion.[479] One can also theoretically predict

the steric strain within coordination metal complexes[480] and modulation of electronic characteristics of the metal ion by complexation.[481] Other properties, such as solvation and stability of binding with commonly encountered biomolecules, may be harder to anticipate, based on empirical considerations.[482]

An ability to tailor the physical properties of the ligand with regard to hydrophilic/ lipophilic balance is of particular importance with respect to transport of metal ions across biological membranes.[483] A stronger affinity between ligand and metal would be expected to alter the in vivo substitution chemistry with endogenous ligands of both low molecular mass (e.g. citrate, ascorbate and glutathione) and high molecular mass (e.g. transferrin and albumin).[484] An available strategy for improving biological functionality may be to include sulphur coordination for potentially useful enzyme binding *in vivo*,[485] or to introduce carbohydrate moieties for preferred membrane transport.[486]

Among the ligands employed so far carboxylic and (poly)carboxylic acids are more relevant to mention in the context of the present work. Outstanding among these organic acids are tricarboxylic as well as dicarboxylic acids. Citric acid, as one of the abundantly encountered tricarboxylic acids, is a biologically relevant molecule existing in biological fluids (at a concentration of ~0.1 mM),[487,488] playing keyroles in a number of catalytic processes, such as the Krebs cycle.[489, 490] In addition, (R)-2-hydroxy-1,2,4-butanetricarboxylic acid [(R)-homocitrate] has been recently reported to be an integral constituent of the inorganic iron-molybdenum cofactor of dinitrogenase.[491,492] Sparse information still exists in the case of a number of vanadium-peroxo–ligand systems, seeking to investigate and to provide clues on low MW species existing in aqueous solutions in the physiological pH range. In the case of the vanadium-peroxo–citrate system, a few reports exist[493-496] on the aqueous chemistry of the two biologically related partners leading to structurally characterized complexes. As a logical sequel to our work, preparation of such compounds and investigation of their reaction profiles are quite in order.

SCOPE OF WORK

As a global concern, one sees rapid increase in recycling initiatives have positive impacts on many aspects of day-to-day living. However, numerous questions remain about the optimum processes, the ultimate yields, and the "true contribution to sustainability'. Chemists deserve to be regarded as trendsetters in recycling practicing, an important aspect of a broad interdisciplinary subject, "Recoverable Catalysts and Catalytic systems". This area is attracting increasing attention and has earned cachet under the awareness for "Green Chemistry." While thinking about inorganic catalysts, one can not afford to ignore metal acetylacetonates. Metal

acetylacetonates are highly versatile compounds and have been used in a multitude of applications. It thus becomes incumbent upon a chemist to explore newer facets of metal acetylacetonate chemistry eventually leading to an entry into the domain of "Recoverable Catalysts and Catalytic systems." One of the rational alternatives is to use a water soluble metal acetylacetonate to study organometallic reactions like Barbier coupling with water as the solvent of choice demonstrating a case of homogeneous catalysis. Importantly, metal acetylacetonate complexes can be well heterogeneized using different techniques like immobilization in organic supports (*c.f.* polystyrene) or inorganic supports such as titania or even in ionic liquids. The catalyst being so heterogeneized should be evaluated in terms their efficacies for important reactions like nitrene transfer reactions with specific references to aziridination and sulfimidation, and also for sulfide oxidations.

In the realm of application of inorganic reagents in organic chemistry, oxo-metal-based oxidants based on chromium(VI) and manganese(VII) perhaps qualify to be the best known oxidizing agents. Indeed these type of reagents are very commonly used in both bench scale as well as on large scale partial oxidation processes. An important point to be noted in this context is that the use of such oxidants on a large scale leads to a rather large volume of toxic metal wastes. Also, most of the processes are based on reactions in solutions. Having been encouraged by the affirmative potential of and the attention received by pyridinium fluorochromate(VI) (**PFC**) since its first report in 1982,[289] and being rightly influenced by the tenets of 'Green Chemistry', it was considered incumbent on us to develop its economic synthesis, since it is so frequently used, and ascertain its efficacy in solvent-free oxidative transformations including selective oxidations, Δ^5-steroidal oxidations, deoximations and deprotections. It may be noted that Δ^5-steroidal oxidations with **PFC**-CH_2Cl_2 or **PFC**-CH_3CN did not work so well. Further, our easy access to many such reagents prompted us to explore solvent-free oxidation chemistry of 3,5-dimethylpyrazolium fluorochromate(VI) (**DmpzHFC**), a companion reagent of **PFC** of very recent origin. Additionally, it would be interesting to look into the possibility of using these reagents as catalysts so as to enable us minimize the amount of chromium wastes.

As a sustained scientific curiosity in reaction chemistries of various inorganic species, our attention was drawn to brominations including oxidative bromination. Bromination of organic molecules is an important chemical process especially when it is used to generate highly useful intermediates for the manufacture of pharmaceuticals, flame retardants, agrochemicals and other specialty chemicals, and to selectively activate functional groups in molecules. General methods that are largely used in practice involve elemental bromine (Br_2) because of its cost-effectiveness and versatility, even though elemental bromine in any of its forms is very toxic,

corrosive being highly detrimental to health and hazardous to the environment. As the cost involved in the use of Br_2 in the processes of transportation and storage, unless it is manufactured at site, is not just a trivial issue. Thus, in order to evade these problems, a rational choice would be to look into the cleaner synthesis of organic ammonium tribromides, 'store houses' of bromine, and investigate their efficacy in solid phase bromination of organics. It is pertinent to mention that solid-phase reactions appear to be very promising alternatives to reactions in solution especially if they are more selective and efficient to afford sensitive products that are rather difficult, tedious, and at times impossible, to obtain in solution.

While dwelling on clean bromination and safer brominating agents, [154,412,413] the contribution of peroxo-metal reaction chemistry, in particular the reactivity of peroxovanadates(V), figures upper most in the mind. Our research group has been highly endowed with the knowledge being gained from the studies on peroxo-vanadium chemistry. In fact it is the consequence of investigation of reaction chemistry of peroxo-vanadium(V)[404-413,154] that provided our research group an entry into the bromo-organic chemistry research including improvising cleaner routes to brominating agents. As a logical extension of our long and extremely rewarding alliance with the peroxo-vanadium chemistry,[386-394,404-413,154] it was considered important to develop newer heteroligated monoperoxovanadates(V), characterize them and then explore their catalytic properties. As a matter of ready information, it may be recalled that a vast majority of our earlier synthetic works on peroxo-vanadium(V) compounds were addressed di and triperoxo-vanadates(V) with very little emphasis on the monoperoxovanadates(V). It was emphasized in our previous studies that the number of coordinated peroxo ligands increases with the increase in pH of the reaction solution and the chances of polymerization decreases with the increase in H_2O_2 concentration. Taking cues from these, it is argued to be quite rational to conduct H_2O_2 – vanadium reactions at pH 3 or 4 and with a relatively excess amount of H_2O_2 if one were to successfully synthesize a monomeric monoperoxo complex of pentavalent vanadium. The choice of heteroligand may go in favor of citric acid for a variety of reasons including the evidence that in the process of purification and characterization of the vanadium enzymes, the bromoperoxidases, (VBrPOs), two operations are directly related to the properties of the peroxo(citrato)vanadates(V). The first of which is the formation of a product with a λmax of 420 nm that gradually converts in slightly acidic solution into a different species with increasing the absorption at 460 nm.[415] Second, a citrate/phosphate buffer is used, and consequently bonding of some citrate to vanadium is likely. In monoperoxovanadate (V) the LMCT bands occur typically between 415 and 430 nm and in

more acidic solution they gradually develop the absorption at 450-460 nm due to the formation of VO-$(O_2)^+$ cation.[440]

One of the major aims would be to first synthesize low molecular weight monoperoxo(citrato)vanadates(V), characterize them as well defined chemical entities and then use as catalysts. Time may not permit during the present Ph.D. research, to evaluate their insulin mimic activity though such complexes would be candidates worth investigating.

The subject matter of the thesis has been divided into six chapters. While the present chapter highlights background of the relevant aspects of catalysis, metal acetylacetonate, oxofluorochromate, tribromide and peroxovanadate chemistries, **it also identifies some of the problems considered imperative and worth investigating thereby providing the scope of the work**. **Chapter 2** describes the sources of chemicals and solvents that were used in the work, methods of preparation of a few starting materials, details of the methods of chemical analyses, and particulars of various instruments and equipment used for physico-chemical studies and characterization of the reported compounds. The main themes of **Chapter 3** are newer preparations of selected metal acetylacetonates, and application of $Co(acac)_2.2H_2O$ in a homogeneous catalytic Barbier coupling of carbonyl with allyl halide in water as well as heterogenization of a few chosen metal acetylacetonates catalysts e.g. $Cu(acac)_2$ and $VO(acac)_2$ for aziridination and sulfimidation, and sulfide oxidation, respectively. **Chapter 4** contains the economic synthesis of pyridinium fluorochromate(VI), $C_5H_5NH[CrO_3F]$ (**PFC**), and solvent-free oxidation of organic substrates with PFC. Also its application as a catalyst for the oxidation of benzylic bromide to benzaldehyde has been brought to attention. In addition, solvent-free as well as catalytic oxidations of organic substrates by 3,5-dimethylpyrazolium fluorochromate(VI), $C_5H_8N_2H[CrO_3F]$ (**DmpzHFC**), has been presented therein. **Chapter 5** focuses on economic as well as solid-phase synthesis of quaternary ammonium tribromides (**QATB**s). In addition, the versatility of quaternary ammonium tribromides (**QATB**s) as brominating agents for solvent-free as well as water assisted bromine-less bromination of some chosen organic substrates are described in the chapter. **Chapter 6**, the concluding chapter of the thesis, gives an account of synthesis and structural assessment of a few peroxo(hetroligand)vanadate(V) complexes of general formula $M[VO(O_2)(C_6H_6O_7)].H_2O$ with citrate ion ($C_6H_6O_7^-$) as the heteroligand of choice and NH_4^+, Na^+, K^+, Rb^+ or Cs^+ as the counter-cation. Preliminary characterization and evaluation of their ability to oxidize bromide, organic sulfide and benzylic and α, β-unsaturated alcohols very efficiently has also been described in the same chapter. It has been endeavored to present each chapter as a self contained one with a

brief introduction, sections on experimental and results and discussion followed by relevant bibliography.

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Method of Preparation of Starting Materials, Elemental Analyses and the Details of Equipment used for Characterization and Structural Assessment of the Compounds

Chapter 2

A comprehensive account of the procedures adopted for preparation of some of the starting materials, the details of the methods used for quantitative determination of various constituents and the relevant particulars of the instruments/equipment used for the characterization and structural assessment of the newly synthesized compounds are described in this chapter.

All the chemicals and solvents used were of analytical grade quality. Following are the sources of the chemicals and solvents: s.d.fine-chem ltd, Qualigens Fine Chemicals, E. Merck (India) Limited, Sisco Research Laboratories Pvt. Ltd, Central Drug House (P) Ltd, Bengal Chemicals and Pharmaceuticals Ltd, Loba Chemie Industries, Spectrochem (India), Ranbaxy Fine Chemical Ltd, Aldrich Fine Chemicals, and Fluka.

Preparation of starting materials

[*N*-(*p*-tolylsulfonyl)imino] phenyl iodinane, PhI=NTs [1]

A suspension of p-toluenesulfonamide (6.5 g, 47 mmol) and 85% KOH (6.5 g, 99 mmol) in methanol (60 mL), was cooled in an ice water bath, and iodosobenzene diacetate (15 g, 47 mmol) was added portion wise over a period of 10-20 min so that the internal temperature could be maintained below $+10^0$C. The reaction mixture was refrigerated at $+5^0$C over night and then filtered. The solid was then dried *in vacuo* over fused $CaCl_2$ affording PhI=NTs as an off-white yellowish solid. Yield:12 g (80%).

1-butyl-3-methyl imidazolium chloride, BMIC [2a]

A mixture of n-butyl chloride (0.40 mol, 37.04 g) and 1-methylimidazole (0.40 mol, 31.9 g) was stirred at 70-80 ^{0}C for 1 or 2 days under nitrogen. The mixture was cooled to room temperature and ethyl acetate (70 mL) was added causing precipitation of 1-butyl-3-methyl imidazolium chloride as a white solid which was recovered by filtration and washed with ethyl acetate followed by ethyl ether. Yield: 43.52 g (63%).

1-butyl-3-methyl imidazolium tetrafluoroborate, BMIM.BF_4 [2a]

The 1-butyl-3-methyl imidazolium chloride salt was added to a suspension of $NaBF_4$ (1.2 equiv, 52.7 g 0.48 mol) in acetone (150 mL). After the mixture was stirred for 48 h at room temperature, the sodium chloride precipitate was removed by filtration and the filtrate concentrated on an oil (~100 mL) by rotary evaporation. This oil still contained some 1-butyl-3-methyl imidazolium chloride because it gave a precipitate when mixed with aqueous silver nitrate. The oil was (~100 mL) was dissolved in methanol (100 mL) and an aqueous solution of $AgBF_4$ (generated from the reaction of Ag_2O with HBF_4) was added drop wise until no more precipitate

was formed. The mixture was filtered through Celite (no. 545), concentrated by rotary evaporation, dissolved in dichloromethane (100 mL), and filtered again to remove insoluble material. The product was purified by column chromatography in three portions on silica gel (~400 g) eluted with dichloromethane/methanol (9:1). The solvent removed under vacuum yielded pale yellow oil. Yield: 78.10 g (72%).

1-butyl-3-methyl imidazolium hexafluorophosphate, BMIM.PF_6 [2b]

To a solution of BMIC (9.3 g, 53.1 mmol) in acetone(50 mL) at room temperature was added sodium hexafluorophosphate (5.83 g, 53.1 mmol). After 24 h of stirring, the reaction mixture was filtered through a plug of celite (l =3 cm) and the volatiles were removed under reduced pressure to obtain the title compound. Yield:10.8 g (90%).

3,5-dimethylpyrazole (dmpz) [3]

A methanolic solution of 25 mL of hydrazine hydrate, $N_2H_4.H_2O$, (25.0 g, 499.4 mmol) was added slowly with stirring to a methanolic solution of 25 mL of acetylacetone (25.0 g, 249.7 mmol) in an ice-cold condition. A light yellow solution was obtained. The solution was concentrated to *ca.* 20 mL on a steam-bath and left overnight in a refrigerator. A white crystalline compound was obtained and this was isolated by filtration, washed 4 or 5 times with water and dried in air. The yield of pure 3,5-dimethylpyrazole (dmpz) was 23.5 g (98 %).

M.p. 107 or 108 °C.

Preparation of 3,5-dimethylpyrazolium fluorochromate(VI), $C_5H_8N_2H[CrO_3F]$, (DmpzHFC) [4]

To a solution of 5.6 g (56 mmol) CrO_3 in 2.5 mL water prepared in a 100 mL polyethylene beaker, 5 mL (120 mmol) of 48% HF was added with stirring. An orange red solution was obtained. The reaction mixture was then cooled in an ice-bath (0-5 °C) and 5.6 g (58.33 mmol) of 3,5-dimethylpyrazole was added in parts with stirring when an orange crystalline compound separated out. This was filtered under vacuum using a polyethylene funnel and washed with petroleum ether (3x10 mL). It was then rapidly dried in a vacuum desiccator and finally stored in a sealed polyethylene bag in a freezer. The isolated yield of the compound was found to be 11.6 g (92%) and melting point was recorded to be 46-48 °C.

Elemental analyses

Vanadium [5]

Vanadium was estimated iodometrically.

An accurately weighed amount (*ca.* 0.1 g) of vanadium compound was dissolved in 100 mL of water. To the solution was added 5 mL of 5M H_2SO_4. The solution was boiled for

10 min to remove peroxide. To this solution was added 5 g of potassium persulphate followed by the addition of one drop of silver nitrate solution. The resultant mixture was boiled for 1 h. After this 15 mL of 5M H_2SO_4 was added and the solution boiled for a further period of 30 min. The solution was allowed to cool to room temperature and *ca.* 2 g of KI was added with stirring. This was then kept in the dark for 15 min. The liberated iodine was titrated with standard $Na_2S_2O_3$ solution using starch as an indicator. The end point was detected by the appearance of a light-blue colour.

1 mL of 0.1 M $Na_2S_2O_3$ = 0.00519 g of vanadium

Chromium [5]

Chromium was estimated iodometrically.

An accurately weighed amount (*ca.* 0.1 g) of a chromium(VI) compound was dissolved in water (*ca.* 120 mL) by slight warming. The solution was cooled to room temperature and acidified with 10-12 mL of 5M H_2SO_4 followed by the addition of *ca.* 2 g of KI with stirring. The whole was kept in the dark for *ca.* 15 min. The liberated iodine was titrated with standard sodium thiosulphate solution in carbon dioxide atmosphere.

1 mL of 0.1 M $Na_2S_2O_3$ = 0.0052 g of chromium

[In case of lowervalent chromium compound (say Cr(IV), it was first oxidized to chromium (VI) with a silver catalyzed persulfate oxidation and then proceeded for the estimation of the metal content.]

Copper [6]

Copper was estimated iodometrically.

An accurately weighed amount (*ca.* 0.1 g) of a copper (II) compound was dissolved in water (*ca.* 120 mL) by slight warming. The solution was cooled to room temperature and acidified with 10-12 mL of 5M H_2SO_4 followed by the addition of *ca.* 2 g of KI with stirring. The whole was kept in the dark for *ca.* 15 min. The liberated iodine was titrated with standard sodium thiosulphate solution in carbon dioxide atmosphere.

1 mL of 0.1 M $Na_2S_2O_3$ = 0.0064 g of copper

Cobalt [7]

Cobalt was estimated gravimetrically.

An accurately weighed amount (*ca.* 0.1 g) of a cobalt compound was dissolved in 200 mL water containing concentrated hydrochloric acid. To it 5-6 mL of oxine reagent (a 10% solution in 20% acetic acid) and 5 g of urea were added. The beaker was covered with clockglass and the whole was heated on an electric hot plate at 95^0C for 2.5 h. Precipitation was complete with the

supernatant liquid, originally greenish yellow, acquiring a pale orange-yellow color. It was allowed to cool and the precipitate was collected in a sintered-glass filtering crucible (porosity no. 3 or 4), washed with a little hot water and finally with cold water. The crucible containing the precipitate was dried at 130^{0}C to constant weight.

Co(II) compound was weighed as $Co(C_9H_6ON)_2$ and Co(III) as $Co(C_9H_6ON)_3$.

Iron [8]

An accurately weighed amount (*ca.* 0.1 g) of a Iron (III) compound was dissolved in water (*ca.* 120 mL) by slight warming. The solution was cooled to room temperature and acidified with 5M H_2SO_4 to maintain a pH of 2-3; Congo red paper was used to the first percipatble color change. It was followed by the addition of 5 drops of variamine blue indicator and the whole was warmed at 40 ^{0}C. The solution was titrated with standard EDTA solution until the initial blue color of the solution turns grey just before the end point, and the final drop of reagent chamges to yellow.

1 mL of 0.1 M EDTA = 0.0056 g of Iron

Sodium, Potassium, Rubidium and Cesium [9]

Sodium, potassium, rubidium and cesium contents were determined by flame photometry. A solution containing sodium or potassium ions was acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Fluoride [9]

An accurately weighed amount (*ca.* 0.1 g) of the fluoride containing compound of chromium was dissolved in 150 mL of water. The solution containing fluorochromate (VI) compound was boiled with 20 – 25 mL of 0.1 M NaOH for *ca.* 30 min. Hydrazine monohydrate was then added to the warm solution drop by drop to reduce Cr(VI) to Cr(III) and precipitate the metal as hydrated Cr(III) oxide [*c.f.* $Cr(OH)_3$]. The solution was digested on a steam-bath for *ca.* 30 min. and filtered to separate the hydrated oxide. The residue was washed thoroughly with water. To the combined filtrate and washings, two or three drops of bromophenol blue indicator and 3 mL of a 10% sodium chloride solution were added and diluted to *ca.* 250 mL. 6 M nitric acid was added to it until the color just changed to yellow followed by the addition of 0.1 M NaOH solution until the color changed to blue. The mixture was then treated with 1 mL of conc. HCl and 5 g of $Pb(NO_3)_2$ and heated on a steam-bath. After all the lead nitrate had dissolved, 5 g of crystallized sodium acetate was added to the solution and the solution digested on a steam-bath for *ca.* 30 min. with occasional stirring. A white precipitate of PbClF formed which was then allowed to stand overnight.

The precipitate was filtered through a Whatman 542 filter paper, washed five or six times with water to make it free from chloride. The precipitate was dissolved in 1% HNO_3 by slight warming. A known excess of standard $AgNO_3$ (0.1 M) solution was added and the suspension of AgCl heated almost to boiling and stirred vigorously. The beaker and its contents were kept in the dark for 1 h, the precipitated AgCl was filtered out and washed with water. The unreacted $AgNO_3$ was finally titrated with standard KSCN solution using $Fe(NO_3)_3$ as indicator. The end point was marked with the appearance of a faint-red brown colour. The volume of $AgNO_3$ in the filtrate thus found was subtracted from the amount that was originally added. The fluoride content was calculated from the volume of $AgNO_3$ solution consumed.

1 mL of 1 M $AgNO_3$ = 0.019 g of fluoride

Bromide [10]

Bromide was estimated volumetrically following Volhard's method.

An accurately weighed amount (*ca.* 0.1 g) of organicammonium tribromide was dissolved in 20 mL of acetonitrile. The solution was treated with 20 mL of a 20% NaOH solution, followed by the addition of 100 mL of water. The solution was boiled for 1 h and acidified with dilute (1:1) HNO_3. The acidified bromide solution was then treated with an excess of 0.1 M silver nitrate solution. The suspension was heated almost to boiling and stirred vigorously. The beaker along with the suspension was kept in the dark for 30 min. The precipitated AgBr was separated out by filtration and washed several times with water. The filtrate and the washings were collected and the unreacted $AgNO_3$ was titrated with standard KSCN solution using $Fe(NO_3)_3$ as indicator. The end point was marked by the appearance of a faint red – brown colour. From the equivalence of standard $AgNO_3$ and standard KSCN solutions, the volume of excess $AgNO_3$ was calculated and this was subtracted from the volume of $AgNO_3$ that was initially added. The difference is the volume of $AgNO_3$ solution consumed.

1 mL of 1 M $AgNO_3$ = 0.0799 g of bromide

Peroxide

(a) Permanganometry [11]

Nearly 1 g of boric acid was dissolved in 100 mL of water taken in a conical flask. To this was added an accurately weighed amount (*ca.* 0.1 g) of peroxo compound followed by the addition of 7 mL of 5M H_2SO_4. The solution was shaken well to dissolve the compound. The

peroxide was then estimated by redox titration with standard $KMnO_4$ solution. The end point was marked by the appearance of a permanent faint pink colour.

1 mL of 0.2 M $KMnO_4$ = 0.016 g of peroxide (O_2^{2-})

(b) Iodometry [11]

To a freshly prepared 2 M sulphuric acid solution, containing an appropriate amount of potassium iodide (~2 g in 100 mL) was added an accurately weighed amount (*ca.* 0.1 g) of a peroxo compound with stirring. The mixture was allowed to stand for *ca.* 15 min in carbon dioxide atmosphere in the dark. The amount of iodine liberated was then titrated with a standard sodium thiosulphate solution, adding 2 mL of freshly prepared starch solution when the colour of the iodine was nearly discharged.

1 mL of 1N $Na_2S_2O_3$ = 0.01701 g of peroxide (O_2^{2-})

[In case of a peroxovanadate(V) complex, this method gives the total amount of peroxide plus vanadium present in the compound. On deduction of the contribution of vanadium (V) from the total amount of iodine liberated, the net peroxide content of the compound is evaluated.]

Carbon, Hydrogen and Nitrogen

The carbon, hydrogen and nitrogen contents were estimated by micro-analytical methods. The results of the analyses were obtained using a 2400 Perkin Elmer Series II CHNS/O Analyzer which is available at Department of Chemistry, IIT Guwahati.

Particulars of Instruments/Equipment used for the following Physico-Chemical Studies

pH Measurement

pH values of the reaction solutions were recorded with a Systronics Type 335 digital pH meter and also by using Merck pH indicator paper.

Solution Electrical Conductance Measurement

Solution electrical conductance measurements were measured on a Systronics Type 304 direct digital reading conductivity meter. Solution strength was maintained at 10^{-3} M in appropriate solvents.

Recording of Melting Point

Melting points of the compounds were recorded using a MP1 V-Scientific melting point apparatus and a Type B-540 Buchi melting point apparatus. The heating rate was maintained at 1°C per min.

Infrared Spectroscopy

Infrared spectra of the compounds were recorded as KBr pellets, as nujol mulls or as thin films using a Nicolet Impact–410 Fourier Transform Infra Red Spectrophotometer.

Electronic Absorption Spectroscopy

UV-visible spectra were recorded, by dissolving a calculated amount of the sample in an appropriate solvent, on a Hitachi UV–visible U–2001 Spectrophotometer.

^{1}H Nuclear Resonance Spectroscopy

^{1}H NMR spectra were recorded either on a Varian 400 MHz NMR spectrophotometer using tetramethylsilane (TMS) as internal standard.

Thermal Studies

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) experiments were conducted on a Mettler-Toledo TGA/SDTA 851^e and DSC 821^e instruments. Experiments were done using either aluminium or platinum crucibles. Pure N_2 gas was used as the flow gas.

Gas Chromatography

Gas chromatographic analysis was done on a Hewlett Packard HP 6890 GC system with the aid of an FID detector by using a SE-30 capillary column. In all cases, nitrogen gas was used as a carrier gas. The results were recorded on an HP 3395 integrator.

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Newer Preparation of Metal Acetylacetonates and a few Heterogeneously and Homogeneously Catalyzed Reactions by Metal Acetylacetonates*

*A part of this chapter constitutes the subject of a patent and a few publications:

1. US Patent Appl. Pub., Pub. No.: US 2004/0126308 A1, Pub. Date: Jul. 1, 2004, Appl. No. 10/335,105, Appl. Date: Dec. 31, 2002
2. *Tetrahedron Letters*, **2003**, *44*, 9029.
3. *Catalysis Letters*, **2004**, *95*, 19.

Chapter 3

Metal acetylacetonates have received significantly increasing attention and the compounds are obviously of great interest considering applications not only in basic research but also in industrial processes.

To begin with it was necessary to address a few issues related to their synthesis, so as to enable us get the compound rather easily and minimize the burden on environment due to waste. In concordance with this, endeavor has been made to first improvise a new synthetic protocol and then develop catalysts with advantages over the existing ones suitable for allylation, aziridination, sulfide oxidation and sulfimidation. Newer preparations of selected metal acetylacetonates, and application of $Co(acac)_2.2H_2O$ in a homogeneous catalytic reaction in water as well as heterogenization of a few chosen metal acetylacetonates catalysts such as $Cu(acac)_2$ and $VO(acac)_2$ are the main theme of **Chapter 3**. The subject matter of this chapter is divided into four sections. **Section 3.1** describes solvent-less and peroxometal(inter)mediated synthesis of selected metal acetylacetonates. The main focus of **Section 3.2** is on $SnCl_2$ mediated and $Co(acac)_2$ catalyzed Barbier coupling of carbonyls with allyl halide. Immobilized copper(II) acetylacetonate catalyst for heterogeneous nitrene transfer reactions has been described in **Section 3.3**, while **Section 3.4** contains $VO(acac)_2$ supported titania catalyzed sulfide oxidation.

Solvent-less and Peroxometal(inter)mediated Synthesis of Selected Metal Acetylacetonates

Section 3.1

Metal acetylacetonates are compounds which find tremendous applications in both basic research as well as industrial processes. Some important applications are (i) as catalysts in polymerization and in important organic chemical transformations,[1-20] (ii) in super critical fluid transport (SFT) CVD of thin films,[21] (iii) in electronic engineering and laser technology,[22,23] (iv) in inorganic crystal engineering,[24] (iv) in nanoparticle synthesis,[25,26] and (v) in diesel fuels as carbon scavengers, and (vi) in rocket fuel, as combustion control catalysts, as components in functional fluids and as components of solid propellants.[27] Because of these and other applications, these compounds have always engaged the attention of researchers over the ages.

In so far as the synthesis of such compounds is concerned, prior to the eighties, an easy access to pure metal acetylacetonate compounds had been somewhat difficult owing to several problems, such as p*H* control, requirement of large excess of buffers, end-product contamination, solubility, involvement of extra preparation steps and difficulties encountered in the handling of air-sensitive and toxic materials that were sometimes required for the preparation of such materials.[28-30] In an effort to alleviate these problems, newer methods of syntheses were reported by our group in the early eighties[31-40] by exploiting separately the chelating ability of acetylacetone and also its potential as a reducing agent. Though the direct syntheses of a host of metal acetylacetonates were possible by those methods, the processes were expensive and wasteful because the reactions were non-stoichiometric and required large excesses of the reagents. Hence improvement of yield was the primary concern and the efficient use of reactants from the standpoint of atom economy was ignored. However, since the multifarious uses of metal acetylacetonates render them commercially important, cost-factor becomes an important consideration.

Furthermore, in recent years, there is also a growing realization of the concepts of 'Green Chemistry' that has resulted in an alteration in the way chemists develop processes and products.[41] The current chemistry scenario therefore demands the development of more and more benign synthetic pathways which in addition to being high yielding, should be simple and exhibiting high atom efficiency, should have reduced number of steps and no waste, are safer and environmentally acceptable.

In keeping with this and as part of our continuing interest in the 'greener' synthesis of 'useful compounds', we describe herein the solvent-less and peroxometal(inter)mediated protocols for the synthesis of metal acetylacetonates, which seem to have by far the best record of atom economy, cost-effectiveness and pollution prevention.

EXPERIMENTAL SECTION

The sources of chemicals and solvents, methods for quantitative determination of elements, and the details of all the equipment used for physico-chemical studies are described in **Chapter 2.**

Preparation of Cobalt(II) Acetylacetonate Dihydrate, $Co(acac)_2.2H_2O$ or $Co(C_5H_7O_2)_2.2H_2O$

Cobalt(II) acetate tetrahydrate (10 g, 40.1 mmol) was dissolved in 200 mL of water in a 500 mL beaker. A 20% aqueous solution of KOH was slowly added with constant stirring. Initially a blue colored precipitate formed which was stirred for 10 min and allowed to stand for half an hour. The blue color of the precipitate turned green and finally to a flesh pink color providing the hydrated metal oxide, as desired (pH~8). The hydrated metal oxide was washed free of alkali by repeated washing with water by decantation followed by filtration through Whatman No.42 filter paper and again washing twice with cold water. The precipitate was then quantitatively transferred into a 100 mL beaker. Distilled acetylacetone (9.1 mL, 88.2 mmol) was added to the precipitate and mixed thoroughly. An exothermic reaction set in leading to the formation of pink shiny crystals of $Co(acac)_2.2H_2O$. It was allowed to stand at room temperature for 30 min and then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No.42 filter paper and dried *in vacuo* over fused $CaCl_2$. Yield: 10.94 g (93%)

Preparation of Copper(II) Acetylacetonate, $Cu(acac)_2$ or $Cu(C_5H_7O_2)_2$

Copper(II) acetate monohydrate (10 g, 50.09 mmol) was dissolved in 300 mL of water in a 500 mL beaker by warming at 60 °C for 15 min. To the cooled solution, 20% aqueous solution of KOH was slowly added with constant stirring to precipitate the metal as its hydrated oxide. The addition of alkali was continued till the pH of the solution was raised to *ca.* 8. The hydrated metal oxide was washed free of alkali by repeated washing with water by decantation, finally followed by filtration through Whatman No. 42 filter paper and again washing twice with cold water. Then the precipitate was quantitatively transferred into a 100 mL beaker. Distilled acetylacetone (11.06 mL, 110 mmol) was added to the precipitate and mixed thoroughly with a glass rod. An exothermic reaction set in leading to the formation of blue shiny crystals of $Cu(acac)_2$. It was allowed to stand at room temperature for 30 min and then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No. 42 filter paper and dried *in vacuo* over fused $CaCl_2$. Yield: 12.49 g (95.3%)

Preparation of Iron(III) Acetylacetonate, $Fe(acac)_3$ or $Fe(C_5H_7O_2)_3$

Iron(III) chloride (15 g, 92.47 mmol) was dissolved in 200 mL of water in a 500 mL beaker followed by addition of 20% aqueous solution of KOH in parts with constant stirring to precipitate the metal as its hydrated oxide. The addition of alkali was continued till the pH of the solution was raised to *ca*. 8. The suspended precipitate was allowed to settle with the supernatant liquid becoming colorless. The flocculent was washed several times with water by decantation, finally by filtration through Whatman No. 42 filter paper and again washing twice with cold water. Then the precipitate was quantitatively transferred to a 250 mL beaker. Distilled acetylacetone (30.5 mL, 295.9 mmol) was added to the slurry and mixed thoroughly with a glass rod. The whole mixture was allowed to stand at room temperature for 30 min with occasional stirring. An exothermic reaction set in leading to the formation of deep red shiny crystals of $Fe(acac)_3$. The reaction container was then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No. 42 filter paper and dried *in vacuo* over fused $CaCl_2$. Yield: 31.1 g (95%)

Preparation of Vanadyl Acetylacetonate, $VO(acac)_2$ or $VO(C_5H_7O_2)_2$

To an aqueous suspension of vanadium pentoxide (5 g, 27.49 mmol) in 20 mL of water taken in a 500 mL beaker, 30% hydrogen peroxide (37.37 mL, 329.88 mmol) was added drop wise in an ice cold condition and stirred till a clear dark solution is formed. To the dark brown colored solution, distilled acetylacetone (19.84 mL, 192.5 mmol) was added drop wise very carefully with continuous stirring. Vigorous effervescence took place after 15 min. Stirring for a period of 30 min led to a precipitation of a brown colored microcrystalline compound. The reaction mixture was heated at 70 °C for 15 min under stirring. The precipitate turned olive green having shiny crystalline appearance with the solution also turning green. The solution was concentrated by heating on a steam bath for 30 min and then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No. 42 filter paper, washed with acetone and dried *in vacuo* over fused $CaCl_2$. Yield: 8.2 g (80%)

Preparation of Cobalt(III) Acetylacetonate, $Co(acac)_3$ or $Co(C_5H_7O_2)_3$

Cobalt(II) acetate tetrahydarte (10 g, 40.1 mmol) was dissolved in 200 mL of water in a 500 mL beaker followed by addition of 20% aqueous solution of KOH with constant stirring to precipitate the metal as its hydrated oxide. Initially a blue colored precipitate formed which was stirred for 10 min and allowed to stand for 30 min. The blue color precipitate turned green, finally a flesh pink color providing the hydrated metal oxide as desired. It was washed free of alkali with water (by decantation), finally by filtration through Whatman No. 42 filter paper and

again washing twice with cold water. Then the precipitate was quantitatively transferred to a 250 mL beaker. Distilled acetylacetone (16.5 mL, 160.4 mmol) was added to the precipitate and mixed thoroughly with a glass rod. An exothermic reaction set in leading to the formation of pink shiny crystals of $Co(acac)_2.2H_2O$. To this was added 30% hydrogen peroxide (11.36 mL, 100.25 mmol) drop wise with constant stirring. A solid to solid conversion of pink $Co(acac)_2.2H_2O$ to green crystalline $Co(acac)_3$ took place with the accompanying solution becoming green. The reaction mixture was heated on a steam bath for complete oxidation of Co(II) to Co(III) and expulsion of hydrogen peroxide. The whole mixture was allowed to stand at room temperature for 30 min with occasional stirring. The reaction container was then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No. 42 filter paper and dried *in vacuo* over fused $CaCl_2$. Yield: 13.95 g (98%)

CHARACTERIZATION OF PRODUCTS

The compounds were characterized by a variety of physical studies. Melting points and analytical data are summarized in **Table 3.1**.

Table 3.1 Melting Points and Analytical Data of Metal Acetylacetonates

Compound (Macac)	m.p. (°C)	% Found (% Calcd)		
		C	H	M (Co, Cu, Fe or V)
$Co(acac)_2.2H_2O$ ($C_{10}H_{18}CoO_6$)	170–172	40.92 (40.97)	6.14 (6.19)	20.24 (20.10)
$Cu(acac)_2$ ($C_{10}H_{14}CuO_4$)	279-283	45.90 (45.88)	5.36 (5.39)	24.33 (24.28)
$Fe(acac)_3$ ($C_{15}H_{21}FeO_6$)	180 or 181	51.2 (51.01)	6.17 (5.99)	15.84 (15.81)
$VO(acac)_2$ ($C_{10}H_{14}VO_5$)	250 or 251	45.11 (45.30)	5.31 (5.32)	19.32 (19.21)
$Co(acac)_3$ ($C_{15}H_{21}CoO_6$)	209	50.21 (50.57)	6.03 (5.94)	16.21 (16.54)

RESULTS AND DISCUSSION

Though the most common way of assessment of the efficiency of a reaction is by calculation of the yield of the product, however, in the context of green chemistry, to grade the reaction as efficient, maintenance of atom economy becomes essential. Atom economy calls for an accounting of the atoms of reactants that are incorporated into the desired product and those that are wasted or incorporated into undesired products.

Solvent-less synthesis of chemical compounds is becoming quite popular world-over in an effort to make synthetic processes more 'green'. In fact, from both economic and environmental standpoint, chemical synthesis without the use of solvents is gradually developing into a powerful methodology.[41] Unfortunately however, while solvent free organic synthesis has become quite common among chemists and chemical technologists, lack of literature evidence suggests that solvent free inorganic synthesis has not really taken any commendable lead as yet. Not withstanding this, demand for increasingly clean and efficient chemical syntheses is continuously becoming more urgent for all kinds of chemistries. This is because solvent-less synthesis facilitates an increase in chemical reactivity, reduction in the amount of initial substances needed; in particular it removes the need for the complex recycling and disposal of solvents. As a part of the programme for the development of atom-economic and solvent-less synthetic protocols, our experience suggests that solvent-less synthesis of metal acetylacetonates might be possible.

As has been mentioned earlier, a few of the metal acetylacetonates described in this chapter had been reported by us a few years ago. Unfortunately, however, these methods of preparation have some disadvantages as far as the efficient use of all atoms was concerned. The importance of the compounds having been largely highlighted, the need for atom economic, cost-effective methods of synthesis of metal acetylacetonates became quite palpable. With this being the pivotal point, atom economic synthetic protocols of metal acetylacetonates were aimed at and success achieved**.**

Accordingly, while retaining the fundamental synthetic philosophies, new atom economic routes to metal acetylacetonates are now defined. Conceptually, in one of the synthetic protocols, *viz*., the solven-less method of synthesis, the slight acidity of acetylacetone is taken advantage of in which there is direct interaction between a metal hydroxide or a hydrated metal oxide with acetylacetone (**Scheme 3.1)**.

$$M(OH)_n + n\ acacH \longrightarrow M(acac)_n.xH_2O$$

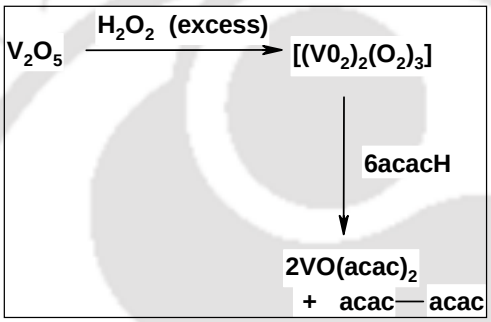
Where M = Co, n = 2 and x=2

M = Cu, n = 2 and x=2, and

M = Fe, n = 3

Scheme 3. 1 Solvent-Less Synthesis of Metal acetylacetonates

While all the preparation procedures reported have distinct advantages in terms of atom economy, the preparation of vanadyl acetylacetonate deserves special mention as it allows the compound to be prepared in 80% isolated yield in about 2 h.



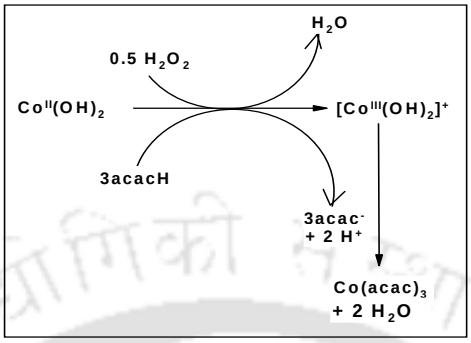
Scheme 3.2 Peroxometal(inter)mediated Route to $VO(acac)_2$

Literature reports[42] that the synthesis of $VO(acac)_2$ is rather tedious, requiring V_2O_5 to be refluxed in almost 33 times its excess of acetylacetone for 24 h. Taking cues from the experiences that we have had with peroxovanadium(V) chemistry, a novel strategy was developed in which the metal was first activated by converting it to its corresponding peroxide, which on treatment with acetylacetone, yielded vanadyl acetylacetonate, as obtained (**Scheme 3.2)**.

The peroxo-metal(inter)mediated protocol provides a route to afford metal acetylacetonates both in higher as well as lower oxidation state. As a typical example, the hydrated metal oxide of cobalt(II) is directly reacted with acetylacetone in the presence of hydrogen peroxide to obtain $Co(acac)_3$ as the product with cobalt being in a higher oxidation state (**Scheme 3.3)**.

The preparation of $Co(acac)_3$ is also quite intriguing, requiring the moist hydrated metal oxide to be mixed thoroughly with the acetylacetone (3.2 equivalent) in ice-cold condition, followed by drop wise addition of the oxidant hydrogen peroxide (0.8 equivalent), setting in an exothermic reaction. The reaction is very facile rendering the product with high crystallinity and in almost quantitative yield. This can be possibly attributed to the fact that flocculent metal

hydroxide, suspended in aceylacetone, is oxidized prior to chelation because of high H^+ concentration which in turn results in an exothermic reaction driving the process to completion.



Scheme 3.3 A New Route to $Co(acac)_3$

The newer preparation protocols have an important advantage in that while it requires no additional amount of acetylacetone, there is an improvement in yield. (**Table 3.2**) Also, in many cases, no extraneous heating is required.

Table 3.2 A Comparison of the Yields

Metal acetylacetonates	Yield (%) (Earlier Reports)	Yield (%) (Present Results)
$Co(acac)_2.2H_2O$	90[37]	93
$Cu(acac)_2$	92[37]	95.3
$Fe(acac)_3$	90[33]	95
$VO(acac)_2$	68[42]	80
$Co(acac)_3$	67-80[43]	98

We thus have at our disposal two efficient and direct methods of synthesis of metal acetylacetonates that seem comply with the commercial requirements of the industries and also conform to the tenets of 'Green Chemistry' in being atom economic and environmentally favorable. Also important is to realize is that with the success in the solvent-less and peroxometal(inter)mediated synthesis of metal actylacetonates, the activity in inorganic synthesis is reinforced.

Barbier Coupling in Water: $SnCl_2$-Mediated and $Co(acac)_2$-Catalyzed Allylation of Carbonyls

Section 3.2

The importance of and the considerable recent upsurge in the study on 'Barbier coupling in water'[45-81] have been emphasized in the literature and appropriately highlighted in **Chapter 1.** Hence our aim was to develop a homogeneous catalytic system that would work efficiently for Barbier coupling in water. Our experience in catalytic organic transformations,[82] in conjuction with the knowledge gathered from recent works on metal mediated C-C bond formation reactions, [45-81] caused us to believe that a combination of a water soluble reductive salt (*c.f.* $SnCl_2$) as a mediator and an appropriately water soluble, redox active, reusable metal complex as the catalyst would perhaps be one of the best options. The bimetallic nature of the reagent and the significant effect of water to facilitate the reaction are important. Important is also the choice of catalyst. Prerequisites for a catalyst to be suitable for the purpose are that it must be cost effective, reusable for several cycles of reactions and, have appreciable shelf life, requisite solubility in water without decomposition or hydrolysis and easily accessible variable oxidation states. It should be applicable to multigram-scale of operations with versatility. Pertinent to mention is that a suitable catalyst is essential since in water $SnCl_2$ alone can not mediate the reaction. To the best of our knowledge, four recent reports using Pd(II),[83] Cu(II)[63, 68] or Ti(III)[69] as the catalyst are of direct relevance to the present work. From the results available on these catalysts, it is clear that they work efficiently on systems that they were applied to. However, Pd and Ti based catalysts are expensive with the former having difficult accessibility and it also needs a biphasic condition, while $TiCl_3$ has inherent stability problems and requires a rather careful handling. The Cu(II) catalyzed reactions are conducted under nitrogen since the active catalyst Cu(I) is prone to easy oxidation. Notably, some of these catalysts do not seem to work well for one category of substrates or the other. For instance, $TiCl_3$ is not efficient for ketones[69] and Cu(II) is poor in allylation of some aldehydes, RCHO, with R being cinnamyl, n-hexyl or 2-furyl.[68] Moreover, it is not clear if carbohydrate allylation would be possible with these catalysts. What would thus be looked for is a combination of $SnCl_2$ as the mediator with a versatile catalyst which would work well in water. The results of the investigations constitute subject matter of this subsection**.**

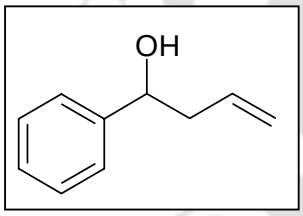
EXPERIMENTAL SECTION

General Proccedure for Carbonyl Allylation

All reactions were carried out in water. To 15 mL of water were added $Co(acac)_2.2H_2O$ (0.1 mmol, 0.029 g), $SnCl_2$ (1.2 mmol, 1.2 g), allyl bromide (1.2 mmol, 0.144 g), and benzaldehyde (1 mmol, 0.106 g) and the reaction mixture was stirred at room temperature for several hours. The reaction was monitered by TLC and after completion of the reaction the product was extracted with ethylacetate directly (3 × 30 mL). The combined organic layer was washed with water several times until the aqueous layer became colorless. After this operation, the organic layer, which contained the crude product, was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography (hexane /ethyl acetate, 90/10, v/v) to afford pure compound. Yield: 0.144 g (97%).

CHARACTERIZATION OF PRODUCTS

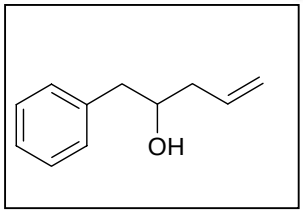
The compounds were characterized by IR and ^{1}H NMR spectral techniques and data for the products are summarized as follows:



Name **1-phenylbut-3-en-1-ol**

IR (cm^{-1}) 3400, 3070, 1641, 1600, 1496, 1446, 1049.

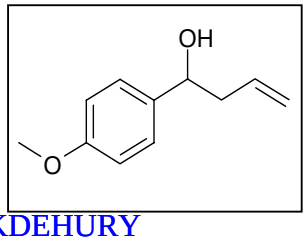
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.40-7.25 (m, 5H), 5.90-5.75 (m, 1H), 5.18 (q, J = 4.95 Hz, 2H), 4.75 (q, J = 3.2 Hz, 1H), 2.50 (m, 2H), 2.20-1.85 (br, 1H).



Name **1-phenylpent-4-en-2-ol**

IR (cm^{-1}) 3362, 3062, 1641, 1603, 1495, 1454, 1045.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.32-7.20 (m, 5H), 5.82 (m, 1H), 5.15 (d, J = 11.1 Hz), 3.87 (m, 1H), 2.80 (m, 2H), 2.20-2.40 (m, 2H), 1.68 (br, 1H).

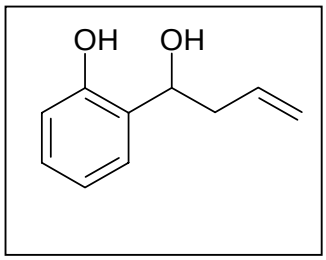


Name **1-(4-methoxyphenyl)but-3-en-ol**

IR (cm^{-1}) 3078, 1643, 1612, 1513, 1463, 1248, 1175.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.27 (d, J = 7.16 Hz, 2H), 6.88 (d, J = 4.95 Hz, 2H), 5.80 (m, 1H), 5.15

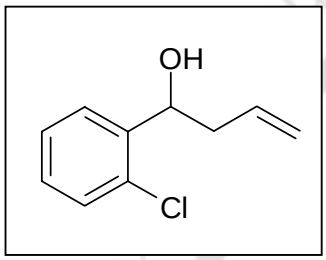
(d, J = 13.2 Hz, 2H), 4.68 (t, J = 6.52 Hz, 1H), 3.79 (s, 3H), 2.50 (m, 2H), 2.10-1.90 (br, 1H).



Name **2-(2-hydroxy)but-3-enylphenol**

IR (cm^{-1}) 3390, 3077, 1642, 1608, 1450, 1106.

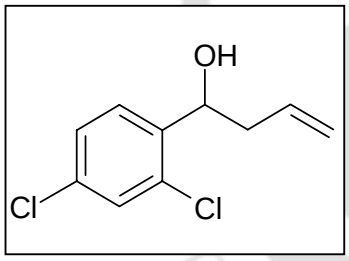
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.00 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 7.0 Hz, 1H), 6.85 (m, 2H), 5.85 (m, 1H), 5.22 (d, J = 13.0 Hz, 2H), 4.88 (s, 1H), 2.68 (s, 1H), 2.61 (s, 2H).



Name **1-(2-chlorophenyl)but-3-en-ol**

IR (cm^{-1}) 3384, 3074, 1641, 1595, 1573, 1473, 1107, 1033.

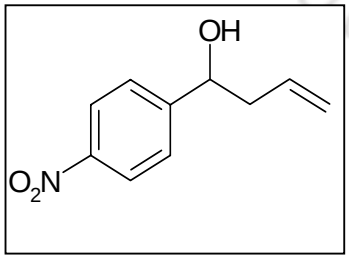
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.56 (d, J = 7.76 Hz, 1H), 7.34-7.20 (m, 3H), 5.80 (m, 1H), 5.20 (m, 3H), 2.62 (m, 1H), 2.40 (m, 1H), 2.10-2.00 (br, 1H).



Name **1-(2, 4-dichlorophenyl)but-3-en-ol**

IR (cm^{-1}) 3280, 3079, 1638, 1590, 1564, 1470, 1102, 1070.

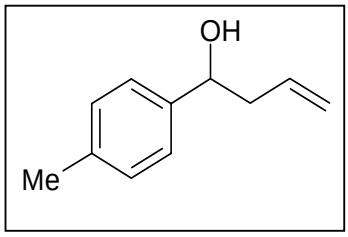
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.51 (d, J = 8.23 Hz, 1H), 7.35 (s, 1H), 7.27 (d, J = 8.5 Hz, 1H), 5.85 (m, 1H), 5.20 (d, J = 12.9 Hz, 2H), 5.12 (t, J = 4.44 Hz, 1H), 2.60 (m, 1H), 2.27 (m, 1H), 2.16 (br, 1H).



Name **1-(4-nitrophenyl)but-3-en-ol**

IR (cm^{-1}) 3400, 3070, 1641, 1600, 1510, 1496, 1459, 1337, 1195, 1056, 831, 737.

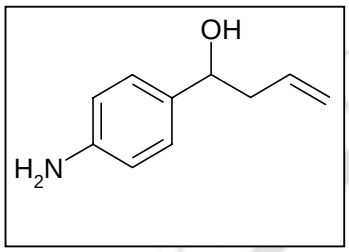
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.96 (d, J = 8.4 Hz, 2H), 7.44-7.27, (d, J = 8.4 Hz, 2H), 5.85 (m, 1H), 5.24 (d, J = 12.1, 2H), 5.05 (t, 4.48Hz, 1H), 2.69 (m, 1H), 2.50 (m, 1H), 2.10-2.00 (br, 1H).



Name **1-(4-methylphenyl)but-3-en-ol**

IR (cm^{-1}) 3385, 3080, 1644, 1594, 1577, 1450.

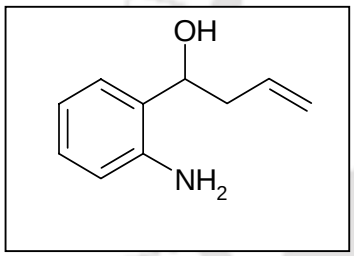
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.25 (d, J = 5.7 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 5.80 (m, 1H), 5.15 (q, J = 5.0 Hz, 2H), 4.71 (t, J = 3.96 Hz, 1H), 2.50 (t, J = 8.18 Hz, 2H), 2.35 (s, 3H), 1.98 (br, 1H).



Name **1-(4-aminophenyl)but-3-en-ol**

IR (cm^{-1}) 3381, 3077, 2974, 1642, 1610, 1510, 1450.

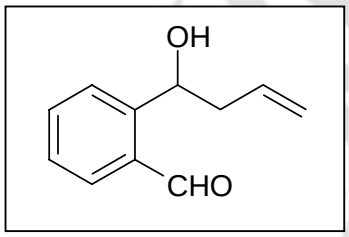
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.15 (d, J = 8.3 Hz, 2H), 6.65 (d, J = 8.22 Hz, 2H), 5.85 (m, 1H), 5.17 (m, 2H), 4.60 (t, J=6.53 Hz, 1H), 3.67 (br, 2H), 2.52 (t, J=6.9 Hz, 2H), 1.90 (br, 1H).



Name **1-(2-aminophenyl)but-3-en-ol**

IR (cm^{-1}) 3387, 3067, 2984, 1648, 1615, 1505, 1461.

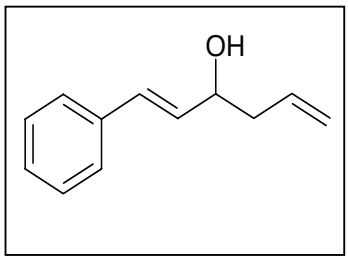
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.12 (d, J = 8.3 Hz, 2H), 6.67 (m, 3H), 5.81 (m, 1H), 5.10 (d, J= 11.5, 2H), 4.63 (t, J=6.57 Hz, 1H), 3.71 (br, 2H), 2.50 (t, J=6.1 Hz, 2H), 1.95 (br, 1H).



Name **2-(1-hydroxybut-3-enyl)benzaldehyde**

IR (cm^{-1}) 3410, 3075, 1710, 1641, 1604, 1491, 1441, 1045

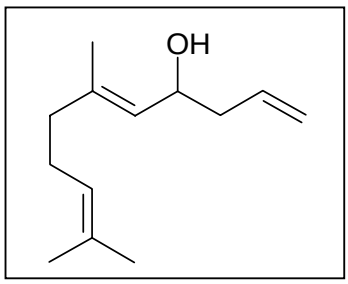
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.78 (s, 1H), 7.83 (d, *J* = 8.31 Hz, 1H), 7.40-7.22, (m, 3H), 5.82 (m, 1H), 5.23 (d, J = 11.1 Hz, 2H), 4.85 (t, J = 6.5 Hz, 1H), 2.64 (m, 1H), 2.46 (m, 1H), 2.10-2.00 (br, 1H).



Name **1-phenylhexa-1,5-dien-3-ol**

IR (cm^{-1}) 3332, 3057, 3027, 1493, 1449, 1417, 1379 1070

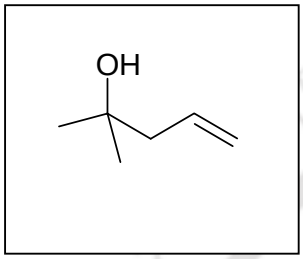
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58 (t, *J* = 8.4 Hz, 1H), 7.42-7.22 (m, 4H), 6.55 (t, *J* = 12.4 Hz, 1H), 5.93-5.71 (m, 1H), 5.16 (m, 3H), 4.78 (q, *J* = 3.4 Hz, 1H), 2.50 (m, 2H), 2.20-1.85 (br, 1H).



Name **6,10-dimethylundeca-1,5,9-triene-4-ol**

IR (cm^{-1}) 3327, 3308, 2968, 2920, 2860, 1668, 1441, 1380, 1094.

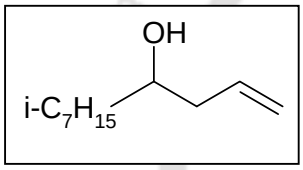
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.93-5.71 (m, 1H), 5.16 (q, *J* = 4.95 Hz, 2H), 5.39 (s, 1H), 5.12 (d, J=6.2, 1H), 3.65 (m, 1H), 2.50 (m, 2H), 2.1 (m, 4H), 1.95 (br, 1H), 1.71 (s, 9H).



Name **2-methyl-pent-4-ene-2-ol**

IR (cm^{-1}) 3374, 3077, 1641, 1151.

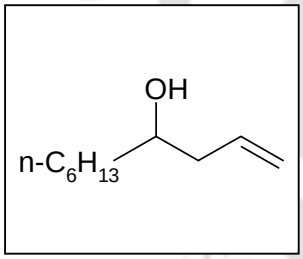
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.86 (m, 1H), 5.15 (d, *J* = 13.3 Hz, 2H), 3.60 (br, 1H), 2.23 (d, J = 7.78 Hz, 2H), 1.70 (br,1H), 1.28 (s, 6H).



Name **5- propyloct-1-en-4-ol**

IR (cm^{-1}) 3355, 3077, 1643, 1101.

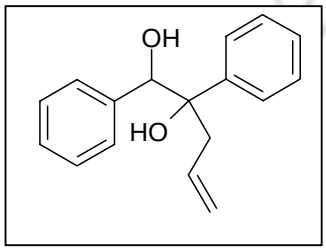
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.80 (m, 1H), 5.13 (d, J = 12.9 Hz, 2H), 3.64 (m, 1H), 2.30 (m, 1H), 2.16 (m, 1H), 1.48-1.21 (m, 12H), 0.88 (s, 3H).



Name **4-methyldec-1-ene**

IR (cm^{-1}) 3358, 3077, 2930, 2858, 1641, 1466.

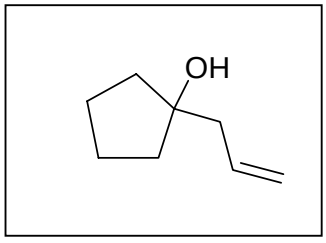
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.76–5.90 (m, 1H), 5.10–5.17 (m, 2H), 3.60–3.68 (m, 1H), 2.26–2.34 (m, 1H), 2.10–2.20 (m, 1H), 1.89 (s, 1H), 1.30–1.46 (m, 10H), 0.89 (t, J = 6.9 Hz, 3H)



Name **1,2-diphenylpent-4-ene-1,2-diol**

IR (cm^{-1}) 3549, 3471, 1633

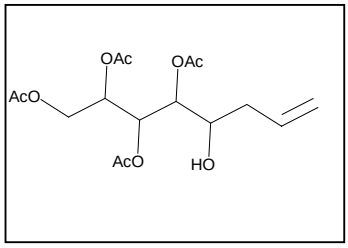
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.96–7.18 (m, 10H), 5.50–5.52 (m, 1H), 5.02–5.14 (m, 2H), 4.75 (s, 1H), 2.88–2.92 (m, 1H), 2.68–2.74 (m, 1H), 2.4–2.7 (br, 2H).



Name **1-allylcyclopentanol**

IR (cm^{-1}) 3391, 3076, 2960, 2874, 1640, 1436, 1194.

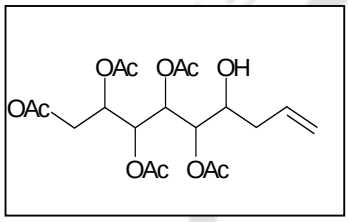
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.83–5.97 (m, 1H), 5.11–5.18 (m, 2H), 2.35 (d, J = 8.4 Hz, 2H), 1.82 (br, 1H), 1.61–1.76 (m, 8H)



Name **1,2,3,4-tetra-O-acetyl-5-hydroxy-6,7,8-trideoxy-gulo-7,8-octenitol**

IR (cm^{-1}) 3394, 3072, 2951, 2862, 1639, 1442, 1199

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.75-5.90 (m, 1H), 5.38 (dd, J = 4.22 and 7.00 Hz, 2H), 5.26 (dd, J=4.17 and 6.61 Hz, 1H) 5.08 (m, 2H), 5.03 (m, 1H), 5.01 (m, 1H) 4.20 (dd, J= 3.39, 12.41 Hz, 1H), 3.77 (m, 1H), 2.39-2.28 (m, 2H), 2.10 (br, 1H), 2.09-2.01 (4s, 12H)



Name **1,2,3,4,5-penta-O-acetyl-6-hydroxy-7,8,9-trideoxy-glyceroman-8,9-octenitol**

IR (cm^{-1}) 3382, 3065, 2971, 2881, 1653, 1441, 1182

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.64 (m, 1H), 5.43 (dd, J = 1.94 and 10.01 Hz, 2H), 5.29 (dd, J=1.84 and 8.62 Hz, 1H) 5.13 (dd, J= 1.85 and 10.03 Hz, 1H), 5.03 (m, 2H), 4.95 (m, 1H) 4.16 (dd, J= 2.85, 12.50 Hz, 1H), 3.77 (m, 1H), 2.17 (m, 2H), 2.10 (br, 1H), 2.09-2.01 (4s, 15H).

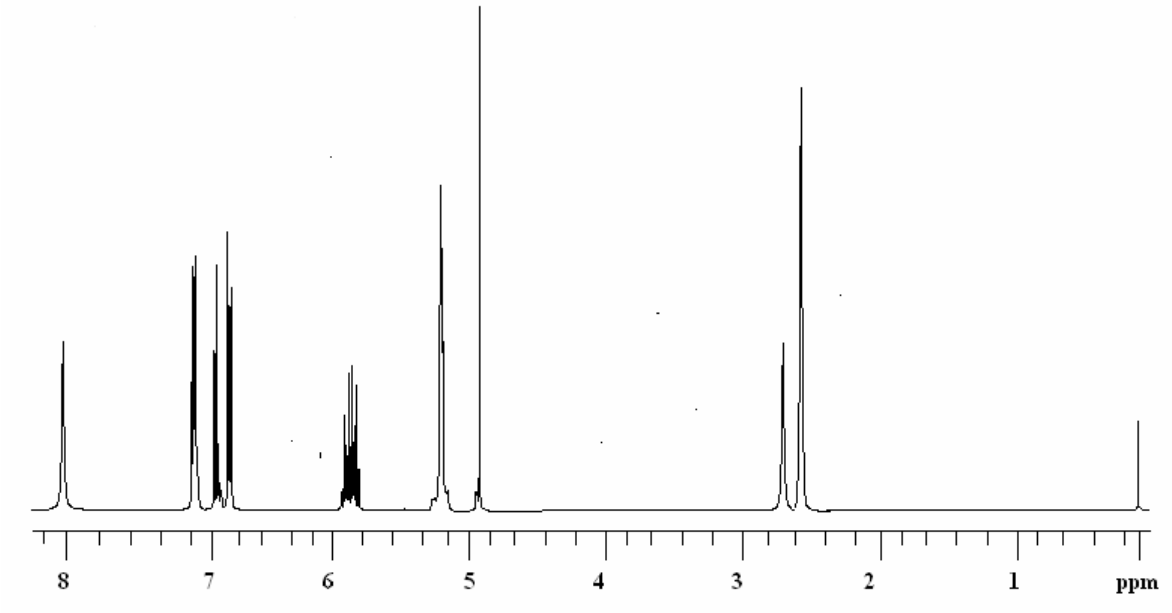


Fig 3.1 ^{1}H NMR Spectrum of 2-(2-hydroxy)but-3-enylphenol

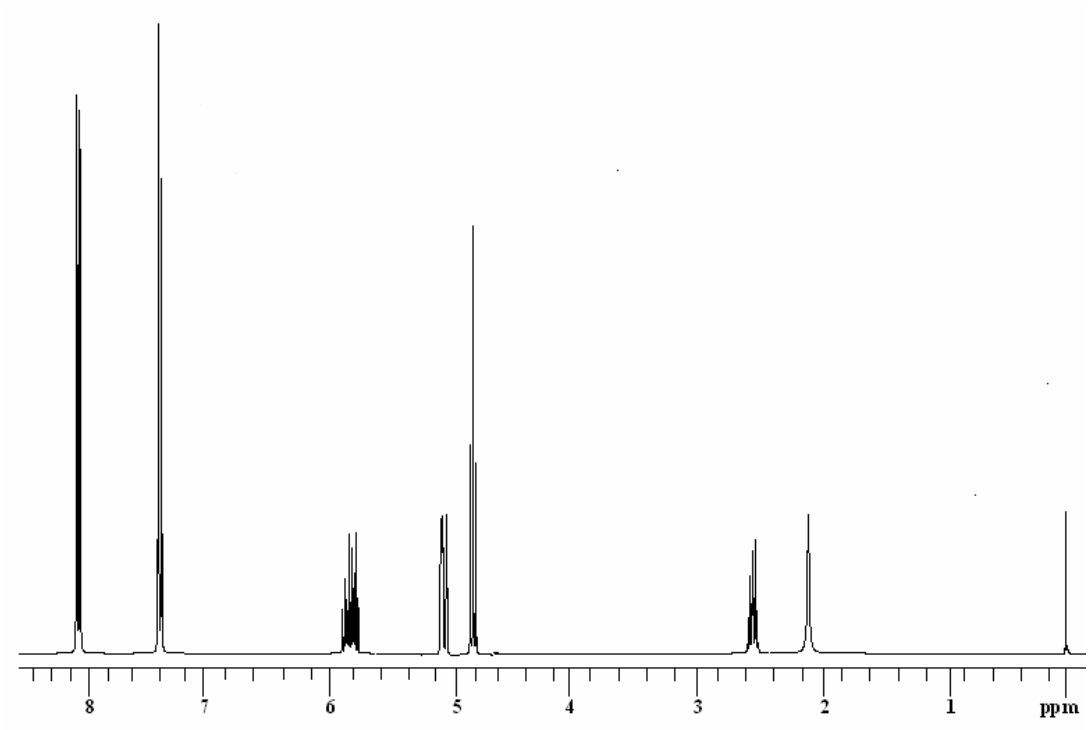


Fig 3.2 ^{1}H NMR Spectrum of 1-(4-nitrophenyl)but-3-en-ol

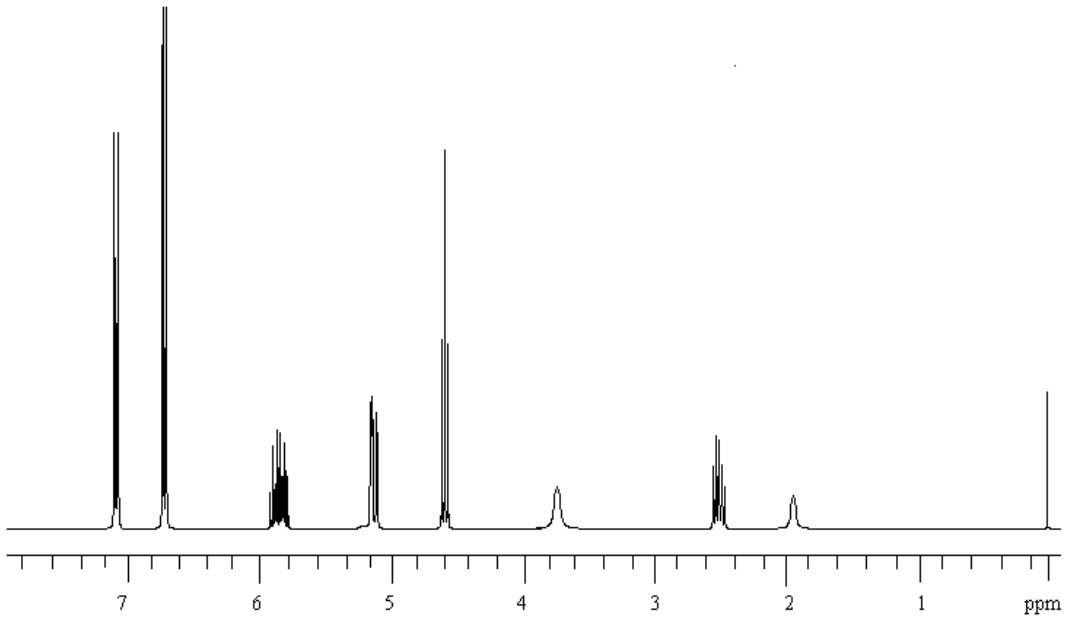


Fig 3.3 ^{1}H NMR Spectrum of 1-(4-aminophenyl)but-3-en-ol

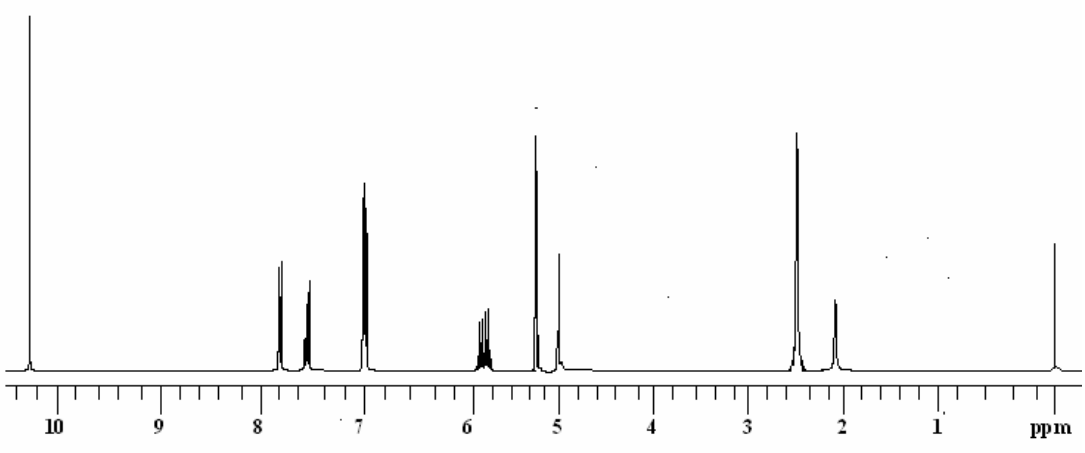
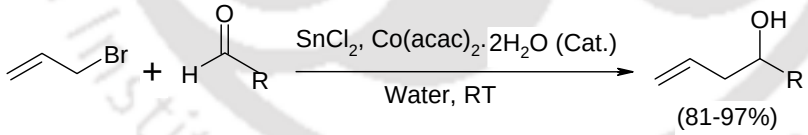


Fig 3.4 ^{1}H NMR Spectrum of 2-(1-hydroxybut-3-enyl)benzaldehyde

RESULTS AND DISCUSSION

We now wish to disclose our results of homoallylation of a variety of substrates using $SnCl_2$/$Co(acac)_2.2H_2O$ as the reagent system. Incidentally, we have a very easy access to metal acetylacetonates including the chosen catalyst, $Co(acac)_2.2H_2O$.[83] The catalyst satisfies the requirement of easily accessible higher oxidation state (*c.f.* Co(III)), has the required solubility in water with no apparent hydrolysis, and is capable of acting as a Lewis acid in water. Herein the results of some of our very recent studies on tin(II) chloride mediated and $Co(acac)_2.2H_2O$ catalyzed Barbier reaction (**Scheme 3.4**) are considered for discussion.

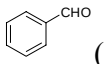
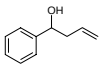
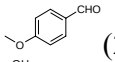
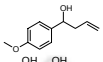
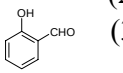
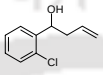
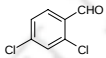
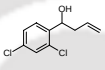
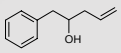
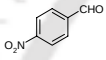
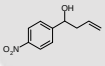
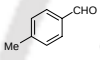
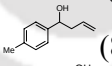
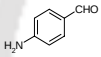
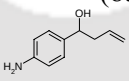
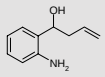
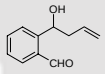
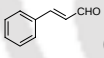
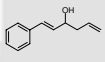
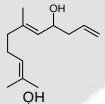
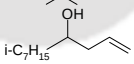
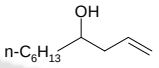
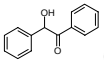
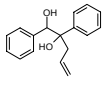
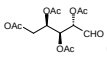
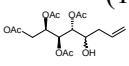
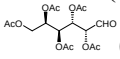
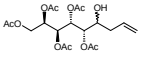


Scheme 3.4 $SnCl_2$ Mediated and $Co(acac)_2.2H_2O$ Catalyzed Barbier Reaction

No organic co-solvent or assistance of ultrasonic irradiation is required thereby showing a clear advantage over those catalyzed by zerovalent metals. The experimental results are summarized in **Table 3.3** to show the efficacy of the protocol using $SnCl_2$/ $Co(acac)_2.2H_2O$ system providing homoallylic alcohols in 81-97% isolated yields.

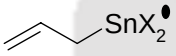
Importantly, both aldehydes and ketones (**1-15** and **16-18**), aliphatic and aromatic carbonyls(**14-15** and **1-13**, and **16-18)** and a nitro substituted substrate (**7**) can be allylated without any difficulty. Some of these reactions are not catalyzed by zerovalent metals. Also for substrate containing active hydrogen (**3**), the protocol works well without any protection.

Table 3.3 $SnCl_2/Co(acac)_2.2H_2O$ Mediated Carbonyl Allylation

Entry	Substrate	Product	Time	Isolated Yield (%)
1.	 (1)	 (1a)	6	97
2.	 (2)	 (2a)	6	93
3.	 (3)	 (3a)	6	91
4.	 (4)	 (4a)	6	94
5.	 (5)	 (5a)	6	93
6.	 (6)	 (6a)	6	96
7.	 (7)	 (7a)	6	94
8.	 (8)	 (8a)	6	92
9.	 (9)	 (9a)	6	95
10.	 (10)	 (10a)	6	91
11.	 (11)	 (11a)	6	90
12.	 (12)	 (12a)	8	92
13.	 (13)	 (13a)	8	85
14.	$i\text{-}C_7H_{15}CHO$ (14)	 (14a)	8	90
15.	$n\text{-}C_6H_{13}CHO$ (15)	 (15a)	8	88
16.	 (16)	 (16a)	18	85
17.	 (17)	 (17a)	18	81
18.	 (18)	 (18a)	18	89
19.	 (19)	 (19a)	18	81
20.	 (20)	 (20a)	18	83

Similarly, for α, β-unsaturated aldehydes (**12-13**) only 1,2-adition products have been obtained. No pinacol coupling has been observed in such reactions. All these results suggest a large scope of $SnCl_2$/ $Co(acac)_2.2H_2O$ system.

Significant is to note that the present protocol works successfully for the alliylation of unprotected sugars in water. Thus, the $SnCl_2/Co(acac)_2.2H_2O$ combination brought about smooth reactions between arabinose acetate (**19**), or mannose acetate (**20**) affording the corresponding homoallylic alcohols in 81-83% yields. In order to further broaden the scope of the present protocol, a few reactions were conducted with allylic chloride. Accordingly, substrates **1, 2** and **3** were allowed to react under conditions similar to those maintained for the corresponding bromoallyles. The reactions were equally facile with homoallylic products being obtained in comparable yields.

In view of the possibility of a facile Co(II)-Co(III) redoxcycling, it is possible that an allyl halide radical is first formed by the transfer of an electron from cobalt(II), which interacts with $SnCl_2$ to give  radical. This would then react with cobalt(III) to produce cobalt(II) and a neutral allylated derivative which would then add to the carbonyl group yielding the homoallylic alcohol, as desired. This reaction might as well be facilitated by simultaneous Lewis acid (*c.f.* Co(II)) catalyzed activation of the carbonyl group. We restrain from making any further comment on the mechanism at the moment, in the absence of the results of the further work in the direction.

Another notable feature of the $Co(acac)_2.2H_2O$ catalyst is its reusability. The results presented in **Fig 3.5** shows that six cycles of the reaction could be conducted with the one time loading of the catalyst with high throughput. After each run, the substrate and $SnCl_2$ were recharged.

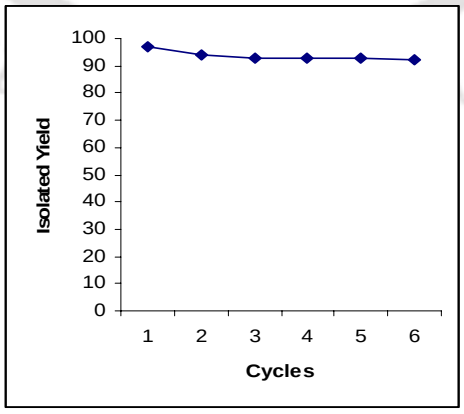


Fig 3.5 Recycling of Catalyst for Allylation of Benzaldehyde

We have carried out allylation of benzaldehyde using different metal acetylacetonate catalysts such as $VO(acac)_2$, $Fe(acac)_3$, $Cr(acac)_3$ and $Co(acac)_2.2H_2O$. The results are summarized in **Table 3.4**. In case of $VO(acac)_2$ and $Fe(acac)_3$, products are isolated with low yields (10-15%) even after allowing the reaction for 30 h. $Cr(acac)_3$ and $Co(acac)_2.H_2O$ were more effective in catalyzing allylations affording the products with very high yields (95-97 %). However, the results suggest that $Co(acac)_2.2H_2O$ should be the preferred catalyst.

Table 3.4 $SnCl_2$ Mediated Allylation of Benzaldehyde using Various Catalysts

Ex. No.	Catalyst	Time (h)	Yield (%)
1.	$Co(acac)_2.2H_2O$	6	97
2.	$VO(acac)_2$	30	15
3.	$Fe(acac)_3$	30	10
4.	$Cr(acac)_3$	18	95

In conclusion, $Co(acac)_2.H_2O$ is used as an effective catalyst for $SnCl_2$ mediated carbonyl allylation of a wide range of aldehydes and ketones, and the chosen carbohydrates. $Co(acac)_2.H_2O$ catalyst can be reused for several cycles with consistent activity. The advantages of $Co(acac)_2.H_2O$ are the ease of preparation, stability, high activity, acceptable solubility in water and cost effectiveness.

Immobilized Copper(II) Acetylacetonate Catalyst for Heterogeneous Nitrene Transfer Reactions

Section 3.3

Section 3.3 comprises of two subsections, a comprehensive account of the results of aziridination of olefins using MC-$Cu(acac)_2$ catalyst and PhI=NTs constitute **Subsection 3.3.1**. Once it was known that $Cu(acac)_2$ microencaspulated in polystyrene efficiently catalyzed aziridination reactions, it appeared quite rational to explore the possibility of sythesis of sulfimide by nitrene transfer to a sulfide using MC-$Cu(acac)_2$ catalyst and PhI=NTs as the nitrene source. In addition, these results prompted us to apply $Cu(acac)_2$ catalyst immobilized in ionic liquid to the synthesis of sulfimides from sulfides and compare the results with those of MC-$Cu(acac)_2$. **Subsection 3.3.2** describes the results of this investigation.

Microencapsulated $Cu(acac)_2$: A Recoverable and Reusable Polymer-Supported Copper Catalyst for Aziridination of Olefins

Subsection 3.3.1

Aziridines are an important class of compounds in organic chemistry[84,85] and especially useful as intermediates for functional group modifications, efficient chiral auxiliaries[86] and ligands in asymmetric catalysis.[87-89]The synthesis of aziridines has therefore been a subject of considerable research interest over the last few years.

A single atom transfer to olefins is the shortest route to three-membered cyclic compounds. Catalytic addition of a carbene moiety to an imine results in the formation of aziridine, but the yields are often low.[90, 91] The transfer of a nitrogen atom onto an olefin offers an attractive synthesis of aziridines.

Evans *et al*. reported Cu(I) and Cu(II) salts[92,93] as the most effective and extensively used homogeneous catalysts for aziridination of olefins using [*N*-(*p*-tolylsulfonyl)imino] phenyl iodinane (PhI=NTs) as the nitrene donor. Taylor and co-workers[94,95] and Ando *et al.*[96] have reported copper-catalyzed aziridination of alkenes using chloramine-T as the source of the nitrene. Hutchings *et al*.[97, 98] have, however, for the first time used heterogeneous copper-exchanged zeolite Y (CuHY) catalyst, using PhI=NTs as a nitrene donor for aziridination reaction. Later, a polymer-supported Ru-porphyrin catalyst,[99] a silica-supported polypyrazolylborate copper complex[100] and a polymer-supported manganese(II) complex[101] were also used for the aziridination of olefins by several other workers. However, these catalysts are limited by tedious catalyst preparation, low yields of aziridines and long reaction times.

Immobilized catalysts have been of great interest due to several advantages, such as ease of product separation, isolation and reuse of the catalyst.[102-104] Recently, Kobayashi *et al*. have reported the use of microencapsulation as a technique for immobilizing metal complexes.[105-108] Microencapsulation is a rather new method for immobilizing catalysts onto polymers accomplished by physical envelopment by the polymers. This allows interactions between the π electrons of benzene rings of the polystyrene-based polymers and vacant orbitals of the catalyst (metal compounds) rendering the catalyst system more effective. This technique has been used in a variety of reactions such as [MC-Sc(OTf)$_3$] in aza Diels-Alder, Strecker, cyanation and alkylation,[109] Mannich-type and aldol reactions,[105] silylation of alcohols[110] and microencapsulated osmium tetroxide [MC-OsO_4] was used for dihydroxylation of olefins[106,111] and [MC-Pd(PPh_3)][108] for allylic substitution, Suzuki coupling and Mizoroki Heck reactions.

Although there have been many applications of Cu(acac)$_2$ in a variety of organic transformations, there are only a few cases known where Cu(acac)$_2$ was used in heterogeneous catalysis. Some of our recent successes have been highlighted in previous sections taking cues from the earlier results, it was considered worthwhile to go for immobilization by microencapsulation of the catalyst in polystyrene, MC-Cu(acac)$_2$, and then try out some nitrene

transfer reactions. Accordingly, a few aziridination reactions of some selected olefins have been carried out to demonstrate that MC-Cu(acac)$_2$ is capable of being used as a recoverable and reusable catalyst for the purpose.

EXPERIMENTAL SECTION

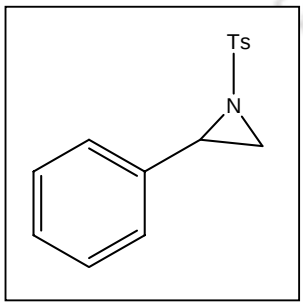
Preparation of Microencapsulated Cu(acac)$_2$

Polystyrene (1.00 g) was dissolved at 40 ^{o}C in cyclohexane (20 mL) and to this solution was added Cu(acac)$_2$ (0.12 g). This mixture was stirred for 1 h at this temperature and then slowly cooled to 0 ^{o}C with vigorous stirring. The polystyrene solidified around the metal catalyst dispersed in the solution. Hexane (30 mL) was added to harden the capsule walls. The mixture was stirred at room temperature for 1 h, and the capsules were washed with acetonitrile several times to remove unencapsulated Cu(acac)$_2$ and then dried under vacuum.

General Procedure: To acetonitrile (3 mL) were added MC-Cu(acac)$_2$ (0.15 g, 5.6 mol%), styrene (0.56 ml, 5 mmol) and PhI=NTs (0.372 g, 1 mmol) and the reaction mixture was stirred at room temperature. The reaction was monitored by disappearance of the PhI=NTs from the reaction mixture. After completion of the reaction, the catalyst was filtered and the filtrate concentrated and purified by column chromatography (hexane /ethyl acetate, 95/5, v/v) to afford pure product as white solid. Yield: 0.251 g, 92%.

CHARACTERIZATION OF THE PRODUCTS

The compounds were characterized by mp, IR and ^{1}H NMR spectroscopy and data for the products are summarized as follows:

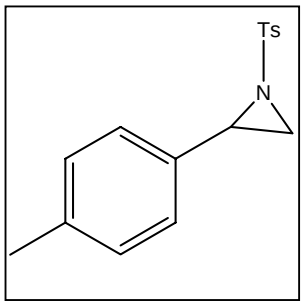


Name N-(*p*-Tolylsulfonyl)-2-phenylaziridine

Mp 88 or 89 ^{0}C

IR (cm^{-1}) 3017, 1327, 1217, 1161, 916, 783, 769, 715, 696, 665

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.86 (d, 2H, J = 8.3 Hz, Ar-H), 7.27 (m, 7H, Ar-H), 3.77 (dd, 1H, J_{cis} = 7.2 Hz, J_{trans} = 4.5 Hz, CHPh), 2.98 (d, 1H, J = 7.8 Hz, cis-CH-aziridine) 2.43 (s, 3H, Ar-Me), 2.38 (d, 1H, J = 4.4 Hz, trans-CH-aziridine).

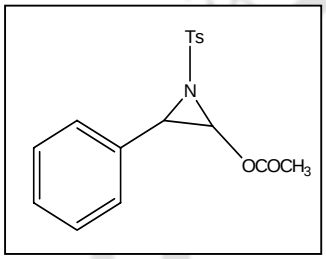


Name N-(*p*-Tolylsulfonyl)-2-(p-methylphenyl) aziridine

Mp 136 or 137 ^{0}C

IR (cm^{-1}) 3034, 1600, 1516, 1380, 1322, 1158, 1092, 1018, 978, 911, 814, 716, 708, 692, 660

^{1}H NMR ($CDCl_3$, 400MHz, ppm) δ 7.86 (d, 2H, J = 8.3 Hz, Ar-H), 7.31 (d, 2H, J = 7.9 Hz, Ar-H), 7.09 (s,4H, Ar-H), 3.73 (dd, lH, J_{cis}, = 7.2 Hz, J_{trans} = 4.5 Hz, CHPh-aziridine), 2.96 (d, lH, J = 7.2 Hz, cis-CH-aziridine), 2.42 (s, 3H, Ar-CH_3), 2.36 (d, lH, J = 4.5 Hz, trans-CH-aziridine), 2.3 (s,3H, Ar-CH_3)

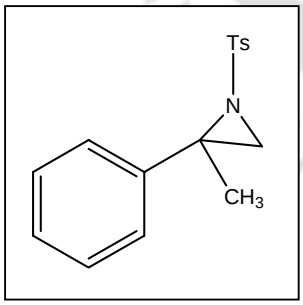


Name N-(*p*-Tolylsulfonyl)-2-carbomethoxy-2-phenylaziridine

Mp 44 or 44 ^{0}C

IR (cm^{-1}) 3068, 3021, 2960, 1750, 1600, 1498, 456, 1440, 1412, 1338, 1306,1292,116,1086,1081, 1004, 938, 906, 834, 812, 709, 692, 646

^{1}H NMR ($CDCl_3$, 400MHz, ppm) δ 7.77 (d, 2H, J=8.3 Hz, Ar-H), 7.31-7.24 (m, Ar-H), 4.44 (d, 1 H, J = 3.9 Hz, CH-aziridine), 3.85 (s, 3H, OCH_3), 3.53 (d, IH, J = 4.0 Hz, CH-aziridine), 2.41 (s, 3H, Ar-CH_3)

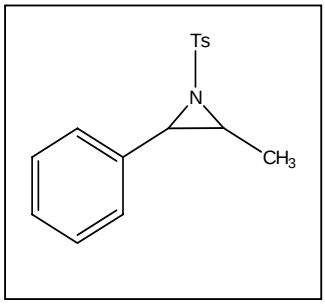


Name N-(*p*-Tolylsulfonyl)-2-methyl-2-phenylaziridine

Mp 83 or 84 ^{0}C

IR (cm^{-1}) 3060, 3028, 2992, 2930, 1600, 1449, 1330, 1267, 1160, 1128, 1089, 1027, 939, 870, 715, 694, 680, 650

^{1}H NMR ($CDCl_3$, 400MHz, ppm) δ 8.03 (d, 2H, J = 8.3 Hz, Ar-H), 7.38-7.12 (m, 5H, Ar-H), 6.92 (d, 2H, J= 8.4 Hz, Ar-H), 2.08 (s, 1H, CH-aziridine) 2.08 (s, 3H, Me), 2.01 (s, 3H, Me)

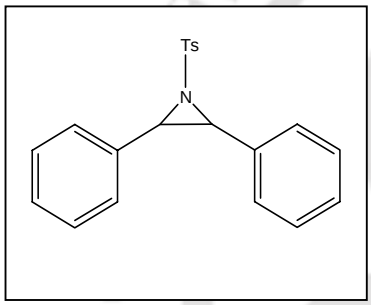


Name N-(*p*-Tolylsulfonyl)-3-methyl-2-phenylaziridine

Mp 72-74 ^{0}C

IR (cm^{-1}) 3031, 1458, 1321, 1306, 1291, 1217, 1159, 1090, 1038, 974, 891, 814, 772, 743,710,698,687, 667

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.82 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.267.20 (m, 5H, Ar-H), 7.13 (d, 2H, *J* =7.9 Hz, *Ar-H),* 3.79 (d, lH, *J* 4.3 Hz, CHPh), 2.9 (dq, lH, *J* = 6.0, 4.4Hz,$CHCH_3$),2.37(s, 3H, Ar-CH_3), 1.83 (d, 3H, J=6.0Hz, CH_3)

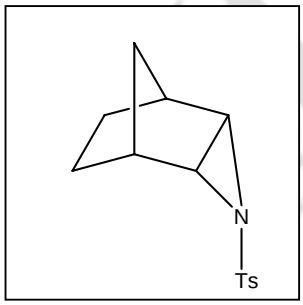


Name N-(*p*-Tolylsulfonyl)-2,3- diphenylaziridine

Mp 139 ^{0}C

IR (cm^{-1}) 3031, 3019, 1327, 1306, 1215, 1161, 1088, 930, 910, 814, 745, 741, 708, 698, 691 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz, ppm) δ 7.62 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.42-7.32 (m, 10H, Ar-*H*), 7.19 (d, 2H, *J* = 8.2 Hz, Ar-H), 4.26 (s, 2H, CH-aziridine) 2.38 (s, 3H, Ar-Me)

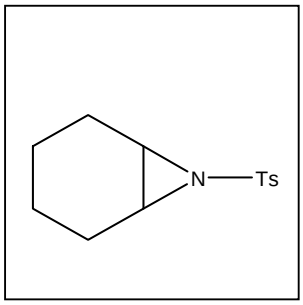


Name N-(*p*-Tolylsulfonyl)-3-azatricyclo[3.2.1.0.^{2,4exo}]octane

Mp 123 or 124 ^{0}C

IR (cm^{-1}) 3017, 1310, 1296, 1277, 1138,1080, 961, 895, 858, 770, 741, 725, 656

^{1}H NMR ($CDCl_3$, 400MHz, ppm) δ 7.97 (d, 2H, J = 8.3 Hz, Ar-H), 6.77 (d, 2H, J = 7.9 Hz, Ar-H), 2.87 (s, 2H, H_3), 1.98 (s, 2H, H_l, H_4), 1.86 (s, 3H,Ar-CH_3), 1.45 (dt, lH,= 2.0, 9.9 Hz, syn-H_7), 0.97-0.92 (m, 2H, H_6, H_5), 0.77-0.71 (m, 2H, 1s, H6),0.32 (d, lH, J= 9.9 Hz, anti-H_7)



Name	N-(*p*-Tolylsulfonyl)-7-azabicyclo[4.1.0]heptane
Mp	55 or 56 ^{0}C
IR (cm^{-1})	3020, 2950, 2860, 1600, 1440, 1395, 1315, 1305, 1155, 1090, 965, 920
^{1}H NMR	($CDCl_3$, 400MHz, ppm): δ 7.82 (d, 2H, J = 8.3 Hz, Ar-H), 7.33 (d, 2H, J = 8.0 Hz, Ar-H), 2.98 (t, 2H, J=1.4 Hz, CH-aziridine), 2.44 (s, 3H, Ar-CHs),1.79 (m, 4H, ring-CH), 1.43-1.36 (m, 2H, ring-CH), 1.26-1.19 (m, 2H, ring-CH)

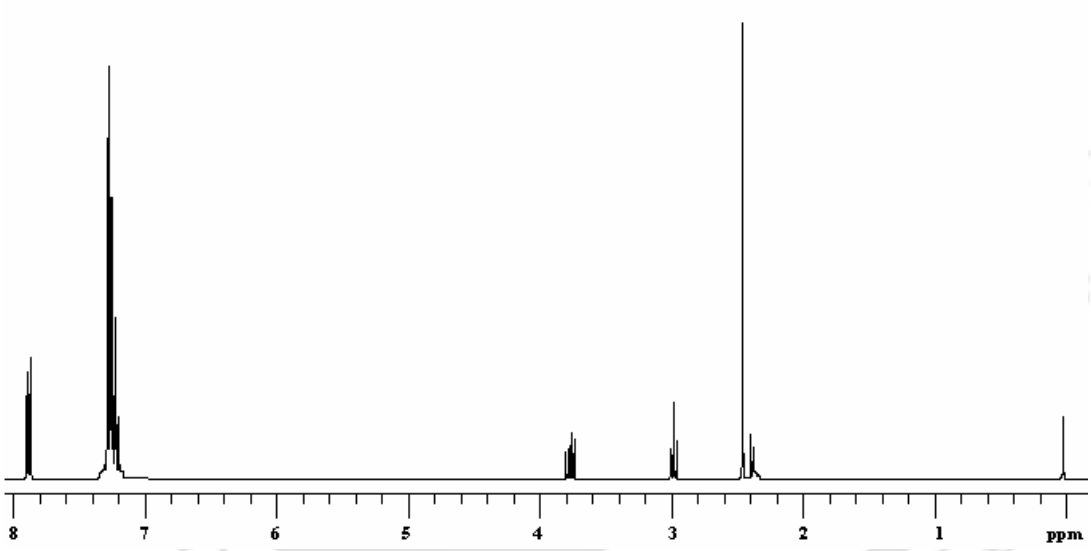


Fig 3.6 ^{1}H NMR Spectrum of N-(*p*-Tolylsulfonyl)-2-phenylaziridine

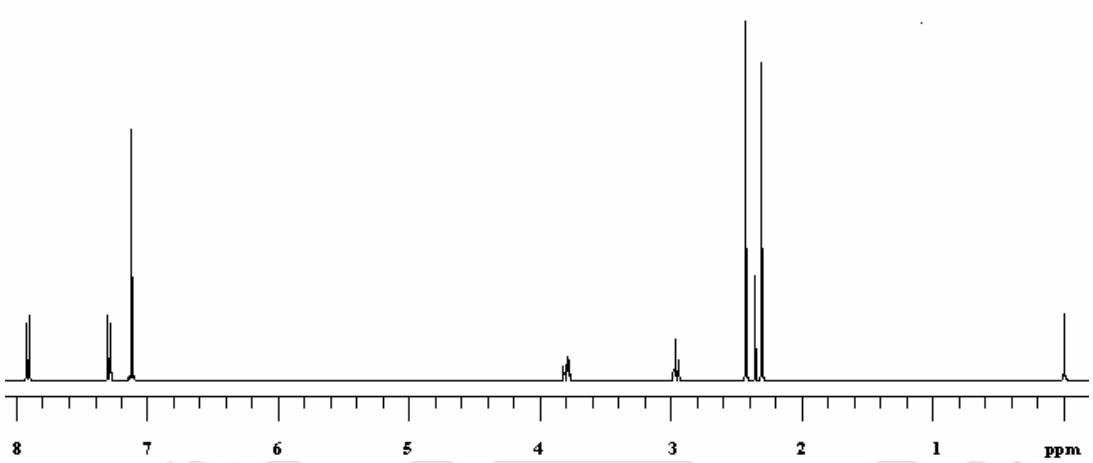


Fig 3.7 ^{1}H NMR Spectrum of N-(*p*-Tolylsulfonyl)-2-(p-methylphenyl)aziridine

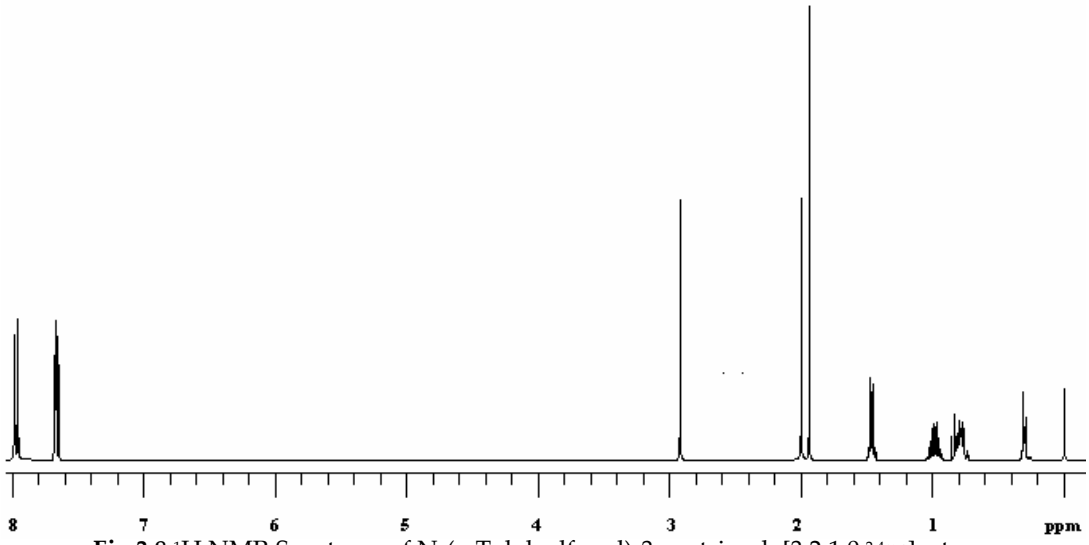


Fig 3.8 ^{1}H NMR Spectrum of N-(*p*-Tolylsulfonyl)-3-azatricyclo[3.2.1.0.^{2,4exo}]octane

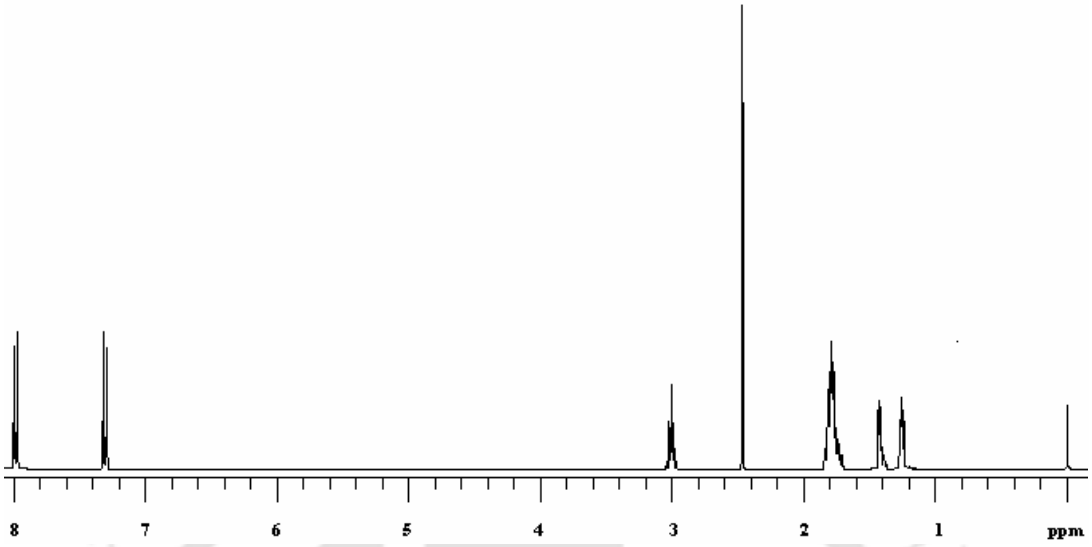
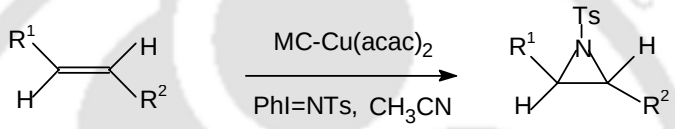


Fig 3.9 ^{1}H NMR Spectrum of N-(*p*-Tolylsulfonyl)-7-azabicyclo[4.1.0]heptane

RESULTS AND DISCUSSION

Considering the advantages of the microencapsulation technique, we have developed a MC-Cu(acac)$_2$ catalyst by immobilizing Cu(acac)$_2$ on polystyrene**.** Incidentally, we have at our disposal a very clean and easy-to-operate method for the preparation of highly pure Cu(acac)$_2$[83] which facilitated the catalyst preparation. The preparation of the MC-Cu(acac)$_2$ is very simple and was accomplished following the Kobayashi protocol[105] using 1 g of polystyrene and 120 mg of Cu(acac)$_2$. Measurement of the mass increase of the resultant MC-Cu(acac)$_2$ indicates that 100 mg of Cu(acac)$_2$ is encapsulated, and the copper content is 0.38 mmol/g.

MC-Cu(acac)$_2$ catalyzes the aziridination of a wide range of alkenes employing [*N*-(*p*-tolylsulfonyl)imino]phenyl iodinane (PhI=NTs) as the nitrogen source (**Scheme 3.5**).



Scheme 3.5 MC-Cu(acac)$_2$ Catalyzed Aziridination of Alkene

We have carried out aziridination of styrene using different nitrene donors such as chloramine-T, bromamine-T and PhI=NTs and the leaching of the metal for these nitrene donors was determined using an Atomic Absorption Spectrometer. The results are summarized in **Table 3.5**. The results confirm that PhI=NTs is the preferred nitrene donor for our catalytic system.

Table 3.5 Aziridination of Styrene using Various Nitrene Donors.

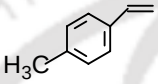
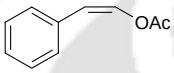
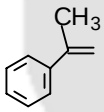
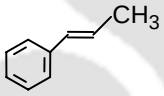
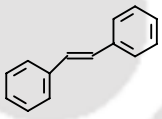
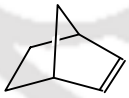
Nirene Donor	Time (h)	Yield (%)[a]	Cu-Leaching (Wt %)
PhI=NTs	1	92	0.025
Chloramine-T	6	36	16.56
Bromamine-T	6	45	10.28

[a] Isolated yields.

A variety of alkenes were examined for this MC-Cu(acac)$_2$ catalyzed aziridination using PhI=NTs. Under the standardized conditions (MeCN, 5.6 mol % catalyst, 1 equiv of PhI=NTs, 5 equiv of olefin, 25 ^{o}C), good yields of aziridines were obtained with both aromatic and aliphatic olefins. The results are summarized in **Table 3.6**. PhI=NTs, like its oxygen analogue PhI=O, is insoluble in a variety of solvents, including MeCN, dissolution of this reagent in the

reaction indicates the completion of the reaction. It is clear from the **Table 3.6** that the catalyst gives best results with phenyl substituted alkenes. The reaction of PhI=NTs with norbornene (entry **7**, **Table 3.6**) occurs from the less hindered *exo* face of the bicyclic nucleus to provide the

Table 3.6 MC-Cu(acac)$_2$ Catalyzed Aziridination of Alkenes[a]

Entry	Alkene	Time (h)	Yields (%)[b]
1		1	92, 90[c] 85[d] 95[e], 62[f]
2		1	85
3		1.5	76
4		1	82
5		2	80
6		2.5	74
7		2	88
8		2	52

[a] Unless otherwise specified reaction conditions were: MeCN, 25 ^{o}C, alkene: PhI=NTs = 5:1; [b] Isolated yield of aziridine based on PhI=NTs; [c] With used catalyst; [d] Styrene: PhI=NTs = 1:1 molar ratio; [e] With 10 mol% of Cu(acac)$_2$[92]; [f] With 5 mol% of CuHY catalyst.[98]

exo adduct in high yield and sterically hindered olefins like *trans*-stilbene (entry **6**, **Table 3.6**) afforded the corresponding aziridines in good yields.

In order to confirm that this process is truly heterogeneous, the catalyst was removed after the reaction run by filtration, fresh aliquots of reactants were added to the filtrate and the reaction was monitored by the dissolution of PhI=NTs**.** No product formation was observed.

Further, the recovered catalyst could be reused for several cycles with consistent activity (**Table 3.7**).

Table 3.7 Recovery and Reuse of the MC-Cu(acac)$_2$- Catalyst for Aziridination of Alkenes[a]

Entry	Cycle no.	Isolated Yield(%)
1	1	92
2	2	92
3	3	92
4	4	90
5	5	90

[a] MeCN, 25 ^{o}C, alkene: PhI=NTs = 5:1.

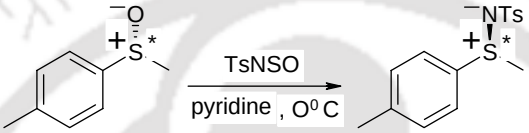
The present microencapsulated catalyst is more active than either its homogeneous analogue Cu(acac)$_2$ or a heterogeneous copper-exchanged zeolite Y (CuHY) catalyst (entry **1**, **Table 3.6**). It is noteworthy that in earlier studies in the homogeneously catalyzed reaction,[23] the yield ofaziridine decreased to 37%, when the molar ratio of styrene: PhI=NTs was 1:1, due to the competing breakdown of the PhI=NTs reagent to yield toluene-*p*-sulfonamide, whereas with our catalyst the yield is 85%. This is a particularly important observation because this procedure can be applied to the aziridination of expensive alkenes.

In conclusion, MC-Cu(acac)$_2$ is used as an effective catalyst for the aziridination of alkenes using PhI=NTs as the nitrene source with low catalyst loading. MC-Cu(acac)$_2$ catalyst can be reused for several cycles with consistent activity. The advantages of MC-Cu(acac)$_2$ are the ease of preparation and high activity.

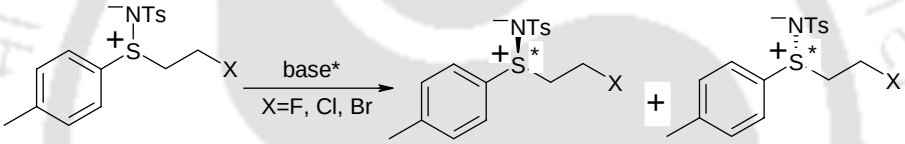
Heterogeneous Catalytic Sulfimidation with PhI=NTs and Immobilized $Cu(acac)_2$

Subsection 3.3.2

Sulfimides are the nitrogen analogues of sulfoxides and sulfonium ylides. Recently, sodium salts of chiral sulfimides were demonstrated as useful asymmetric methylidene tranfer reagents to prochiral carbonyl groups, leading to optically active epoxides.[112] Although the chemistry of chiral sulfoxide[113-115] and sulfonium ylides[116-121] has been investigated with a pledge of accomplishment, the study of their nitrogen analogues sulfimides[122] remain underdeveloped. It is partly because the multi-step methods for preparation of enantiomerically enriched sulfimides comprise of the conversion of chiral sulfoxides to the corresponding enantiomerically pure sulfimides, as reported by Cram *et al.*[123] (**Scheme 3.6**), and the kinetic resolution of recimic sulfimides reported by Annuziata *et al.*,[124] (**Scheme 3.7**).



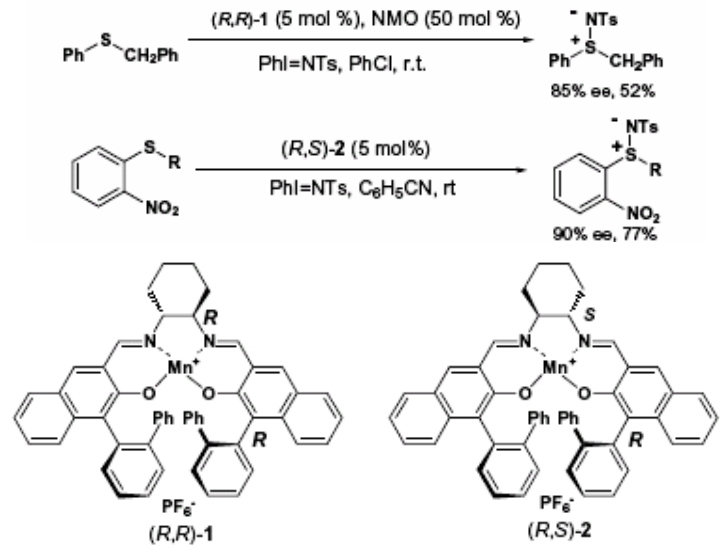
Scheme 3.6 Asymmetric Sulfimation of Sulfide



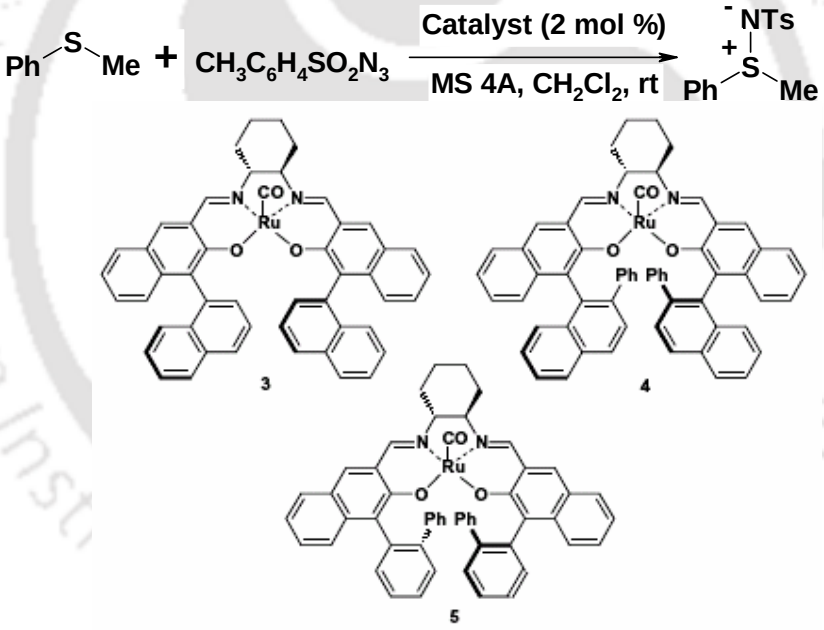
Scheme 3.7 Kinetic Resolution of Recimic Sulfimides

Recently, highly diastereoselective sulfimidations have also been reported by Gaggero *et al.* and Uemura *et al.*[125-127] On the other hand, Umera *et al.* reported catalytic asymmetric sulfimidation using chiral Cu(I) bis(oxazoline) complex as a catalyst and also the racemic synthesis of sulfimides using $Cu(OTf)_3$ as a catalyst and PhI=NTs as a nitrene donor, albeit at moderate enantioselectivity and longer reaction times, respectively.[128-131] Katsuki *et al*[132,133] found that optically active Mn(salen)s **1** and **2** served as efficient catalysts for enantioselective sulfimidation showing good enantioselectivity (**Scheme 3.8**). Later on they have also demonstrated that chiral ruthenium(II)(salen) complexes[134,135] **3, 4** and **5** bearing an apical CO ligand is an excellent catalyst for asymmetric sulfimidation using toluenesulfonyl azide as the nitrene donor **(Scheme 3.9)**. These catalysts have some limitations such as the requirement of longer reaction times and are not reusable. Thus, development of a simple new method for asymmetric synthesis of sulfimides is most timely.

One of the most efficient approaches for the catalyst separartion and recycling and easy separation of products is the use of room temperature ionic liquids.[136,137] They offer an alternative and ecologically sound medium compared to conventional organic liquids as they are non-volatile, recyclable and non-explosive. The catalysts having polar or ionic character can be



Scheme 3.8 Mn(salen) Complex Catalyzed Enantioselective Sulfimidation



Scheme 3.9 Ru(salen) Complex Catalyzed Enantioselective Sulfimidation

immobilized without additional structural modification and thus the ionic solutions containing the catalyst can be easily separated from the reagents and products. Ionic liquids have proven to be excellent solvents for many organic reactions.[138, 139]

Considering the advantages of these techniques, aziridination of olefins using PhI=NTs as a nitrene donor by microencapsulated $Cu(acac)_2$[140] and $Cu(acac)_2$ immobilized in ionic liquids[141] have recently been reported. And the promising results prompted us to explore the synthesis of sulfimides by microencapsulated $cu(acac)_2$ and $cu(acac)_2$ immobilized in ionic

liquids in presence of PhI=NTs. To the best of our knowledge, this is the first example of sulfimidation reaction using a heterogeneous catalyst.

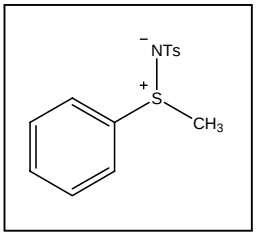
EXPERIMENTAL SECTION

General Procedure for Sulfimidation using MC-Cu(acac)$_2$: To acetonitrile (3 mL) were added MC-Cu(acac)$_2$ (0.15 g 5.6 mol%), methyl phenyl sulfide (0.124 g, 1 mmol) and PhI=NTs (0.372 g, 1 mmol) and the reaction mixture was stirred at room temperature. The reaction was monitored by disappearance of the PhI=NTs from the reaction mixture. After completion of the reaction, the catalyst was filtered and the filtrate concentrated and purified by column chromatography (ether/methanol, 96/4, v/v) to afford pure product as white solid. Yield: 0.252 g, 86%.

Typical Experimental Procedure for Sulfimidation using Cu(acac)$_2$ Immobilized in Ionic Liquid: Cu(acac)$_2$ (0.01 g, 7.7 mol%), methyl phenyl sulphide (0.124 g, 1mmol) and PhI=NTs (0.372 g, 1 mmol) were added to the ionic liquid (1 mL) and the reaction mixture was stirred at room temperature. The reaction was monitored by the disappearance of PhI=NTs. After completion of the reaction, the product was extracted with ether (3x4 mL) by simple decantation and purified by column chromatography on silica gel (ether/methanol, 96/4, v/v as an eluent) to afford pure product as white solid. Yield: 0.252 g, 85%.

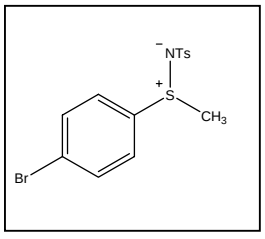
CHARACTERIZATION OF THE PRODUCTS

The compounds were characterized by ^{1}H NMR and data for the products are summarized as follows:



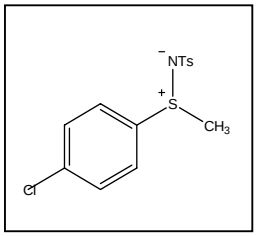
Name *S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 2.34 (s, 3H, CH_3) 2.81 (s, 3H, CH_3) 7.12-7.71 (m, 9H, Ar-H).



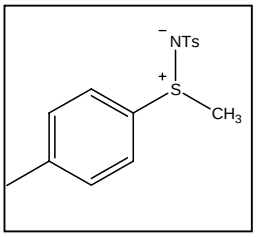
Name *S*-Methyl-*S*-(4-bromophenyl)-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 7.12-7.81 (m, 8H, Ar-H), 2.85 (s, 3H, CH_3). 2.38 (s, 3H, CH_3).



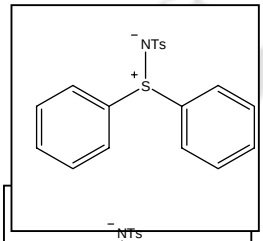
Name *S*-Methyl-*S*-(4-chlorophenyl)-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 7.12-7.95 (m, 8H, Ar-H), 2.81(s, 3H, CH_3). 2.32 (s, 3H, CH_3).



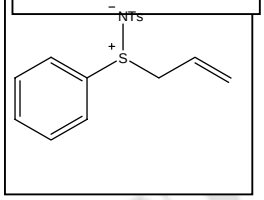
Name *S*-Methyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 2.34 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.81 (s, 3H, CH_3) 7.13-7.73 (m, 8H, Ar-H).



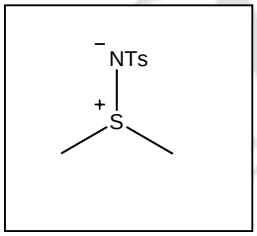
Name *S*, *S*-Diphenyl-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 2.43 (s, 3H, CH_3), 7.29-7.83 (m, 14H, Ar-H).



Name *S*-Allyl-*S*-phenyl-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 7.12-7.71(m, 9H, Ar-H), 3.52 (d, J= 7.4 Hz, 2H, CH_2). 2.32 (s, 3H, CH_3).



Name *S*,*S*-dimethyl-*N*-(*p*-tolylsulfononyl)sulfilimine

^{1}H NMR ($CDCl_3$, 200 MHz, ppm) δ 7.12-7.71(m, 4H, Ar-H), 2.81 (s, 6H, CH_3). 2.34 (s, 3H, CH_3).

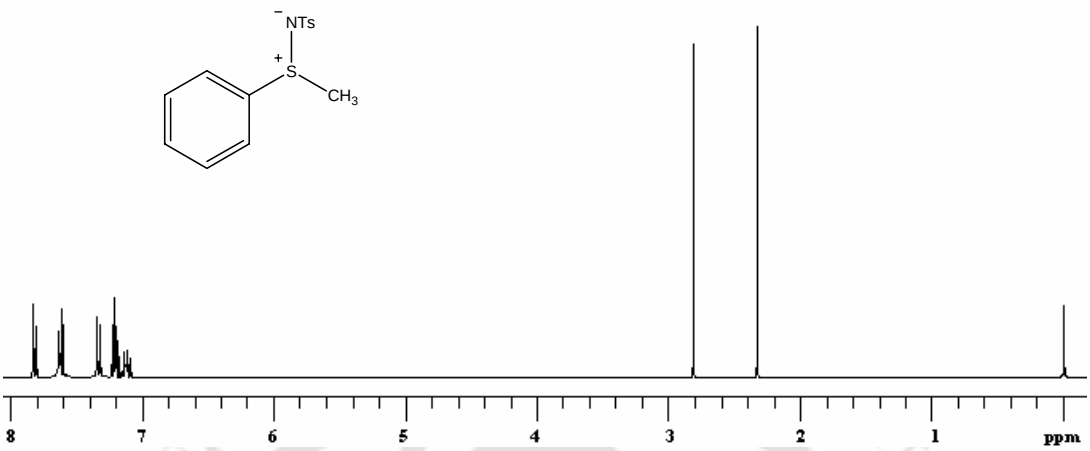


Fig 3.10 ^{1}H NMR Spectrum of *S*-Methyl-*S*-phenyl-*N*- (*p*-tolylsulfononyl)sulfilimine

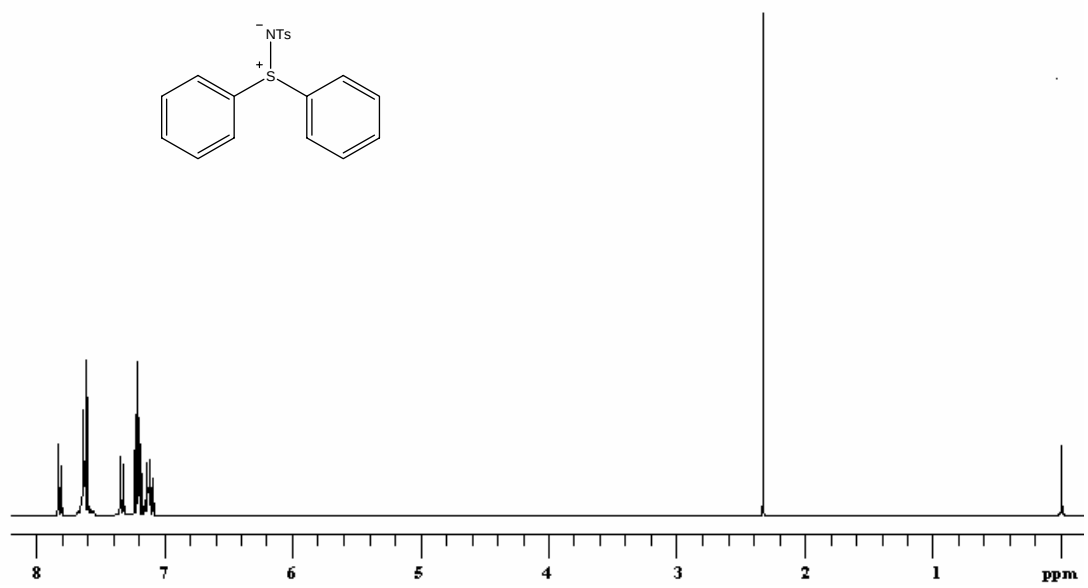


Fig 3.11 ^{1}H NMR Spectrum of *S, S*-Diphenyl-*N*-(*p*-tolylsulfononyl)sulfilimine

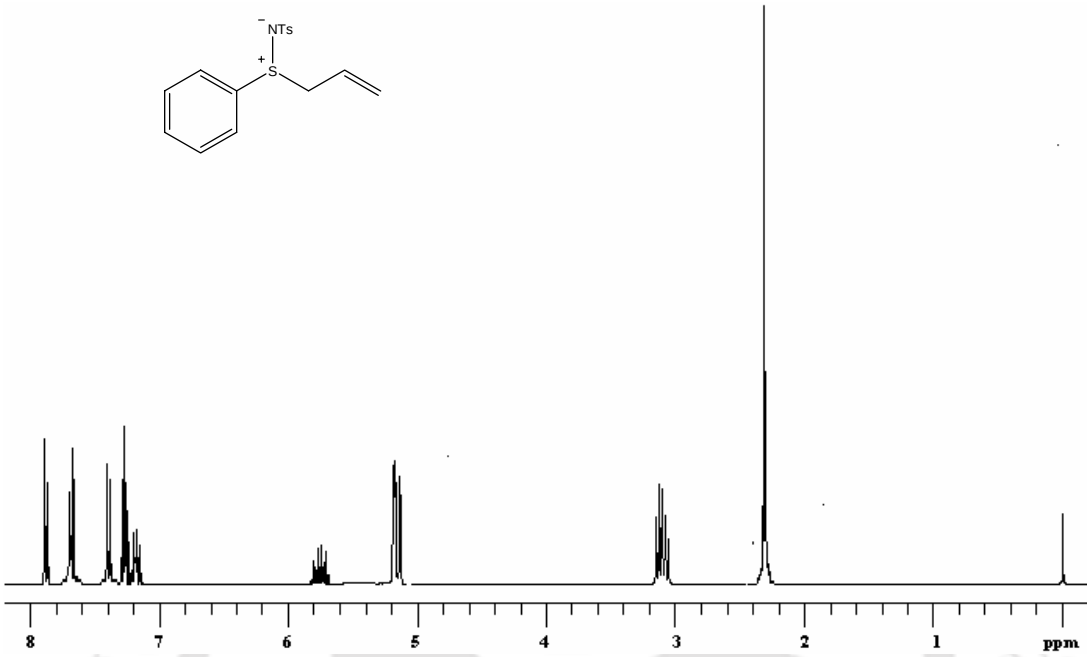


Fig 3.12 ^{1}H NMR Spectrum of *S*-Allyl-*S*-phenyl-*N*-(*p*-tolylsulfononyl)sulfilimine

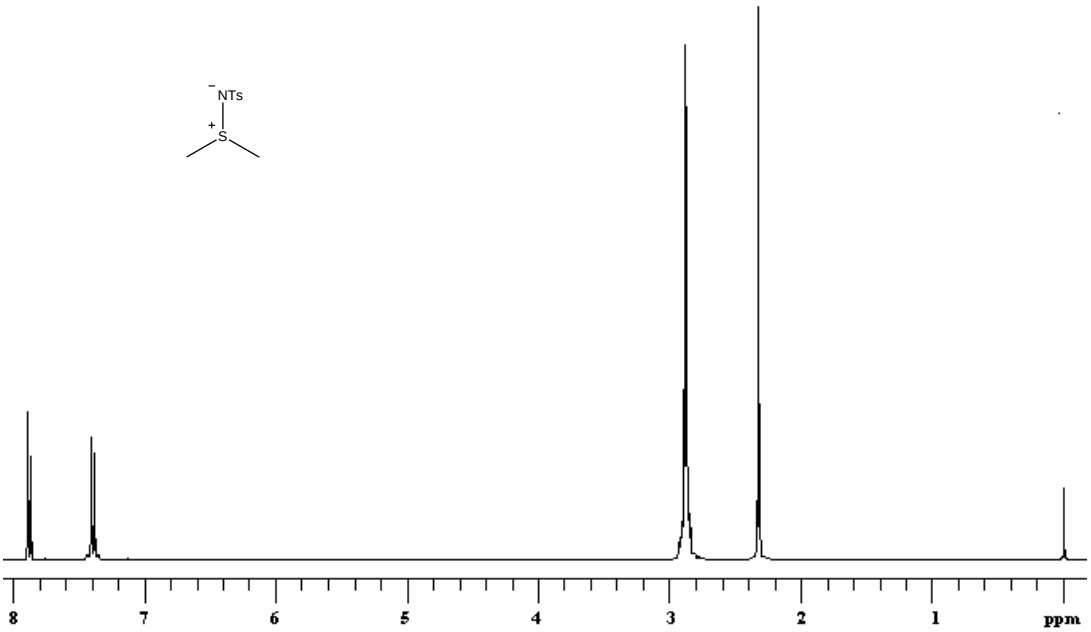
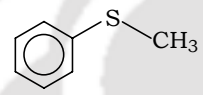
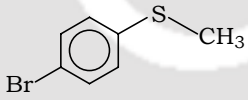
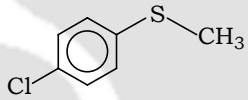
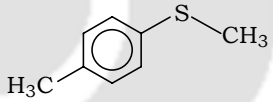
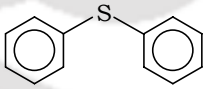
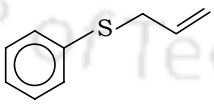
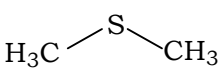


Fig 3.13 ^{1}H NMR Spectrum of *S,S*-dimethyl-*N*-(*p*-tolylsulfononyl)sulfilimine

RESULTS AND DISCUSSION

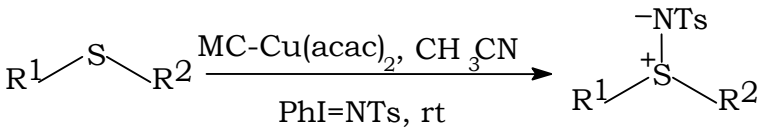
A variety of sulfides were subjected to sulfimidation reaction in the presence of 5.6 mol% of MC-Cu(acac)$_2$ in MeCN , one equivalent PhI=NTs and 1mmol of sulfide at 25 °C to afford the corresponding sulfimides in high yields, as reported. The results are summarized in **Table 3.8**. Aliphatic sulfides gave higher yields compared to the aromatic sulfides (entry **7**).

Table 3.8 Sulfimidation of Sulfides with PhI=NTs using MC-Cu(acac)$_2$

		MC-Cu(acac)$_2$	
Entry	Substrate	Time (h)	Yield (%)[a]
1		1	86, 85[b]
2		5	75
3		6	78
4		1	88
5		6	75
6		2	84
7		0.33	92

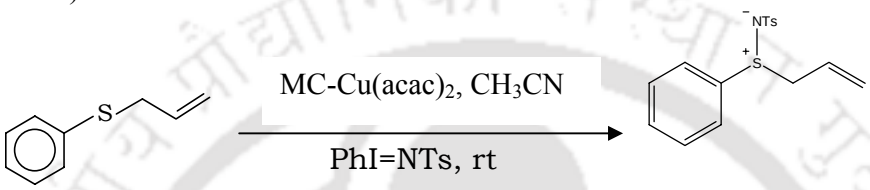
[a] Isolated yields, [b] With recycled catalyst

Aromatic sulfides bearing electron-releasing groups (entry **4**) are found to be more reactive than those bearing electron withdrawing groups in the sulfimidation reaction (**Scheme 3.10**).



Scheme 3.10 MC-Cu(acac)$_2$ Catalyzed Sulfimidation

When the reaction is applied to allylic sulfides, aziridination to the double bond did not occur instead allylic sulfenamide was obtained selectively in good yields (entry **6**, **Table 3.8**) (**Scheme 3.11**).



Scheme 3.11 MC-[Cu(acac)$_2$] Catalyzed Sulfimidation of Allylic Sulfide

In order to confirm that this process is truly heterogeneous, the catalyst was removed after the reaction run by filtration, fresh aliquots of reactants were added to the filtrate and the reaction was monitored by the dissolution of PhI=NTs**.** No product formation was observed. Further, the recovered catalyst could be reused for 5 cycles with consistent activity (**Fig 3.14**).

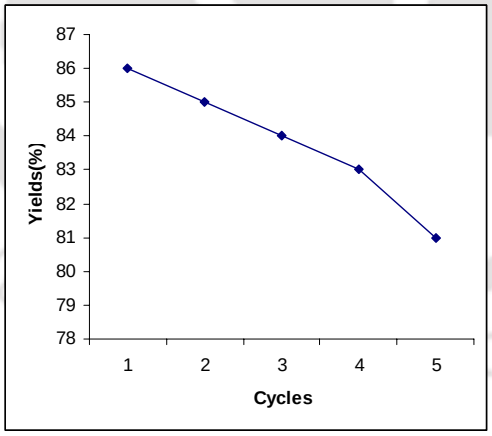
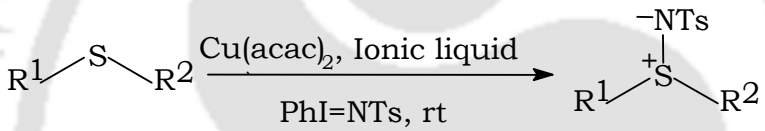


Fig 3.14 Recycling of the MC-Cu(acac)$_2$ Catalyst for Sulfimidation of S-methyl-S-phenyl sulfide

On the other hand ionic liquids provide innocent solvent systems for biphasic catalysis, heterogeneizing the catalyst and product into two separate and immiscible phases without loosing the selectivity and efficiency inherent in homogeneous catalysis. While the catalyst residing in solution in one of the two phases, the substrate resides in the other phase. During reaction, the catalyst and the substrate are allowed to interact by stirring the mixture vigorously.

Reactions can be accelerated in ionic liquids with improved selectivity. In fact an increased stability of the catalyst is observed in the ionic liquid, for instance. Finally their nonvolatile nature enables significant advantage for distillative product separation, and the catalyst solution is available for immediate reuse.

Hence, in separate experiments the synthesis of sulfimides were carried out using $Cu(acac)_2$ immobilized in ionic liquids. $BmimBF_4$ and $BmimPF_6$ ionic liquids were synthesized according to the procedures reported in the literature[14] and used in the present investigation. A variety of alkenes were subjected to sulfimidation reaction in the presence of 7.7 mol% of $Cu(acac)_2$ in 1mL of ionic liquid, 1 equivalent of PhI=NTs and 1mmol of sulfide at 25 °C and very good yields of sulfimides were obtained with both aromatic and aliphatic sulfides. The results are summarized in **Table 3.9**. It may be mentioned that both $BmimBF_4$ and $BmimPF_6$ seemed to have shown almost similar activities in so far as the sulfimidation reactions are concerned.



Scheme 3.12 Sulfimidation Catalyzed $Cu(acac)_2$ Immobilized in Ionic Liquid.

Finally upon completion of a reaction, the ionic liquid phase containing $BmimBF_4$ or $BmimPF_6$ and $Cu(acac)_2$ was almost quantitatively recovered by simple extraction of the product with Et_2O. The recovered ionic liquid phase containing the catalyst was reused for several additional cycles with consistent activity (entry **1**, **Table 3.9**). Further, it is evident from the results that the product yields are almost similar to those of MC-$Cu(acac)_2$ reactions, however, the reactions proceeded with much alacrity in the ionic liquids.

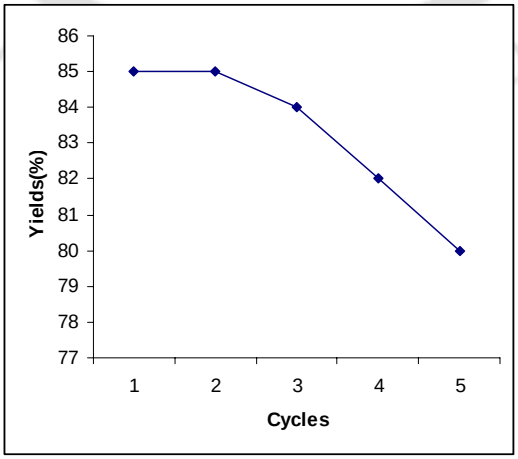
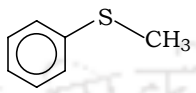
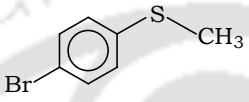
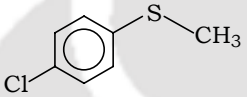
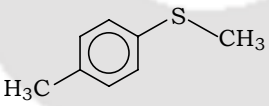
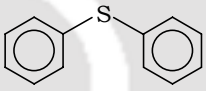
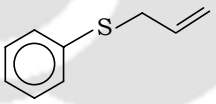
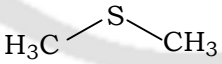


Fig 3.15 Recycling of the $Cu(acac)_2$-catalyst Immobilized in Ionic Liquid for Sulfimidation of S-methyl-S-phenyl sulfide

Table 3.9 Sulfimidation of Sulfides with PhI=NTs using $Cu(acac)_2$ Immobilized in Ionic Liquid

		$BmimBF_4$	
Entry	Substrate	Time (min)	Yield (%)[a]
1		15	85, 85[b] 84[c]
2		15	77
3		20	78
4		15	87
5		20	78
6		20	85
7		5	94

[a]Isolated yields, [b] With recycled catalyst, [c] With $BmimPF_6$

In conclusion, MC-$Cu(acac)_2$ and $Cu(acac)_2$ immobilised in ionic liquids are used as effective catalysts for the synthesis of sulfimides from the reactions of sulfides with PhI=NTs as the nitrene donor in very good yields. We have also demonstrated that ionic liquids can act as powerful media not only for facilitating the catalyst recycling but also for accelerating the reaction rate in $Cu(acac)_2$ catalyzed sulfimidation reactions.

$VO(acac)_2$ Supported on Titania: A Heterogeneous Catalyst for the Selective Oxidation of Sulfides using TBHP

Subsection 3.4

The discovery of new catalysts leading to applications in synthetic organic chemistry is of much current interest in heterogeneous catalysis, in view of the following advantages, for example, easy work-up, reusability, atom economy, and reduction of waste. The vast chemistry of sulfoxides and sulfones makes them very useful reagents in organic synthesis in general and useful synthetic intermediates for the construction of various chemically and biologically significant molecules in particular.[142,143] For this reason the oxidation of sulfides to chiral/achiral sulfoxides or sulfones has been the subject of extensive studies and a number of synthetic procedures are now available.[144-165] To date, the most important method for preparing sulfoxides or sulfones involves the oxidation of sulfides. Various oxidising reagents used for this purpose include nitric acid,[147,148] $KMnO_4$,[149] MnO_2,[150] $NaClO_4$,[151] *m*-chloroperbenzoic acid,[152] sodium metaperiodate,[153,154] bromine,[155] nitrogen tetraoxide,[156,157] oxaziridine,[158] benzeneseleninic peracid,[159,160] *tert*-butyl hydroperoxide,[161] sulfinyl peroxy compounds,[162] iodosobenzene diacetate[163] and 4-methylmorpholine *N*-oxide with osmium tetraoxide.[164] Unfortunately most of these reagents are not satisfactory for medium to large scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavourable by-products, and high cost. Singlet oxygen or molecular oxygen combined with 2-methylpropanal and Co(II) complexes[165,166] has, however, been used with reasonable success.

Catalytic homogeneous reactions were preferred over reactions that use stoichiometric quantities, since the stoichiometric reactions are not only corrosive and hazardous at times, but they also generate copious amounts of heavy metal waste. For instance, the oxidation of sulfides has been performed under homogeneous conditions using aqueous hydrogen peroxide as oxidant in the presence of a metal catalyst, such as H_2WO_4,[167] $[C_5H_5N(n\text{-}C_{16}H_{33})]_3PO_4[W(O)(O_2)_2]_4$,[168] and Na_2WO_4 + $[n\text{-}C_4H_9)_4N]Cl$[179] in addition to Na_2MoO_4 + $(n\text{-}C_4H_9)_3PO$,[170] $TiCl_3$,[171] CH_3ReO_3.[172] Recently, Noyori *et al.*[173] reported oxidation of sulfides to sulfoxides and sulfones with 30% H_2O_2 using Na_2WO_4 under solvent and halogen free conditions. A phosphonic acid promoter and an acidic quaternary ammonium salt, $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ were used along with the catalyst making the process cumbersome. Moreover, the catalyst could not be recovered for further cycles.

An ideal system for such reactions is a solid catalyst capable of working under heterogeneous conditions. This would allow easy separation of the catalyst from the reaction mixture and adaptability in large-scale production to conform to the class of greener technologies. In recent years selective oxidation of sulfides to sulfoxides or sulfones has been carried out with a number of supported reagents or catalysts.[174-182] For instance, titanium silicates (TS-1 and TS-2)[180] promote sulfide oxidation but the use of bulky sulfides is precluded by their

limited access to the relatively small Ti active sites. In order to overcome this limitation, mesoporous materials have been used. Thus, Ti-MCM-41 allows the oxidation of bulky sulfides[183] but with the loss of selectivity. Subsequently, Fraile *et al.*[184] introduced $Ti(O^iPr)_4$ supported on silica as an efficient and selective catalyst for the oxidation of sulfides to sulfoxides but the drawback is the gradual leaching of titanium during the reaction. Recently, some of our collaborators reported the catalytic oxidation of sulfides by tungstate-exchanged Mg-Al-LDH catalyst (LDH-WO_4) in quantitative yields at faster rate in aqueous media.[185]

Although many reagents have been employed for the oxidation of sulfides,[186] there is still a need for ones that are efficient, selective and environmentally acceptable. One oxidant that meets the last criterion, in addition to being inexpensive and safe to handle even in large quantities,[187,161] is *tert*-butyl hydroperoxide [$(CH_3)_3COOH$]. However, used alone it is a poor oxidizing agent. Thus it requires a metal or solid support to activate.[187]

With an ever-increasing level of global competition and environmental consciousness, there is much incentive to find new and strategically important processes using a robust and recyclable catalyst that provides higher atom utilization, preferably close to theoretical values, to eventually minimize pollution levels using greener ingredients. The challenge is to perform a truly heterogeneous catalytic reaction for the oxidation of sulfides in the laboratory, bulk and fine chemical industries.

We herein report a heterogeneous catalytic system comprising of a vanadium complex supported on titania for the oxidation of sulfides using *tert*-butyl hydroperoxide (TBHP) as an oxidant in dichloromethane in quantitative yields at room-temperature (equation 1). We have a very clean and easy method for the preparation of highly pure $VO(acac)_2$[83] which facilitated the catalyst preparation.

EXPERIMENTAL SECTION

Preparation of $VO(acac)_2$ Supported on Titania ($VO(acac)_2$ - TiO_2)

To a solution of $VO(acac)_2$ (265 mg) in anhydrous THF (50 mL), TiO_2 (1.0 g) was added and stirred at 293 K for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed several times with anhydrous THF and finally dried *in vacuo*. Measurement of the mass increase of the resultant $VO(acac)_2$-TiO_2 indicates that 170 mg of $VO(acac)_2$ is supported, and the vanadium content is 0.64 mmol/g.

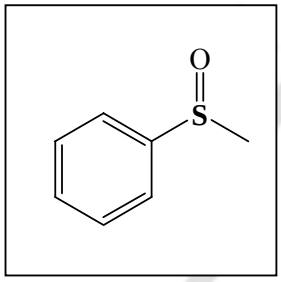
Typical Procedure for the Oxidation of Methyl Phenyl Sulfide

To the stirred mixture of methyl phenyl sulfide (121 mg, 1 mmol) and $VO(acac)_2$ - TiO_2 (50 mg, 0.032 mmol) in dichloromethane (10 mL), was added anhydrous TBHP (0.44 mL, 2.56

M in isooctane*)* in 2 or 3 portions at room temperature. After completion of the reaction (followed by TLC), the catalyst was filtered off and washed with ethyl acetate (2 × 10 mL), dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to afford the crude product. Analytically pure compound was obtained after column chromatography (silica gel, hexane–ethyl acetate). The yield was 128 mg (93%).

CHARACTERIZATION OF THE PRODUCTS

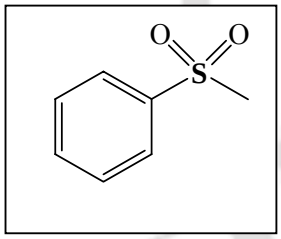
The compounds were characterized by IR and ^{1}H NMR and data for the product are summarized as follows:



Name Methylsulfinylbenzene

IR (cm^{-1}) 1047

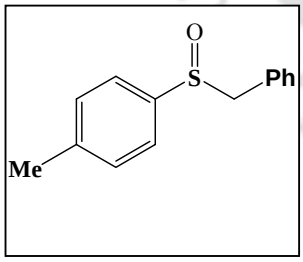
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 2.78 (3H, s, Me), 7.44–7.66 (m, 5H, Ph)



Name Methylsulfonylbenzene

IR (cm^{-1}) 1320, 1164

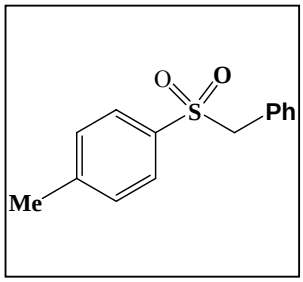
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 3.0 (3H, s, Me), 7.44–7.64 (m, 3H, Ph), 7.84–7.95 (2H, d, Ph–H, J = 8.1 Hz)



Name 1-((*p*-tolylsulfinyl)methyl)benzene

IR (cm^{-1}) 1038

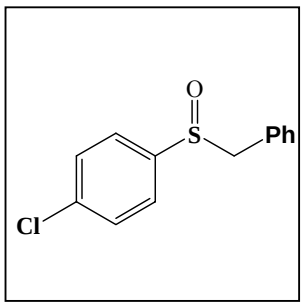
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 2.4 (3H, s, Me), 3.9 (1H, d, CH_2,J = 12.7 Hz), 4.05 (1H, d, CH_2, J = 12.7 Hz), 6.9 (2H, m, Ph–H) 7.18 (7H, m, Ph–H)



Name 1-Benzylsulfonyl-4-methylbenzene

IR (cm^{-1}) 1309, 1151

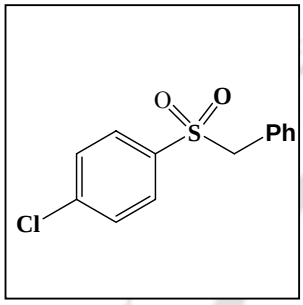
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 2.42 (3H, s, Me), 4.22 (2H, s, CH_2), 7.06 (2H, m, Ph–H), 7.22 (3H, m, Ph–H), 7.4 (2H, m,Ph–H), 7.62 (2H, m, Ph–H)



Name 1-Benzylsulfinyl-4-chlorobenzene

IR (cm^{-1}) 1040

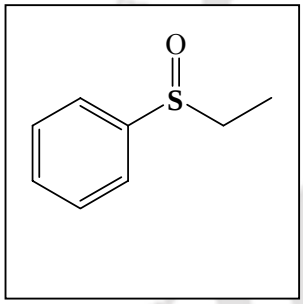
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 3.98 (1H, d, CH_2, J = 12.7 Hz), 4.04 (1H, d, CH_2 J = 12.7 Hz), 6.95 (2H, d, Ph–H, J = 6.8 Hz), 7.3 (5H, m, Ph–H), 7.38 (2H, d, Ph–H, J = 6.8 Hz)



Name 1-Benzylsulfonyl-4-chlorobenzene

IR (cm^{-1}) 1310, 1150

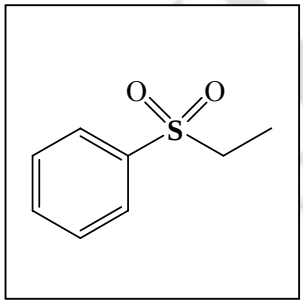
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 4.24 (2H, s, CH_2), 7.01 (2H, d, Ph–H, J = 6.8 Hz), 7.32 (3H, m, Ph–H), 7.42 (2H, d, Ph–H, J = 6.8 Hz), 7.58 (2H, d, Ph–H, J = 6.8 Hz)



Name 1-Ethylsulfinylbenzene

IR (cm^{-1}) 1062

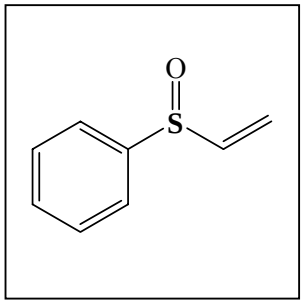
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 1.2 (3H, t, Me, J = 6.6 Hz), 2.7–2.75 (1H, q, CH_2, J = 6.6 Hz), 2.9 (1H, q, CH_2, J = 6.6 Hz), 7.1–7.45 (3H, m, Ph–H), 7.45–7.8 (2H, m, Ph–H)



Name 1-Ethylsulfonylbenzene

IR (cm^{-1}) 1320, 1146

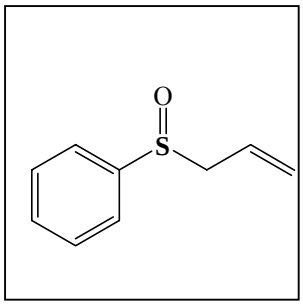
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 1.3 (3H, t, Me, J = 7.0 Hz), 3.1 (2H, q, CH_2 J = 7.0 Hz), 7.5 (3H, m, Ph–H), 7.9 (2H, m, Ph–H)



Name 1-Vinylsulfinylbenzene

IR (cm^{-1}) 1053

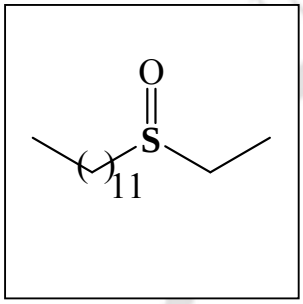
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 5.89 (1H, d, CH, J = 10.2 Hz), 6.2 (1H, d, CH, J = 15.3 Hz), 6.5–6.8 (1H, m, CH), 7.5–7.8 (5H, m, Ph–H)



Name 1-Allylsulfinylbenzene

IR (cm^{-1}) 1044

^1H NMR ($CDCl_3$, 300MHz, ppm) δ 3.45 (2H, s, CH_2), 5.1 (1H, d, CH, *J* = 15 Hz), 5.32 (1H, d, CH, *J* = 11 Hz), 5.65 (1H, m, CH), 7.55 (5H, m, Ph–H)



Name 1-Ethylsulfinyldodecane

IR (cm^{-1}) 1046

^1H NMR ($CDCl_3$, 300MHz, ppm) δ 1.2–1.5 (m, alkyl, 21H), 1.7–1.9 (2H, m, CH_2), 2.55–2.75 (2H, m, CH_2), 2.95– 3.0 (2H, m, CH_2)

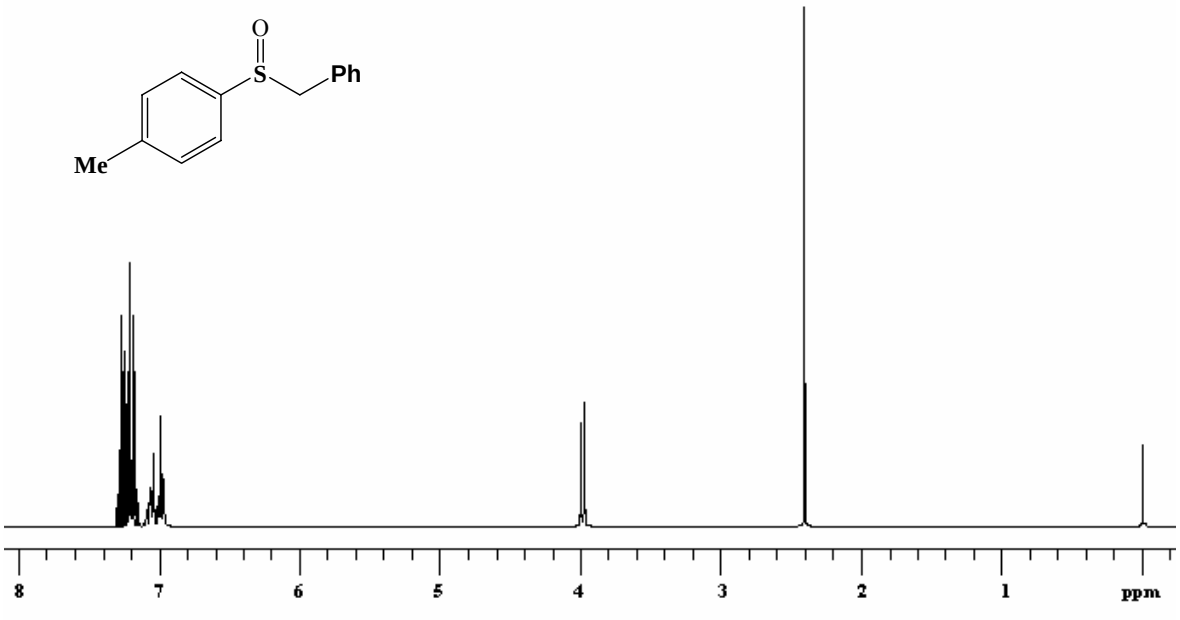


Fig 3.16 ^1H NMR Spectrum of 1-((*p*-tolylsulfinyl)methyl)benzene

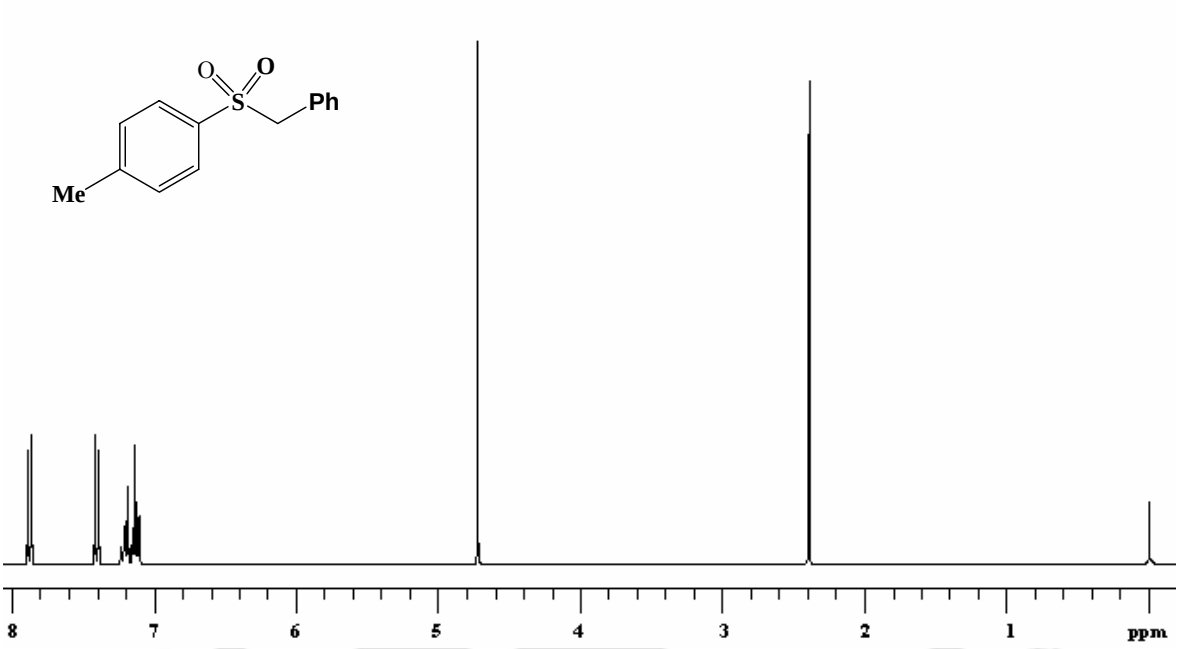


Fig 3.17 ^{1}H NMR Spectrum of 1-Benzylsulfonyl-4-methylbenzene

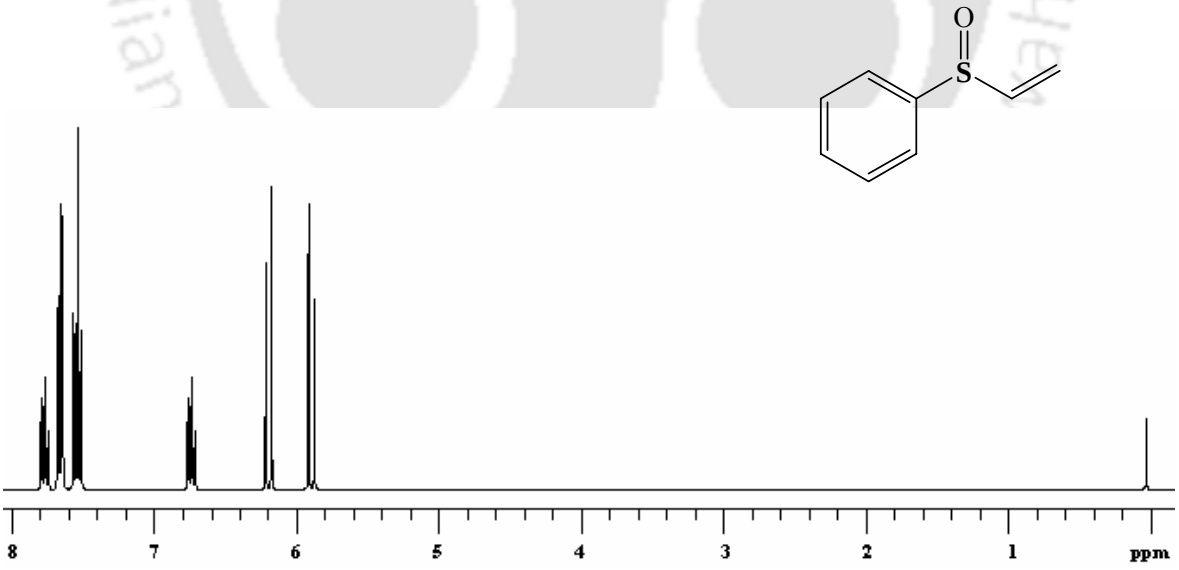


Fig 3.18 ^{1}H NMR Spectrum of 1-Vinylsulfinylbenzene

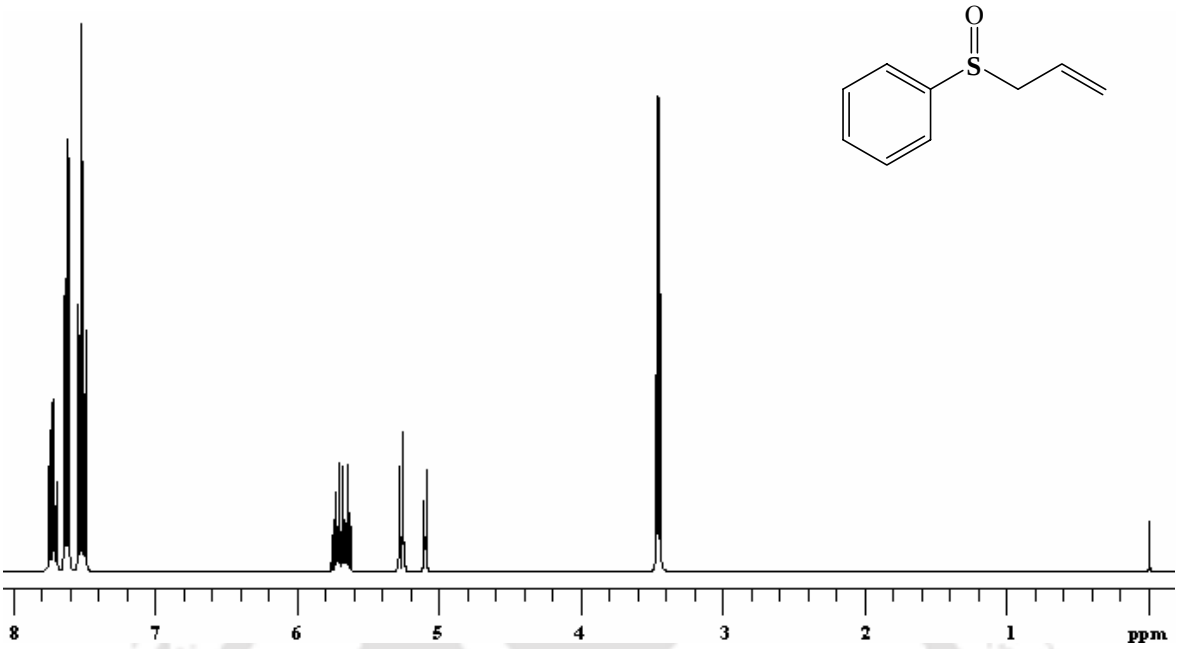
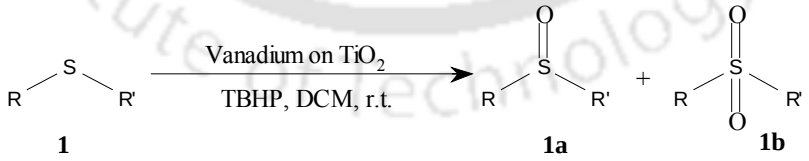


Fig 3.19 ^{1}H NMR Spectrum of 1-Allylsulfinylbenzene

RESULTS AND DISCUSSION

We report in this section a heterogeneous catalytic system comprising of a vanadium complex supported on titania catalyst for the oxidation of sulfides using *tert*-butylhydroperoxide (TBHP) as an oxidant in methylene chloride in quantitative yields at room temperature (**Scheme 3.13**). A similar reaction using H_2O_2 as an oxidant afforded the conversion to sulfoxides in the range of 53-76% after 24 hours,[188] as opposed to the present reaction which is far more facile.



1 **1a** **1b**

Scheme 3.13 Oxidation of Sulfides by $VO(acac)_2$ Supported on Titania using TBHP

The vanadium supported titania catalyst and its homogeneous analogues were evaluated for the oxidation of thioanisole in order to identify the best catalytic system using anhydrous TBHP, and results are presented in **Table 3.10** It is evident from the results that $VO(acac)_2$ supported on TiO_2 (anatase) (Cat 1) showed excellent activity in the oxidation of thioanisole by TBHP as an oxidant. Incidentally, Cat 2 also afforded comparable results. From this study, it is

concluded that the use of anatase or rutile form of titania in the oxidation of thioanisole does not influence the selectivity or yield (entry **1** and **2**, **Table 3.10**) of the products. No reaction occurred without the catalyst, in the oxidation of thioanisole using TBHP alone as an oxidant (entry **6**, **Table 3.10**), as evident.

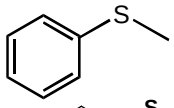
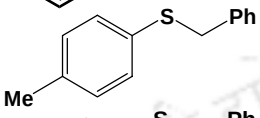
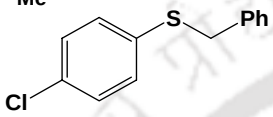
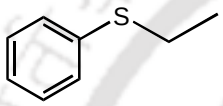
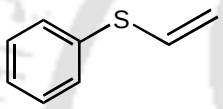
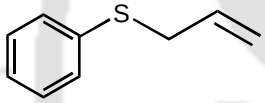
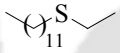
Table 3.10 Catalytic Oxidation of Thioanisole by TBHP using Various Catalysts[a]

Ex. No	Catalyst	Time (h)	Conversion (%)	Selectivity	
				Sulfoxide	Sulfone
1	TiO_2 (anatase)	24	99	56	44
2	TiO_2 (rutile)	24	99	51	49
3	TiO_2 (anatase)-$VO(acac)_2$ (Cat **1**)	1.5	99	97	03
4	TiO_2 (rutile)-$VO(acac)_2$ (Cat **2**)	2.0	99	98	02
5	$VO(acac)_2$	0.25	99	86	14
6	None	2	No reaction	-	-
		24	70	100	-

[a]All reactions were carried out with 1 mmol of substrate, 100 mg of catalyst in 10 mL methylene chloride, 0.44 mL of anhydrous TBHP (2.56M) at room temperature.

In an effort to understand the scope of the reaction, a series of sulfides having varied R groups attached to the sulfur atom were subjected to oxidation using the vanadium supported titania (Cat **1**)-TBHP system and the results are presented in **Table 3.11**. It is significant to note that the vinylic and allylic sulfides afford the form corresponding sulfoxides/sulfones without the cleavage of carbon–carbon bonds (entries **5** and **6, Table 3.11**). The studies on the conversion as well as selectivity as a function of time in the oxidation of sulfides show higher selectivities towards sulfoxides at lower conversions. With increasing time, the conversion increases but selectivity is reduced. In most cases, sulfoxide is obtained as the major product (*ca*. >90 %).

Table 3.11 Oxidation of Sulfides by $VO(acac)_2$ - TiO_2 using TBHP[a]

Entry	Sulfide **1–10**	Time (h)	Conversion (%)[b]	Sulfoxide **1a–10a**	Sulfone **1b–10b**
1		1.5	99 90[c]	97 95	03 05
2		2	99	87	13
3		5	99	93	7
4		6.5	99	46	54
5		4.5	99	100	-
6		6	99	100	-
7		2.5	99	100	-

[a]Reaction conditions are as exemplified in **Table 3.10**, in footnote *a*; [b]Isolated yield; [c]Conversion after 5th cycle

It is important to note that the catalyst is recycled for five times without significant loss of activity and selectivity as represented in **Figure 3.20**.

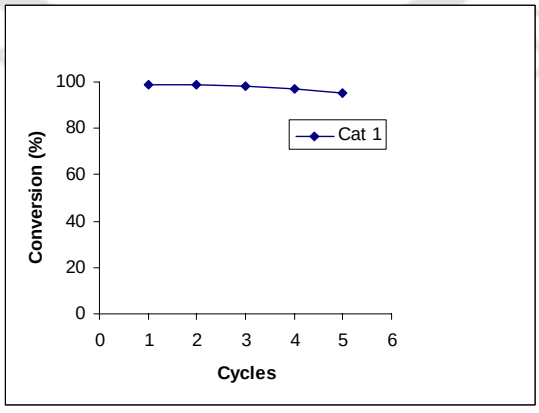
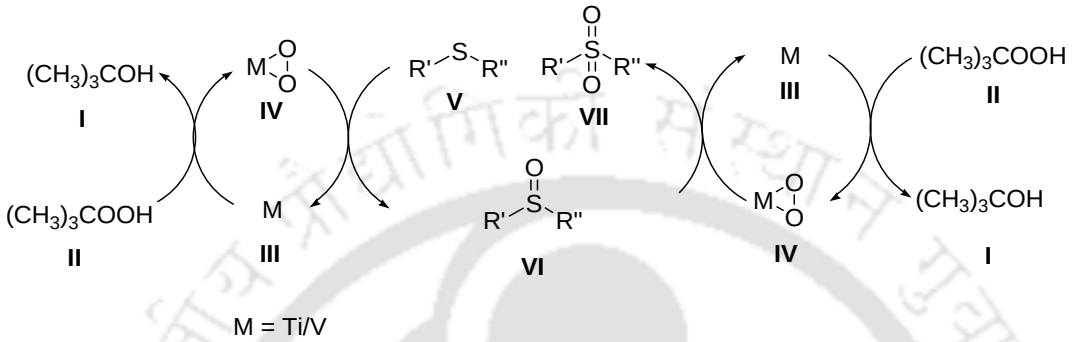


Figure 3.20 Conversion obtained with multiple cycles of the catalyst (Cat **1**) in the oxidation of thioanisole using TBHP. Reaction conditions: 1 mmol of thioanisole, 100 mg of catalyst in 10 mL methylene chloride, 0.44 mL of anhydrous TBHP (2.56M) at room temperature.

Although the exact mechanism of oxidation is only predictive at this moment, yet being guided by our long experience on the peroxo-chemistry of titanium[189] and vanadium,[190-192] it is believed that the catalyst, (Cat **1) III** interacts with TBHP to form a peroxometal intermediate of the type **IV** thereby activating the bound peroxide. The oxidation is then likely to proceed via metal-oxygen transfer mechanism as shown below.[185]



Scheme 3.14 Plausible mechanism for the oxidation of sulfides by supported vanadium on titania using TBHP.

The plausible catalytic cycle in the oxidation of sulfides to sulfoxides or sulfones may be presented as depicted in **Scheme 3.14.** In the present reaction the ease of transfer of electrophilic oxygen from the peroxometal species, **IV**, to the nucleophilic sulfide **V** facilitate the formation of sulfoxide **VI**. The sulfoxide **VI** may further react with another mole of active peroxometal species, **IV,** to form sulfone **VII** with the eventual regeneration of the catalyst **III**.

In summary, the present study represents the first example wherein the vanadium supported on titania is used in catalytic amounts for the oxidation of sulfides to sulfoxides and/or sulfones. With the broader scope of utility as applied for bulky sulfoxides and consistent activity over a number of cycles, the present catalytic system is superior to the other heterogeneous catalysts reported so far. The high throughput of the product obtained using the vanadium supported on titania catalyst using TBHP as an oxidant lowers the inventories of the process to offer a potentially competitive and economically viable process.

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187. $(CH_3)_3COOH$ is commercially available, has high thermal stability, and is safer to handle than CH_3CO_3H or HOOH because of its much lower sensitivity to decomposition catalyzed by trace metallic impurities.[14] Moreover, its byproduct of oxidation, $(CH_3)_3COH$, is easily removed from reaction mixtures by distillation or

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Solvent-free and Catalytic Oxidations with Chromium(VI) Based Reagents and Catalyst*

* A part of this chapter constitutes the subject matter of a patent and a publication:

1. US Patent Appl. Publ., Pub. No.:US 2004/0133003 A1, Pub. Date: Jul. 8, 2004.
2. *Synthetic Communications*, **2004**, *22*, 4077.

Chapter 4

Economic synthesis[1] of frequently used chemicals and solvent-free chemical transformations[2-5] have drawn significant attention in contemporary chemistry research due to the concerns for eco-benevolence. While the former produces zero waste, reactions under solvent-free conditions are expected to have several advantages such as improved yield, selectivity, procedural simplicity and redundancy of detrimental organic solvents during reactions; such reactions are especially important in the context of 'Green Chemistry'[1] and may have potential applications in combinatorial chemistry. [6]

Partial oxidations of organic substrates have always been commercially very important [1] and for this purpose no other reagent could be as popular, as useful and as successful as the chromium(VI) reagents have been. Some of the important entries in the list of chromium(VI) reagents are the Collin's reagent,[7] chromium-trioxide-3,5-dimethyl-pyrazole complex,[8] pyridinium chlorochromate (**PCC**),[9,10] pyridinium dichromate (**PDC**)[11] and 2,2′-bipyridinium chlorochromate (**BiPCC**).[12] In addition, there are a few other systems which work as reagents in combination with chromium(VI), e.g., chromium(VI)—*t*-butylhydroperoxide,[13-16] chromium(VI)— peroxocarbonate[17,18] and chromium(VI) — peroxoborate.[19]

Our participation in the development of newer chromium reagents led to the introduction of reagents like pyridinium fluorochromate (**PFC**),[20-23] quinolinium fluorochromate (**QFC**)[24] and 3,5-dimethylpyrazolium fluorochromate(VI), **DmpzHFC**, $C_5H_8N_2H[CrO_3F]$,[25] as oxidants with improved properties in terms of higher solubility and controlled acidity. An ever-increasing use of **PFC** as a versatile oxidant attests to its credibility as a popular reagent. This reagent has not only survived the test of time but also been continuously showing newer applications with the passage of time.[26-32] All these investigations were conducted in solutions. Pertinent to mention is that solvent-free oxidations have already begun to appear in literature[33-37] and there is a large scope of further research. Having been encouraged by the affirmative potential of and the attention received by **PFC** since its first report in 1982,[20] and being guided by the tenets of 'Green Chemistry', it was considered incumbent on us to develop its economic synthesis, since it so frequently used, and to ascertain its efficacy in solvent-free oxidative transformations including selective oxidations, Δ^5-steroidal oxidations, deoximations and deprotections. It may be noted that Δ^5-steroidal oxidations with **PFC**-CH_2Cl_2 or **PFC**-CH_3CN did not work. Preliminary results of investigation suggest that the reactions are relatively facile.

Notably for alcohol oxidations, it is advisable that the reactions are performed in anhydrous conditions in order to exclude the formation of geminal diol. Thus, one could conduct oxidation reactions under solvent-free conditions. Apart from this, if oxidations are carried out

in an acidic environment, formation of hemiacetals from reaction of oxidized product and the unreacted alcohol seem to cause problems. In order to circumvent many of these practical problems, one would like to opt for the reactions under solvent-free conditions with a reagent having inherently controlled acidity. In fact, far less acidic character of **DmpzHFC** (pk_a, 7.8)[25] in comparison to that of its companion reagents PCC (pk_a, 1.4), PFC (pk_a, 2.7) and QFC (pk_a, 4.7) in conjunction with many other desired properties, as enumerated above, encouraged us to explore its solvent-free oxidation chemistry. Additionally, we have been interested in exploring the possibility of using this reagent as a catalyst so as to enable us minimize the amount of chromium waste. Accordingly, the investigation of oxidation of organic substrates with H_2O_2 as the oxidant and **DmpzHFC** as the catalyst was included in the agenda of the present study. It was thought that an internal comparison of the results would enable us comment on the viability of one protocol over the other. Report herein are: the economic synthesis of **PFC,** the results of oxidation of a variety of organic substrates under solvent-free conditions using **PFC** and **DmpzHFC,** respectively, and **DmpzHFC** catalyzed oxidations using H_2O_2 as the oxidant.

EXPERIMENTAL SECTION

The sources of chemicals and solvents, the methods for quantitative determination of elements and the details of all the equipment used for physico-chemical studies are described in **Chapter 2.**

A. The Economic Synthesis of Pyridnium Fluorochromate(VI)

A sample of chromium(VI) oxide, CrO_3 (150 mmol, l5.0 g) was taken in a 250 mL polyethylene beaker and 48% hydrofluoric acid , HF (150 mmol, 6.25 mL) was added drop wise with continuous stirring with a teflon rod. The stirring was continued for 8-10 min. This exercise was followed by drop wise addition of 9 mL of water under stirring over a period of 15min leading to a clear orange colored solution. The whole was cooled in a ice-water bath for 15min and distilled pyridine (150.02 mmol, 12.11 mL) was added drop wise to this solution with vigorous stirring. An exothermic reaction set in leading almost instantaneously to the formation of bright orange crystals of pyridinium fluorochromate, PFC. The whole was allowed to stand first in ice-water bath for 30 min and then at room temperature for 30 min. The compound was washed twice with hexane. The product was finally dried *in vacuo* over conc. H_2SO_4 or fused $CaCl_2$. Yield: 29.63 g (99.2%).

Melting Point: 106-108 ^{0}C. The chemical analyses of the compound match very well with those reported in literature.[20]

Analytical data: $C_5H_6FCrNO_3$:

Calc. C, 30.16; H, 3.04; N, 7.04; F, 9.54; Cr, 26.12%.

Found. C, 30.1; H, 3.07; N, 6.96; F, 9.6; Cr, 26.2%.

B. Solvent-Free Oxidation of Organic Substrate with PFC as the reagent

PFC was added to the substrate in a mortar maintaining the appropriate stoichiometry as reported (**Table 4.1**). The whole was mixed thoroughly and left at room temperature with occasional agitation or grinding for the time period shown against each entry in **Table 4.1**. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. Upon completion of the reaction, the mixture of the organic components was extracted with dichloromethane (3 x 15 mL). Evaporation of the organic solvent and purification of product by column chromatography (hexane /ethyl acetate, 95/5, v/v) afforded the compounds in good yields (**Table 4.1**).

C. Solvent-Free Oxidation of Organic Substrate with DmpzHFC as the Reagent

DmpzHFC was added to the substrate in a mortar maintaining the appropriate stoichiometry as reported (**Table 4.3**). The whole was mixed thoroughly and left at room temperature with occasional agitation or grinding for the time period shown against each entry in **Table 4.3**. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. Upon completion of the reaction, the mixture of the organic components was extracted with dichloromethane (3 x 15 mL). Evaporation of the organic solvent and purification by column chromatography in a manner similar to what has been described under **B** yielded the products in good yields (**Table 4.3**).

D. Oxidation of Benzyl Bromide to Benzaldehyde by H_2O_2 as the Oxidant and PFC as a catalyst

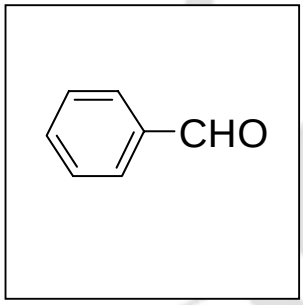
First H_2O_2 (8.82 mmol, 1 mL) and then PFC (0.01 mmol, 1.99 mg) were added to the benzyl bromide (1 mmol, 171 mg) in a mortar. The whole was mixed and left at room temperature with occasional agitation & grinding for 4 h. The progress of the reaction was monitored by TLC of the ethyl acetate solution over silica gel. Anhydrous Na_2SO_4 was added to the reaction mixture and then the product is extracted with dichloromethane. Evaporation of the organic solvent and purification by column chromatography in a manner similar to what has been described under **B** yielded the product. Yield: 26.5 mg (25%)

E. Oxidation of Organic Substrates by H_2O_2 as the Oxidant and DmpzHFC as a Catalyst

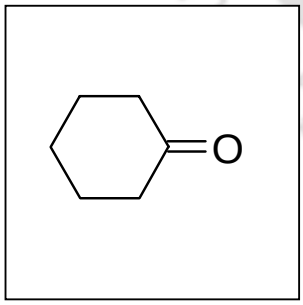
First H_2O_2 and then DmpzHFC were added to the substrate in a mortar in amounts as given in **Table 4.4**. The whole was mixed and left at room temperature with occasional agitation and grinding for the time period as given in the **Table 4.4**. The progress of the reaction was monitored by TLC of the ethyl acetate solution over silica gel. Upon completion of the reaction anhydrous Na_2SO_4 was added to the reaction mixture and then the product is extracted with dichloromethane. Evaporation of the organic solvent and purification by column chromatography in a manner similar to what has been described under **B** yielded the products in good yields (**Table 4.4**).

CHARACTERIZATION OF THE PRODUCTS

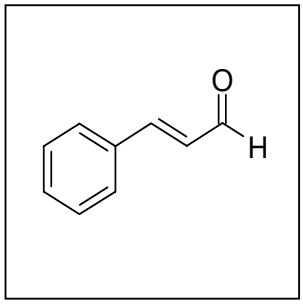
The compounds were characterized by IR and ^{1}H NMR and data for the product are summarized as follows:



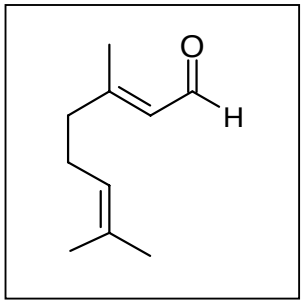
Name Benzaldehyde
IR (cm^{-1}) 1716
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 9.87 (s, 1H, COH), 7.85 (d, J=8.4, 2H, ArH), 7.57 (t, J=8.2, 1H, ArH), 7.43 (m, 2H, ArH)



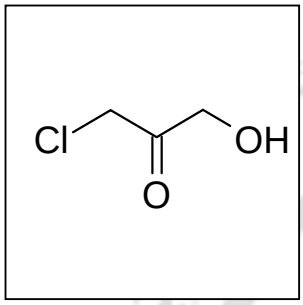
Name Cyclohexanone
IR (cm^{-1}) 1713
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 2.25 (t, J=6.1, 4H, $COCH_2$), 1.87 (m, 4H, $COCH_2$ CH_2), 1.75 (t, J=6.51, 2H, $COCH_2$ CH_2 CH_2CH_2)



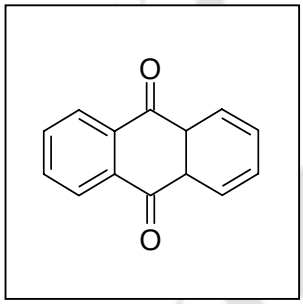
Name Cinnamaldehyde
IR (cm^{-1}) 1682
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 9.68 (d, 1H, OCH), 7.55 (d, J=15.1, 2H, ArH), 7.51 (d, 1H, ArCH), 7.45 (m, 3H, ArH), 6.70 (dd, J=7.1, 6.3, 1H, -CHCO)



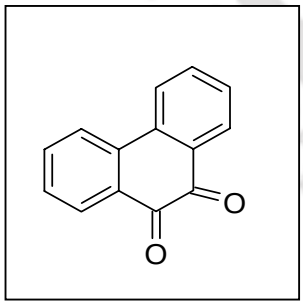
Name Geranial
IR (cm^{-1}) 1675
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.68 (d, J=6.3, 1H, OCH), 5.39 (s, 1H), 5.12 (d, J=6.2, 1H), 2.1 (m, 4H), 1.71 (s, 9H).



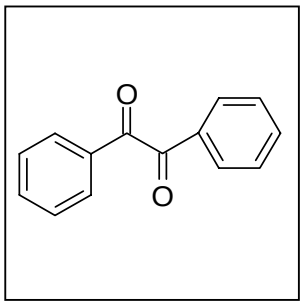
Name 1-chloro-3-hydroxypropoan-2-one
IR (cm^{-1}) 1720
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 4.81(d, 2H, J=4.1, $-CH_2OH$), 4.64 (s, 2H, $-CH_2Cl$), 2.10 (br, 1H, -OH).



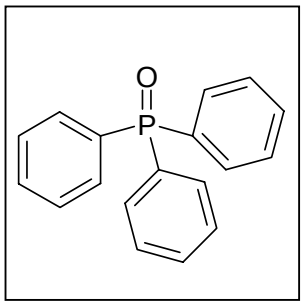
Name Anthracene-9,10-dione
IR (cm^{-1}) 1673
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.75 (q, J=8.3, 4H, ArH), 8.31 (d, J=8.4, 4H, ArCH)



Name Phenanthrene-9,10-dione
IR (cm^{-1}) 1678
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.45 (t, J=8.6, 2H, ArH), 7.65 (t, J=8.1, 2H, ArH), 8.02 (d, J=8.1, 2H, ArH), 8.21 (d, J=8.6, 2H, ArH)



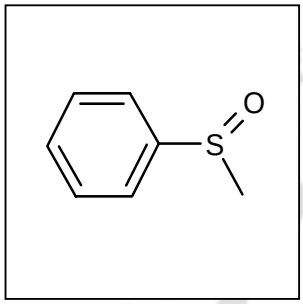
Name Benzil
IR (cm^{-1}) 1660
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.97 (d, J=8.6, 4H, ArH), 7.68 (t, J=8.1, 2H, ArH), 7.46 (d, J=8.1, 4H, ArH)



Name Triphenylphosphine oxide

IR (cm^{-1}) 452, 500, 542, 696, 722, 752, 996, 1071, 1118, 1189, 1437, 3052,

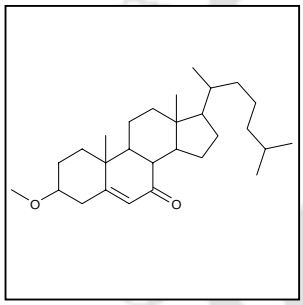
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.35-7.55 (m, 9H, ArH), 7.61-7.75 (m, 6H, ArH),



Name Methylsulfinylbenzene

IR (cm^{-1}) 1047

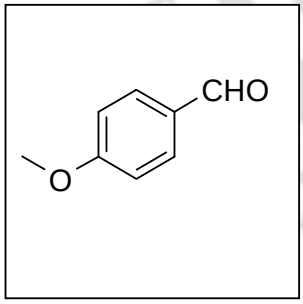
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 2.78 (s, 3H, Me), 7.44–7.66 (5H, m, Ph)



Name 3-Acetoxy-7-Keto-cholesterol

IR (cm^{-1}) 1741, 1671

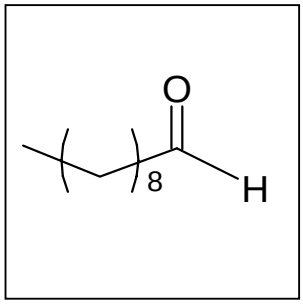
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 0.78 (d, J=5.1, 6H, $-CH_3$), 0.90(s, 3H, $-CH_3$), 1.2 (d, J=4.1, 3H, CH_3), 2.01(s, 3H, $OCOCH_3$), 4.68 (m, 1H, $-CHOCOCH_3$), 5.7 (s, 1H, -CO-CH=).



Name 4-methoxybenzaldehyde

IR (cm^{-1}) 1688

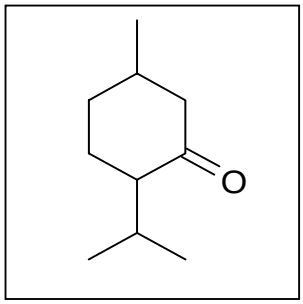
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.92 (s, 1H, -CHO), 7.81 (d, J=8.6, 2H, ArH), 6.98 (d, J=8.1, 2H, ArH), 3.84 (s, 3H, $-OCH_3$)



Name 1-decanal

IR (cm^{-1}) 1727

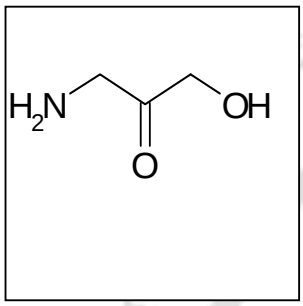
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.78 (s, 1H, -CHO), 2.42 (t, J=4.1, 2H, $-CH_2CHO$), 1.58 (m, 2H, $-CH_2CH_2CHO$), 1.40-1.20(b, 12H, $-CH_2$), 0.91(t, J=6.1, 3H, CH_3)



Name Menthone

IR (cm^{-1}) 1710

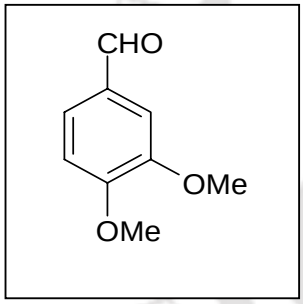
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 2.32 (d, J=6.1, 2H, $-CH_2CO$), 2.20-1.75 (m, 7H), 1.01 (d, 3H, $-CH_3$), 0.95-0.85 (d, J=6.5, 6H, $-CH_3$)



Name 1-amino-3-hydroxypropoan-2-one

IR (cm^{-1}) 1715

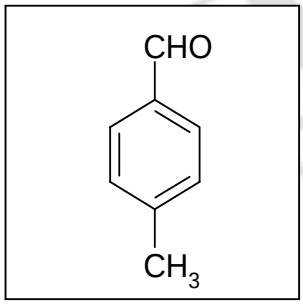
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 4.69(d, J=4.5, 2H, $-CH_2OH$), 3.81 (s, 2H, $-CH_2Cl$), 2.71 (br, 2H, $-NH_2$), 2.10 (br, 1H, -OH).



Name 3,4-Dimethoxybenzaldehyde

IR (cm^{-1}) 1685

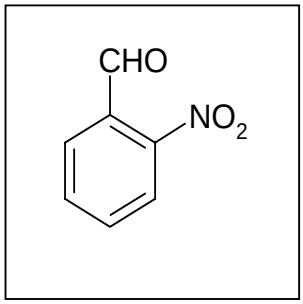
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.87 (s, 1H, -CHO) 7.50 (d, J=8.3, 1H, ArH), 7.45 (s, 1H, ArH), 6.98 (d, J=8.2, 1H, ArH), 3.98 (s, 3H, $-OCH_3$), 3.90 (s, 3H, $-OCH_3$).



Name p-Tolualdehyde

IR (cm^{-1}) 1692

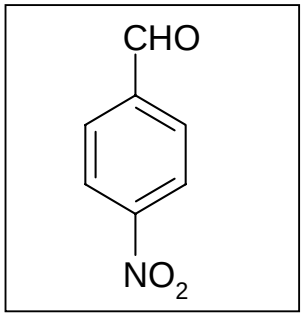
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.94 (s, 1H, -CHO) 7.72 (d, J=8.1, 2H, ArH), 7.25 (d, J=8.6, 2H, ArH), 2.25 (s, 3H, $-CH_3$).



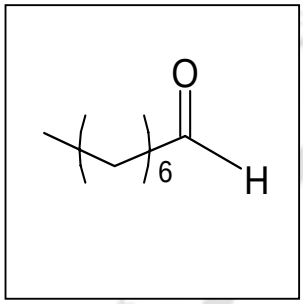
Name 2-Nitrobenzaldehyde

IR (cm^{-1}) 1701

^1H NMR ($CDCl_3$, 300MHz, ppm) δ 10.24 (s, 1H, -CHO) 8.47 (d, J=8.7, 1H, ArH), 8.15 (d, J=8.5, 1H, ArH), 7.95-7.90 (m, 2H, ArH).



Name	4-Nitrobenzaldehyde
IR	(cm^{-1}) 1707
^{1}H NMR	($CDCl_3$, 300MHz, ppm) δ 10.20 (s, 1H, -CHO) 8.45 (d, J=8.5, 2H, ArH), 8.18 (d, J=8.3, 2H, ArH).



Name	Octanal
IR	(cm^{-1}) 1720
^{1}H NMR	($CDCl_3$, 300MHz, ppm) δ 9.75 (s, 1H, -CHO), 2.41 (t, J=6.1, 2H, $-CH_2CHO$), 1.70 (m, 2H, $-CH_2CH_2CHO$), 1.40-1.20(b, 10H, $-CH_2$), 0.84 (t, J=5.4, 3H, CH_3).

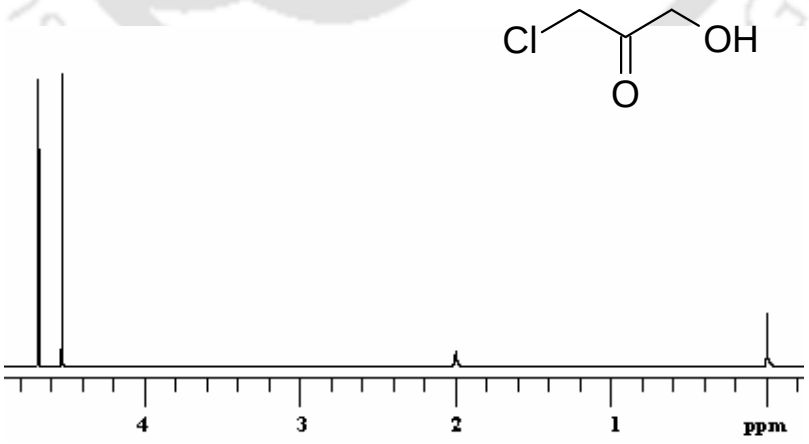


Fig 4.1 ^{1}H NMR Spectrum of 1-chloro-3-hydroxypropoan-2-one

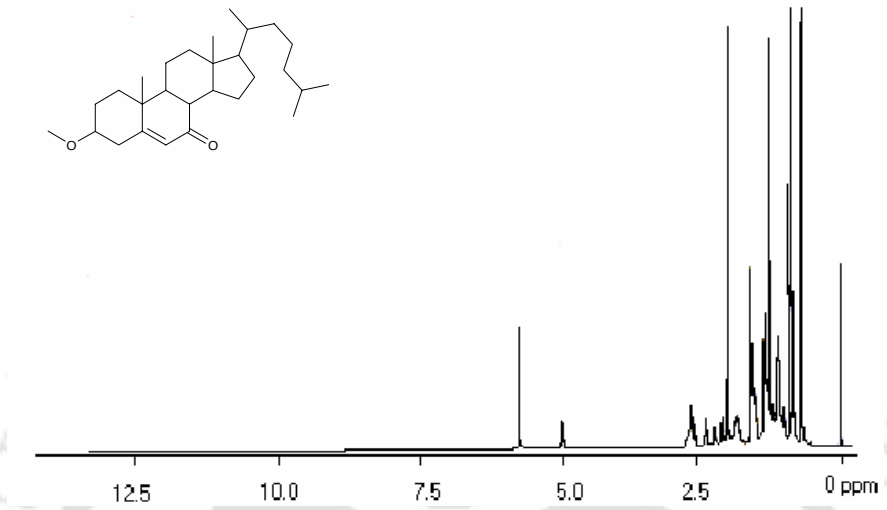


Fig 4.2 ^{1}H NMR Spectrum of 3-Acetoxy-7-Keto-cholesterol

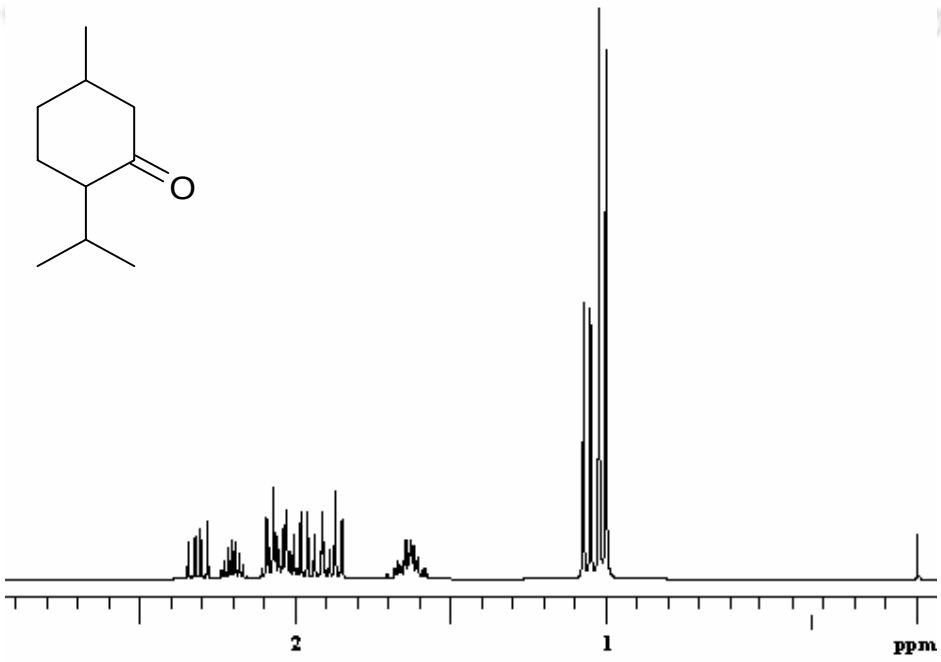


Fig 4.3 ^{1}H NMR Spectrum of Menthone

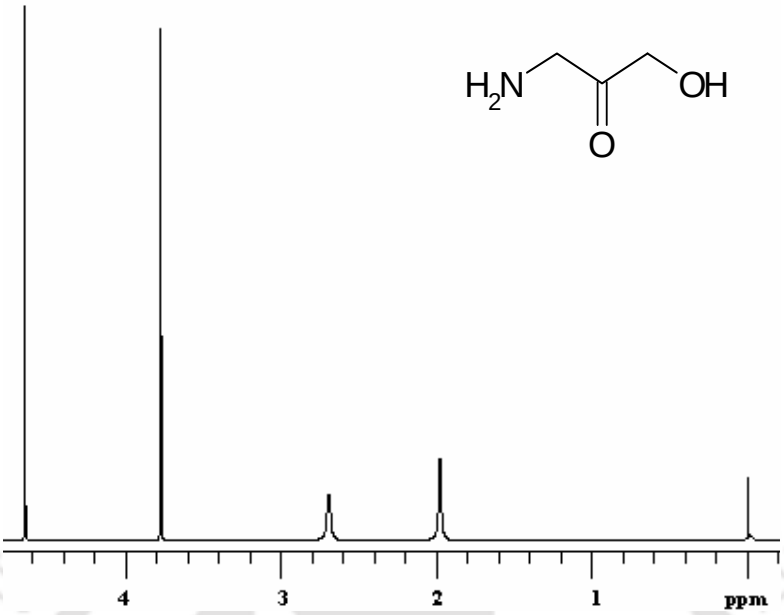


Fig 4.4 ^{1}H Spectrum of 1-amino-3-hydroxypropoan-2-one

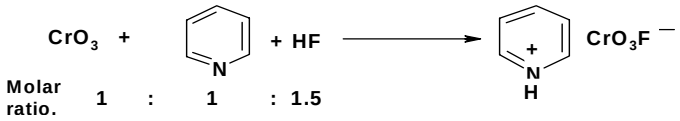
RESULTS AND DISCUSSION

Economic Synthesis of PFC

In order to get rid of the inherent stability problem of pyridinium chlorochromate, **PCC**, the development of its fluoro analogue pyridinium fluorochromate, **PFC**, was essential. Thus, while philosophizing on **PFC** it was conjectured that replacement of Cl by F to coordinate with the Cr(VI) centre would enhance the stability of the resultant compound in addition to increasing its potential as oxidant. This is because oxidation of F^- to ½ F_2, unlike Cl^- to ½ Cl_2, is not possible by the metal, while the higher electronegativity of the fluoride ion contributes to the enhancement of the electron transfer ability of the reagent. Another contributing factor to the stability of the reagent is the high propensity of fluoride to react with higher valent metal to form a stable species (HSAB concept).

Thus, in a typical protocol, in the reaction between CrO_3 and hydrofluoric acid, chromium(VI) oxide first reacts with F^- ion in an acidic medium, to form the distorted tetrahedral fluorotrioxo-chromate(VI), CrO_3F^- ion, which is then precipitated by the counter cation $C_5H_5NH^+$ (PyH^+), obtained by the addition of pyridine in the acidic medium. Notably, in the previous method,[20] a higher amount of hydrofluoric acid than what is actually required was used (**Scheme 4.1**). And this procedure has been used world wide for the preparation of the reagent. However, the use of a relatively higher amount of HF was a matter of concern to us

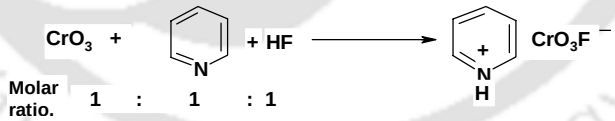
over several years. Since this reagent was originated from our lab, it became incumbent on us to address this issue. And it is there where the hub of the present work lies.



Scheme 4.1 Previous Method of Preparation of **PFC**

The goal of the present work is to prepare pyridinium fluorochromate(VI) by economic and environmentally favourable process. The requirement of only one equivalent of fluoride and one equivalent of H^+ ion, with HF having no other role in the process, caused us to anticipate that the tenet of atom economic principle could be successfully applied to achieve the goal. Again, because of the fact that $C_5H_5NH[CrO_3F]$ (**PFC**) is soluble in water, it was but natural to predict a higher yield by the possible use of a lesser amount of water. In addition, the use of a lesser amount of water was expected to allow a relatively strong inter ionic interaction thereby making the reaction effectively more exothermic which in turn would render the extraneous heating redundant. Indeed all the strategies articulated above worked well leading to the success of the present protocol.

Thus, in a typical economic synthesis, to a solution of 15.0 g (150 mmol) of CrO_3 in 6.25 mL (150 mmol) of 48% HF and 9.0 mL of water in a polyethylene beaker was added under stirring 12.11 mL (150.02 mmol) of pyridine leading to an exothermic reaction to afford 29.63 g (99.2%) of orange colored crystalline pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$ (**PFC**) (**Scheme 4.2**).



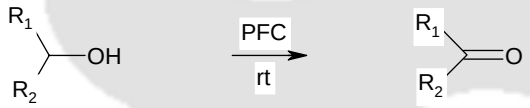
Scheme 4.2 Atom Economic Synthesis of **PFC**

PFC melts at 106-108° C and the results of analysis and characterization data compare very well with those reported in literature.[20] No recrystallisation is required. The reaction can be scaled up, if desired.

Oxidation of Organic Substrates by PFC under Solvent-Free Conditions

Prepared in aforementioned way pyridinium fluorochromate(VI), **PFC**, worked very well under solvent-free conditions and the reactions proceeded with alacrity. The reactions were carried out by agitating the mixture of stoichiometric amounts of the substrate and the reagent in

an agate mortar or in a silica boat with an agate pestle, either at ambient temperature or at relatively higher temperatures between 50 and 70 ^{o}C in a hot air oven for the time period as shown against the entry in **Table 4.1**. The solid substrates and the reagent were powdered separately before mixing together. The progress has been monitored with TLC. The reactions were worked up by extracting the product with diethylether (*ca*.50 mL/mmol of substrate) followed by filtration through a short silica gel column. The solvent was removed in a rotary evaporator to get the product. This procedure was adapted for **1-5**, **8-10** and **12-15**. However, for **6**, **7** and **11**, crude product was purified by column chromatography over a short pad of silica gel using ethylacetate-hexane (1:9) as eluent. Isolation of anthraquinone (**6a**) was also possible by sublimation from a mixture after conducting a separate reaction. This represents a case of all-solid-phase reaction. In all cases, the transformations were selective, and the conversions were quantitative except for **6**, **7** and **11**. Isolated yields are reported in **Table 4.1**. As evident, the reagent worked extremely well by readily converting primary including allylic (**3** and **4**) and secondary (**2,5** and **8**) alcohols to the corresponding carbonyls:

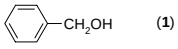
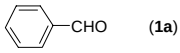
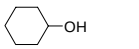
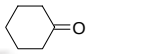
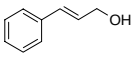
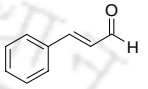
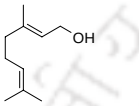
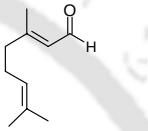
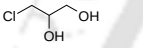
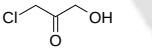
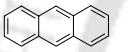
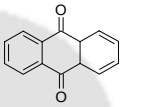
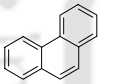
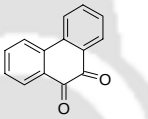
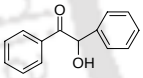
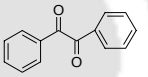
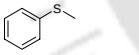
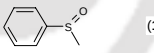
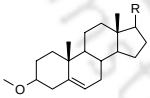
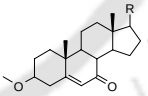
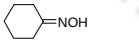
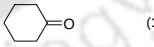
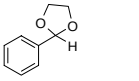
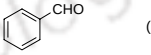
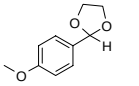
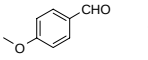
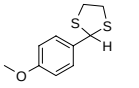
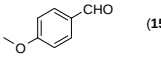


Scheme 4.3 Solvent-Free Oxidation of Alcohols with **PFC**

Importantly, the acid sensitive transformation like geraniol (**4**) to geranial (**4a**) occurred smoothly. Such reactions in solution often require buffer to provide the conducive conditions. Notably important are also the selective oxidation of a secondary alcohol in presence of a primary alcoholic group (**5** to **5a**). Oxidation of poylcyclic hydrocarbons generally requires stringent conditions. Under the present experimental conditions, both anthracene **(6)** and phenanthene **(7)** were readily oxidized to 9, 10-anthraquionone (**6a)** and phenanthrene-9,10-quinone (**7a)**, respectively. The very facile oxidation of PPh_3 **(9)** to $O{=}PPh_3$ **(9a)** provides a good example to show that an oxo-transfer reaction can be carried out easily in a solid-phase reaction with stiochiometric amount of the reagent. This may serve as a method of choice for similar or related transformations. Also important is the oxidation of organic sulfide to the corresponding sulfoxide (**10** to **10a**) without over oxidation. Incidentally, selective oxidation of sulfides to sulfoxides is an important synthetic problem for which not many suitable reagents and protocols are available in literature.[19]

An important concern of the present investigation was oxidation of Δ^5- steroids to the corresponding α,β-unsaturated ketone owing to the intrinsic importance of the product.[38-44] This was because the literature methods have one or more of the following limitations, *viz*.,

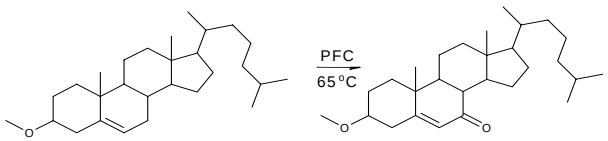
Table 4.1 Solvent-Free Oxidative Transformations of some Organic Substrates using **PFC**

Entry	Substrate	Sub. /PFC molar ratio	Temp. (^{o}C)	Time	Product	Yield*
1	 (1)	1:1	rt	10 min	 (1a)	93
2	 (2)	1:1	rt	15 min	 (2a)	86
3	 (3)	1:1	rt	10 min	 (3a)	85
4	 (4)	1:1	rt	10 min	 (4a)	82
5	 (5)	1:1	rt	7 min	 (5a)	87
6	 (6)	1:2.2	50	2 h	 (6a)	75
7	 (7)	1:2.2	70	2 h	 (7a)	79
8	 (8)	1:1	55	30 min	 (8a)	85
9	PPh_3 (9)	1:1	55	5 min	$O=PPh_3$ (9a)	95
10	 (10)	1:1	rt	5 min	 (10a)	65
11	 (11)	1:4	65	2 h	 (11a)	64
12	 (12)	1:2	60	30 min	 (12a)	85
13	 (13)	1:2	60	25 min	 (13a)	82
14	 (14)	1:2	60	20 min	 (14a)	86
15	 (15)	1:6	70	2 h	 (15a)	83

* Isolated yields are reported.

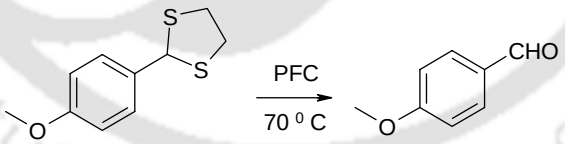
requirement of a large excess of the oxidants, use of very expensive reagents, stringent reaction conditions, and very sluggish reactions with poor yields of the products in many instances. Significantly, under the solvent-free conditions 3-acetoxy cholesterol (**11**) was typically

oxidized by **PFC** to 3-acetoxy-7-keto- cholesterol (**11a**) in 64% isolated yield in *ca.* 2 h at 65 ^{o}C. It is relevant to mention that a similar oxidation by **PFC** in CH_2Cl_2 or CH_3CN under prolonged refluxing conditions did not afford any promising results.[45]



Scheme 4.4 Solvent-Free Oxidation of 3-Acetoxy Cholesterol with **PFC**

The efficacy of the protocol is demonstrated also by the alacrity with which the deoximation of **12** to the corresponding ketone (**12a**) occurred. Deoximations are important as alternative pathways to the synthesis of aldehydes and ketones from non-carbonyl subtrates. Pertinently, conventional oxidations do not seem to work satisfactorily especially because of long reaction times and low yields. To generalize the superiority, similar solvent-free transformations with another oxidant such as **QFC** are now underway. The results obtained so far are in the affirmative. In order to extend the scope of the protocol, the possibility of deprotection of dioxolanes and a dithiolane were investigated. This attracted our attention especially because selective protection and deprotection of carbonyl groups constitute key steps in many synthetic reactions.[46] Moreover, the deprotection of thioacetals, which are important as acyl carbanion equivalent in organic synthesis, is rather challenging because of their stability towards normal acidic and basic conditions. The deprotection of dioxolanes(**13** and **14**) and a dithiolane (**15**) went off very readily to afford the corresponding aldehydes (**13a**, **14a** and **15a**, respectively) in high isolated yields.

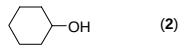
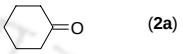
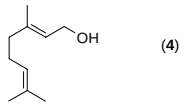
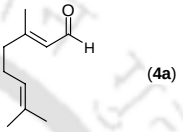
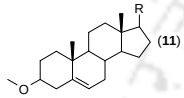
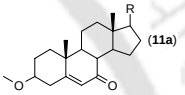


Scheme 4.5 Solvent-Free Deprotection with **PFC**

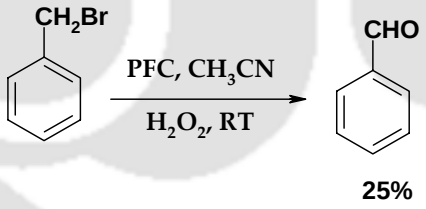
A comparison of the results of **PFC** oxidations in solvents,[20] with those obtained under solvent-free conditions evidences that the reactions work much faster without solvent (present results). Three selected examples are cited in **Table 4.2** for comparison. Rapidity of solid-phase reaction is believed to be facilitated by the intervention of a liquid phase, especially when both substrate and the reagent are solid, owing to the existence of a lower melting eutectic which might have formed from the interaction of a small amount of the product, formed at the initiation of the reaction, with the reagent. Indeed, the appearance of a liquid or melt phase was observed in each reaction reported herein. This might have imbued the individual molecules

with required mobility for productively important reactive collisions thereby allowing for rapid reactions to take place between two solid reactants (i.e. substrate and reagent).

Table 4.2 Comparison of In-Solvent versus Solvent-Free Oxidations by **PFC**

Substrate	PFC-CH_2Cl_2 or CH_3CN / Time	Yield (%)	PFC, Solvent-free/ Time	Yield (%)	Product
 (2)	3.5h	89	15min	86	 (2a)
 (4)	2h	80	20min	82	 (4a)
 (11)	10-12h	Very poor	2h	64	 (11a)

In another experiment we attempted to ascertain the catalytic behavior of **PFC** by carrying out the oxidation of benzyl bromide to benzaldehyde using catalytic amount of **PFC** and excess H_2O_2 as oxidant. However we could able to isolate on 23% of product even after 6h of reaction.



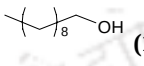
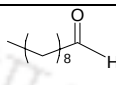
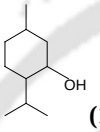
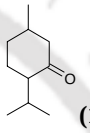
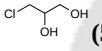
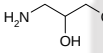
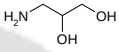
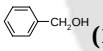
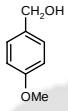
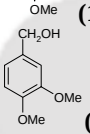
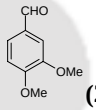
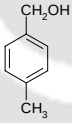
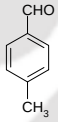
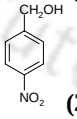
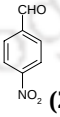
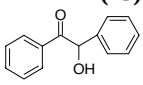
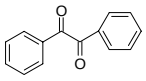
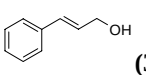
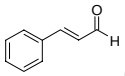
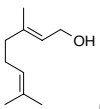
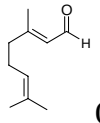
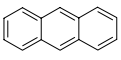
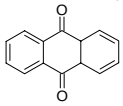
Scheme 4.6 PFC Catalyzed Oxidation of Benzyl Bromide with H_2O_2

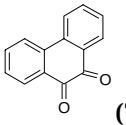
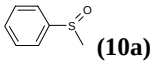
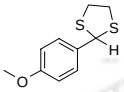
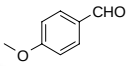
Oxidation of Organic Substrates by DmpzHFC under Solvent-free Conditions

In a separate set of experiments, oxidation of organic substrates were conducted under solvent-free condition using **DmpzHFC** as the oxidant. The results of the investigations reveal that **DmpzHFC** oxidizes primary (Entry **1**, **Table 4.3**), secondary (Entry **2** and **3**, **Table 4.3)**, benzylic (Entry **6-12**, **Table 4.3)** and allylic (Entry **13** and **14**, **Table 4.3)** alcohols to the corresponding carbonyls, and secondary alcohols in the presence of primary alcohols (Entry **4** and **5**, **Table 4.3)**, polycyclic hydrocarbons (Entry **15** and **16**, **Table 4.3)** to cyclic ketones, PPh_3 (Entry **18**, **Table 4.3)** to $O{=}PPh_3$, methylphenyl sulfide (Entry **17**, **Table 4.3)** to sulfoxide,

cyclohexanone oxime (Entry **19**, **Table 4.3)** to cyclohexanone, and deprotection of dithiolanes (Entry **20**, **Table 4.3)** to aldehydes very efficiently.

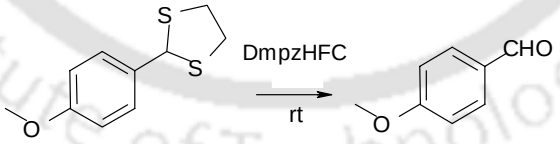
Table 4.3 Solvent-Free Oxidations of some Organic Substrates using DmpzHFC as the Oxidant

Entry	Substrate	Sub. / DmpzHFC Molar ratio	Time (min)	Product	Yield(%)
1	 **(16)**	1:1	2	 **(16a)**	84
2	 **(2)**	1:1	2	 **(2a)**	85
3	 **(17)**	1:1	2	 **(17a)**	91
4	 **(5)**	1:1	2	 **(5a)**	79
5	 **(18)**	1:1	2	 **(18a)**	72
6	 **(1)**	1:1	1	 **(1a)**	70
7	 **(19)**	1:1	2	 **(19a)**	90
8	 **(20)**	1:1	2	 **(20a)**	94
9	 **(21)**	1:1	2	 **(21a)**	75
10	 **(22)**	1:1	45	 **(22a)**	98
11	 **(23)**	1:1	60	 **(23a)**	89
12	 **(8)**	1:1	10	 **(8a)**	90
13	 **(3)**	1:1	2	 **(3a)**	81
14	 **(4)**	1:1	2	 **(4a)**	93
15	 **(6)**	1:2.1	20	 **(6a)**	71

16	 **(7)**	1:2.1	20	 **(7a)**	58
17	 **(10)**	0.66	2	 **(10a)**	96
18	PPh_3 **(9)**	1:1	2	$O{=}PPh_3$ **(9a)**	81
19	 **(12)**	1:1	2	 **(12a)**	90
20	 **(15)**	1:6	5	 **(15a)**	73

Scheme 4.7 Solvent-Free Oxidation of Alcohols with **DmpzHFC**

Notably, benzyl alcohols (Entry **6-12, Table 4.3**) undergo oxidation selectively to the corresponding benzaldehyde without any over oxidation. The reactions proceed with great alacrity providing products in high yields. Experiments were carried out with a series of benzyl alcohols having both electron-donating and electron-withdrawing groups. Oxidation of substrates having electron donating groups e.g., $-CH_3$ (Entry **9, Table 4.3**)and $-OCH_3$(Entry **7** and **8, Table 4.3**), has been faster compared to those having electron withdrawing groups e.g. $-NO_2$. Notably, 2-nitrobenzyl alcohol (Entry **10, Table 4.3**) is oxidized at a comparatively faster rate than 4-nitrobenzyl alcohol (Entry **11, Table 4.3**).



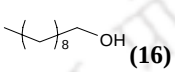
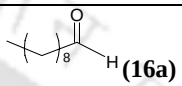
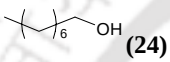
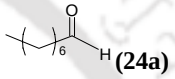
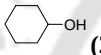
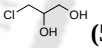
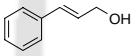
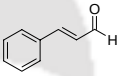
Scheme 4.8 Solvent-Free Deprotection with **DmpzHFC**

Additionally, a very facile deprotection of dithiolanes with chromium(VI) reagent under solvent-free conditions is unprecedented to our knowledge. In order to demonstrate efficacy of the present protocol, the deprotection of diathiolane (Entry **20, Table 4.3**)was conducted with **DmpzHFC** in the solid phase. The reaction was complete in 5 min. The TLC profile showed 100 % conversion, though the isolated yield of the product was 83%. Some amount of the product must have been lost in the work up.

It was one of our main concerns to ascertain if DmpzHFC would act as an oxidation catalyst so as to enable metal waste reduction. Thus, a selected number of reactions have been

conducted using catalytic amount of **DmpzHFC** and H_2O_2 as the oxidant without using any additional solvent. In a typical reaction, to the substrate H_2O_2 was added in small portions followed by the addition of DmpzHFC. The whole was mixed thoroughly and kept at room temperature for a period mentioned in **Table 4.4**. The reaction strategy worked well for a variety of substrates affording the products in high yields (**Table 4.4**).

Table 4.4 **DmpzHFC** Catalyzed Oxidation of selected Organic Substrates with H_2O_2

Entry	Substrate	Substrate/ DmpzHFC/ H_2O_2 molar ratio	Time (min)	Product	Yield (%)
1	 **(16)**	1: 0.01: 2	5	 **(16a)**	81
2	 **(24)**	1: 0.01: 2	5	 **(24a)**	82
3	 **(2)**	1: 0.01: 2	3	 **(2a)**	82
4	 **(5)**	1: 0.01: 2	2	 **(5a)**	80
5	 **(3)**	1: 0.01: 2	2	 **(3a)**	84
6	 **(4)**	1: 0.01: 2	5	 **(4a)**	87
7	 **(10)**	1: 0.01: 2	30	 **(10a)**	75
8	PPh_3 **(9)**	1: 0.01: 2	5	$O{=}PPh_3$ **(9a)**	85

Oxidations, expect for phenyl methyl sulfide were very facile. The reaction of phenyl methyl sulfide (Entry **7, Table 4.4**) not only took relatively more time but was also less selective in that the sulfoxide to sulfone ratio was found to be 75:25. It may be mentioned that on addition of the catalyst to the mixture of substrate and H_2O_2, a violet color is first formed which turned brown as the reactions proceeded. It is believed that H_2O_2 interacts with DmpzHFC to form peroxo-chromium complexes which oxidize the alcohols to aldehydes.

An internal comparison of the results of solid-phase stoichiometric oxidations with those of the catalytic oxidations (**Table 4.5**) suggests that reactions under the two different experimental conditions generally proceeds with equal alacrity, except for phenyl methyl

sulfide, giving comparable yields of the products. However, abiding by the tenets of 'Green Chemistry', the catalytic oxidations may be preferred over the stoichiometric reactions.

Table 4.5 Internal Comparison of Solvent-Free and Catalytic Oxidations by **DmpzHFC**

Substrate	Solvent-free		Catalytic	
	Time (min)	Yield (%)	Time (min)	Yield (%)
16	2	84	5	81
2	2	79	2	80
5	2	85	3	82
3	2	81	2	84
4	2	93	5	87
10	2	96	30	75
9	2	81	5	85

It is pertinent to mention that **DmpzHFC** is a relatively new chromium (VI) reagent being first reported in 2001 along with its efficiency as an oxidant in solution phase.[25] Considering the results reported earlier in conjunction with those of the present studies, it is clear that this reagent is possibly one of the most appropriate chromium (VI) oxidants which is capable of being used in solution, under solid phase condition without a solvent, and as an oxidation catalyst. The oxidations under solid phase and catalytic conditions (present work) seem to be comparatively more facile (**Table 4.6**).

Table 4.6 Comparison of In-Solvent, Solvent-Free and Catalytic Oxidations by **DmpzHFC**

Substrate	Time (%Yield)		
	In-solvent[25]	Solvent-free	Catalytic
2	30min (70)	2min (85)	3min (82)
3	1.5h (70)	2min (81)	2min (84)
4	1.5h (95)	2min (93)	5min (87)

A comparison of the results of oxidation of organic substrates with PFC under solvent-free conditions with those of by DmpzHFC under solvent-free and in catalytic oxidations reveals that reactions proceeds with much alacrity in the absence of solvent on both the cases. Additionally, DmpzHFC oxidizes the substrates with a faster rate compared to that of PFC. Further DmpzHFC attests as an efficient catalyst for oxidation of alcohols using H_2O_2 as oxidizing agent rendering the product with high yield (**Table 4.7)**.

Table 4.7 Comparison of Solvent-Free or/and Catalytic Oxidations by **PFC** and **DmpzHFC**

Substrate	Time (%Yield)		
	PFC	**DmpzHFC**	
	Solvent-free	Solvent-free	Catalytic
2	15min (86)	2min (85)	3min (82)
3	10min (85)	2min (81)	2min (84)
4	10min (82)	2min (93)	5min (87)

Notable in conclusion is that **PFC** is capable of being synthesized in a highly economic way and very effectively used as an oxidant under solvent-free conditions. The new protocol is not only facile and selective but also more versatile in that it can readily oxidize certain substrates (*c.f.* Δ^5–steroidal systems), which were not possible in the corresponding solution phase reaction. Further, 3,5-dimethylpyrazolium fluorochromate(VI),$C_5H_8N_2H(CrO_3F)$, **DmpzHFC**, works more efficiently under solvent-free conditions. Its controlled acidity is an additional advantage for oxidations of acid sensitive substrates. Its role as a catalyst in H_2O_2 oxidation of organic substrates seems to be remarkable in that it catalyses some substrates, organic sulfides for instance, more efficiently than its companion reagents **PFC** and **QFC**. From the results of some of our incomplete investigations, it is expected that DmpzHFC-H_2O_2 is likely to evolve as a highly effective system for oxidations.

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Ecomonic and Solid-Phase Synthesis of Quaternaryammonium Tribromides and Solvent-Free Bromine-Less Bromination of Organic Substrates*

* A part of this chapter constitutes the subject of a patent:

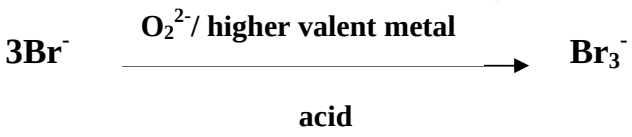
US Patent Appl. Pub., Pub. No.: US 2004/0126308 A1, Pub. Date: Jul. 1, 2004, Appl. No. 10/335,105, Appl. Date: Dec. 31, 2002

Chapter 5

There has been increasing use of bromoorganics in general and bromoaromatics in particular in the manufacture of a range of bulk and fine chemicals including flame-retardants, disinfectants, antibacterial and antiviral drugs.[1] Of the nearly 3200 known naturally occurring organohalogen compounds, more than 1600 contain bromine. These bromoorganics, which range in structural intricacy from the simple but enormously abundant bromoform ($CHBr_3$) and bromomethane to the highly complex bryozoan bromine containing indole alkaloids, are produced by marine and terrestrial plants, marine animals (sponges, tunicates, bryozoans, gorgonians, sea hares, nudibranchs), bacteria, fungi, some higher animals, and a few mammals including humans.[2-4]

Owing to the significance of such bromoorganics or organic bromo derivatives, bromination of organic molecules though constitutes a rather small area of activity yet considered to be an important chemical process. Traditional protocols for bromination involve use of hazardous molecular Br_2 or HBr or both of the two in combination with environmentally unacceptable solvents and auxiliaries.[5-7] In addition, the use of bromine is fraught with problems of handling and the low atom efficiency of substitution reactions (50% maximum with bromide by-poduct). For these reasons work has been carried out using bromide and an oxidant to generate bromine (or electrophilic Br species) for electrophilic aromatic brominations.[8] Consequently, what is needed is a methodology that would be environmentally friendly and clean and yet efficient, siteselectiive, operationally simple, and cost effective.

Fortunately, the group which the present author is associated with has a long standing experience on synthesis, isolation, structural assessment and reactivity of peroxo-vanadium compounds.[9, 10] Our group has also demonstrated that peroxovanadate(V) can oxidize Br^- and in presence of suitable cations such as organicammonium ions, one of its oxidized form *viz*. Br_3^- can be isolated as organicammonium tribromide.[11-13] Taking cues from here we developed a synthetic protocol for organicammonium tribromides (**Scheme 5.1**).



Scheme 5.1 Peroxo-Metal Catalyzed Oxidation of Br^-

However the reported solution method for organic ammonium tribromides[11, 13] involves higher stiochiometry of H_2O_2 and H_2SO_4 thus making the process wasteful. In addition, the reactions were tedious and needed at ice cold conditions. Being guided by the recent trends of sustainable chemistry, we believe that in the chemical sciences there is a need to develop benign

synthetic pathways which, in addition to being high yielding, are simple and exhibit high atom efficiency, hence no waste, are safe, and environmentally acceptable.[14] This philosophy prompted us to develop economic as well as solvent-less procedures for the synthesis of quaternaryammonium tribromides (**QATB**s) with QA being tetramethylammonium (TMA), tetraethylammonium (TEA), tetrabutylammonium (TBA), cetyltrimethylammonium (CTMA) or benzyltrimethylammonium (BTMA). A comprehensive account of the results of the investigation constitutes a part of this chapter.

As far as brominations of organic substrates are concerned, in many instances these are carried out using suitable organic solvents. Furthermore, removing organic solvent in chemical synthesis is important in the drive towards benign chemical technologies. Organic solvents are high on the list of toxic or otherwise damaging compounds because of the large volumes used in industry, and difficulties in containing volatile compounds.[14] Replacement of reaction media includes ionic liquids,[15-18] liquid and supercritical CO_2,[19-21] and water,[22-27] and polyethylene and polypropylene glycol.[28] Nevertheless, the best solvent from an ecological point of view is without doubt no solvent[29] and one of the best alternatives is not to use a reaction media, the so called solvent-free reactions.[14] Co-incidentally, laboratory experiments involving oxidation of organic substrates by chromium(VI) reagents[30] suggest that reactions proceeds with much alacrity in the absence of organic solvent. This knowledge guided us to develop solvent-free bromine-less bromination of organic substrates using quaternaryammonium tribromides (**QATB**s) as brominating agent. The substrates, which are chosen for bromination, are of significant relevance. For instance, phenol and aniline were chosen because it is acknowledged that most aromatic and heteroaromatic parent bromometabolites are phenols, aniline and their derivatives.[31] Again, the selection of anthracene and phenanthrene went in their favor because among many other implications, bromoanthracenes also allow metal exchange reactions to be possible leading to the synthesis of compounds such as vinyl anthracene, an important precursor in polymerization reactions. It is evident from literature that bromination of imidazoles is not always an easy task.[31] In addition, brominated imidazoles have some catalytic activity and are believed to be capable of reactivating phosphorylated acetylcholinesterase.[32] Similarly, chalcones represent yet another class of substrates having biochemical relevance for they are important precursors in flavonoid synthesis.[33]

Further, in order to enhance bromination in a non-organic solvent, we have carried out water-assisted bromination using a few drops of water. The results of all these investigations are described in this chapter.

EXPERIMENTAL SECTION

The sources of chemicals and solvents, methods for quantitative determination of elements, and the details of all the equipment used for physico-chemical studies are described in **Chapter 2**.

ECONOMIC SYNTHESIS

Synthesis of Tetramethylammonium Tribromide, TMATB (From TMAB)

A sample of molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.32 mmol, 0.058 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (176.37 mmol, 20 mL) was added to it. The mixture was stirred for 30 min at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept on an ice-water bath. Tetramethylammonium bromide, TMAB (32.45 mmol, 5 g) and potassium bromide, KBr (129.83 mmol, 15.45 g) dissolved in H_2SO_4 (0.8M) (40 mmol, 50 mL) was added to this solution slowly with continuous stirring leading to the formation of a golden colored precipitate. The mixture was stirred in ice-water bath for another ~1 h and then kept standing on ice-water bath for 2 h to get orange yellow tetramethylammonium tribromide, **TMATB**. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and recrystallized from acetonitrile. Yield: 9.35 g (91.79%)

Synthesis of Tetramethylammonium Tribromide, TMATB (From TMAC)

A sample of molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.46 mmol, 0.082 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (264.55 mmol, 30 mL) was added to it. The mixture was stirred for 30 min at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept on an ice-water bath. Tetramethylammonium chloride, TMAC (45.61mmol, 5 g) and potassium bromide, KBr (268.91 mmol, 32 g) dissolved in H_2SO_4 (1M) (100 mmol, 100 mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was stirred in ice-water bath for another ~1 h and then kept standing on ice-water bath for 2 h to get orange yellow tetramethylammonium tribromide, **TMATB**. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and recrystallized from acetonitrile. Yield: 13.35 g (93.25%)

Synthesis of Tetraethylammonium Tribromide, TEATB (From TEAB)

A sample of molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.24 mmol, 0.043 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (23.81 mmol, 2.7 mL) was added to it. The mixture was stirred for 30 min at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept on an ice-water bath. Tetraethylammonium bromide, TEAB (23.79 mmol, 5 g) and potassium bromide, KBr (47.56 mmol, 5.66 g) dissolved in H_2SO_4 (0.5M) (23.79 mmol, 47.58 mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was stirred in ice-water bath for another ~1 h and then kept standing on ice-water bath for 2 h to get orange yellow compound of tetraethylammonium tribromide, **TEATB**. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and recrystallized from acetonitrile. Yield: 8.36 g (94.99%)

Synthesis of tetrabutylammonium tribromide, TBATB (From TBAB)

A sample of molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.16 mmol, 0.029 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (15.52 mmol, 1.76 mL) was added to it. The mixture was stirred for 30 min. at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept on the ice-water bath. Tetrabutylammonium bromide, TBAB (15.51 mmol, 5 g) and potassium bromide, KBr (31.01 mmol, 3.69 g) dissolved in H_2SO_4 (0.3M) (15.52mmol, 51.70mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was stirred in ice-water bath for another ~1h and then kept standing on ice-water bath for 2 h to get orange yellow tetrabutylammonium tribromide, **TBATB**. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and recrystallized from acetonitrile. Yield: 7.23 g (96.7%)

Synthesis of Cetyltrimethylammonium Tribromide, CTMATB (From CTMAB)

A sample of molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.14 mmol, 0.025 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (13.76 mmol, 1.56 mL) was added to it. The mixture was stirred for 30 min. at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept on the ice-water bath. Cetyltrimethylammonium bromide, CTMAB (13.72 mmol, 5 g) and potassium bromide, KBr (27.48 mmol, 3.27 g)

dissolved in H_2SO_4 (0.3M) (13.72 mmol, 45.73 mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was stirred in ice-water bath for another ~1 h and then kept standing on ice-water bath for 2 h to get orange yellow cetyltrimethylammonium tribromide, CTMATB. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and recrystallized from acetonitrile. Yield: 7.11 g (98.86%)

SOLID-PHASE SYNTHESIS

Synthesis of Tetraethylammonium Tribromide, TEATB (From TEAB)

Molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.24 mmol, 0.043 g), potassium bromide, KBr (47.56 mmol, 5.66 g) and tetraethylammonium bromide, TEAB (23.79 mmol, 5 g) were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a boat kept on an ice-water bath and 30% hydrogen peroxide, H_2O_2 (23.81 mmol, 2.7 mL) was added drop wise with continuous grinding for 15 min, followed by drop wise addition of H_2SO_4 (10M) (23.80 mmol, 2.38 mL). It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline compound of tetraethylammonium tribromide, **TEATB**. The compound was dried over fused $CaCl_2$ and extracted with ethyl acetate by dissolving in minimum amount of solvent followed by filtration through Whatman No. 42 filter paper. Aqueous phase, if present, could be removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange tetraethylammonium tribromide, **TEATB**, which was recrystallized from acetonitrile. Yield: 8.44 g (95.89%)

Synthesis of Tetrabutylammonium Tribromide, TBATB (From TBAB)

Molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.16 mmol, 0.029 g), potassium bromide, KBr (31.01 mmol, 3.69 g) and tetrabutylammonium bromide, TBAB (15.51 mmol, 5 g) were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a boat kept on an ice-water bath and 30% hydrogen peroxide, H_2O_2 (15.52 mmol, 1.76 mL) was added drop wise with continuous grinding for 15 min, followed by drop wise addition of H_2SO_4 (10M) (15.5 mmol, 1.55 mL). It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline tetrabutylammonium tribromide, **TBATB**. The compound was dried over fused $CaCl_2$ and extracted with ethyl acetate by dissolving in minimum amount of solvent followed by filtration through Whatman No.42 filter paper. Aqueous phase, if present, could be removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange

tetrabutylammonium tribromide, **TBATB**, which was recrystallized from acetonitrile. Yield: 7.2 g (96.26%)

Synthesis of Benzyltrimethylammonium Tribromide, BTMATB (From BTMAB)

Molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.13 mmol, 0.023 g), potassium bromide, KBr (26.06 mmol, 3.1 g) and benzyltrimethylammonium bromide, BTMAB (13.03 mmol, 3.0 g) were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a boat kept on an ice-water bath and 30% hydrogen peroxide, H_2O_2 (13.23 mmol, 1.5 mL) was added drop wise with continuous grinding for 15 min, followed by drop wise addition of H_2SO_4 (10M) (13.0 mmol, 1.3 mL). It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline benzyltrimethylammonium tribromide, **BTMATB**. The compound was dried over fused $CaCl_2$ and extracted with ethyl acetate by dissolving in minimum amount of solvent followed by filtration through Whatman No. 42 filter paper. Aqueous phase, if present, could be removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange benzyltrimethylammonium tribromide, **BTMATB**, which was recrystallized from acetonitrile. Yield: 4.17 g (82.04%)

Synthesis of Benzyltrimethylammonium Tribromide, BTMATB (From BTMAC)

Molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.27 mmol, 0.049 g), potassium bromide, KBr (83.36 mmol, 9.92 g) and benzyltrimethylammonium chloride, BTMAC (26.92 mmol, 5 g) were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a boat kept on an ice-water bath and 30% hydrogen peroxide, H_2O_2 (40.56 mmol, 4.6 mL) was added drop wise with continuous grinding for 15 min, followed by drop wise addition of H_2SO_4 (10M) (40.6 mmol, 4.06 mL). It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline benzyltrimethylammonium tribromide, **BTMATB**. The compound was dried over fused $CaCl_2$ and extracted with ethyl acetate by dissolving in minimum amount of solvent followed by filtration through Whatman No. 42 filter paper. Aqueous phase, if present, could be removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange benzyltrimethylammonium tribromide, **BTMATB**, which was recrystallized from acetonitrile. Yield: 10 g (95.25%)

Synthesis of Cetyltrimethylammonium Tribromide,CTMATB (From CTMAB)

Molybdic acid monohydrate, $H_2MoO_4.H_2O$ (0.14 mmol, 0.025 g), potassium bromide, KBr (27.48 mmol, 3.27 g) and cetyltrimethylammonium bromide, CTMAB (13.72 mmol, 5 g) were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a

boat kept on an ice-water bath and 30% hydrogen peroxide, H_2O_2 (13.76 mmol, 1.56 mL) was added drop wise with continuous grinding for 15 min, followed by drop wise addition of H_2SO_4 (10M) (13.72 mmol, 1.372 mL). It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline cetyltrimethylammonium tribromide, **CTMATB**. The compound was dried over fused $CaCl_2$ and extracted with dichloromethane by dissolving in minimum amount of solvent followed by filtration through Whatman No. 42 filter paper. Aqueous phase, if present, could be removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange cetyltrimethylammonium tribromide, **CTMATB**, which was recrystallized from acetonitrile.
Yield: 7.17 g (99.7%)

General Procedure for Solvent-Free Bromination

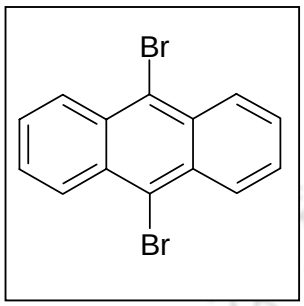
Crystals of cetyltrimethylammonium tribromide, **CTMATB**, were finely powdered by grinding with a pestle in a mortar for a few minutes. To it the subtrate was added maintaining the appropriate stoichiometry as reported (**Table 5.4**). The whole was mixed thoroughly and at the given temperature with occasional agitation or grinding for the time period shown against each entry in **Table 5.4**. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. Upon completion of the reaction, 20 mL of water was added to the reaction mixture and stirred for 10 min. The reaction mixture was filtered, washed with water and air-dried to afford the compounds in good yields (**Table 5.4**).

Procedure for Water-Assisted Bromination of Chalcone by TBATB

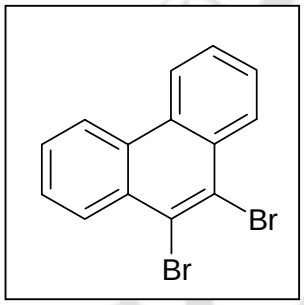
Crystals of tetrabutylammonium tribromide, **TBATB**, (0.524 g, 1 mmol) were finely powdered by grinding with a pestle in a mortar for a few minutes. To it chalcone (0.416 g, 1 mmol) and 0.5 mL of water were added. The whole was mixed thoroughly and left at room temperature with occasional agitation or grinding for 15 min. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. Upon completion of the reaction, 20 mL of water was added to the reaction mixture and stirred for 10 min. The reaction mixture was filtered, washed with water and air-dried to afford the compounds.
Yield: 0.7 g (95%).

CHARACTERIZATION OF THE PRODUCTS

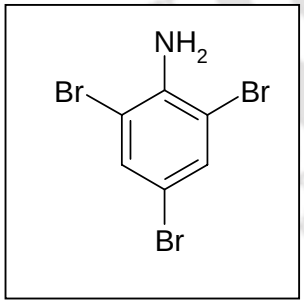
The compounds were characterized by mp, IR and ^{1}H NMR and data are summarized below:



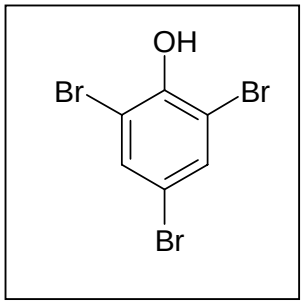
Name 9,10-dibromoanthracene
Mp 220-225 ^{0}C
IR (cm^{-1}) 2928, 2855, 1624, 1460, 1380, 1311, 1264, 955, 927, 880, 845, 768, 729, 536.
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.85 (d, J= 8.5, 4H, ArH), 7.42 (t, J=8.7, 4H, ArH)



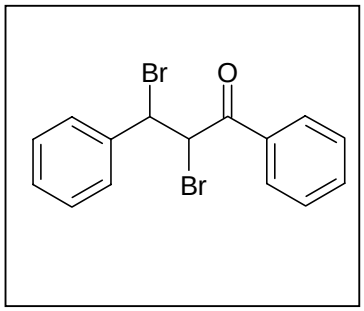
Name 9,10-dibromophenanthrene
Mp 180-183 ^{0}C
IR (cm^{-1}) 2935, 2845, 1630, 1458, 1356, 1302, 1252, 945, 920, 864, 825, 756, 713, 552.
^{1}H NMR ($CDCl_3$, 300MHz) δ 8.94 (d, J=8.1, 2H, ArH), 8.12 (d, J=8.6, 2H, ArH), 7.80-7.90 (m, 4H, ArH)



Name 2,4,6-Tribromoaniline
Mp 120-122 °C
IR (cm^{-1}) 3151, 1548, 1491, 1359, 1179, 1156, 1063, 1011, 917, 866, 773, 724, 590
^{1}H NMR ($CDCl_3$, 300MHz) δ 7.45-7.50 (s, 2H, ArH), 4.35-4.45 (br, 2H, $-NH_2$)



Name 2,4,6-Tribromophenol
Mp 92-94 ^{0}C
IR (cm^{-1}) 3400, 2920, 2855, 1563, 1470, 1380, 1330, 1265, 1220, 1170, 964, 740, 708, 675, 555
^{1}H NMR ($CDCl_3$, 90MHz) δ 7.57 (2H, s, Ar-H), 5.88 (1H, brs, -OH)



Name 2,3-dibromo-1,3-diphenyl-propan-1- one

Mp 159-160 ^{0}C

IR (cm^{-1}) 2920, 2865, 1681, 1600, 1460, 1400, 1380, 1276

^{1}H NMR ($CDCl_3$, 300MHz) δ 7.4-7.81 (m, 10H, ArH), 5.83 (d, 1H, *J*=11.5, ArCOCH-), 5.65 (d, 1H, *J*=11.4, ArCH-)

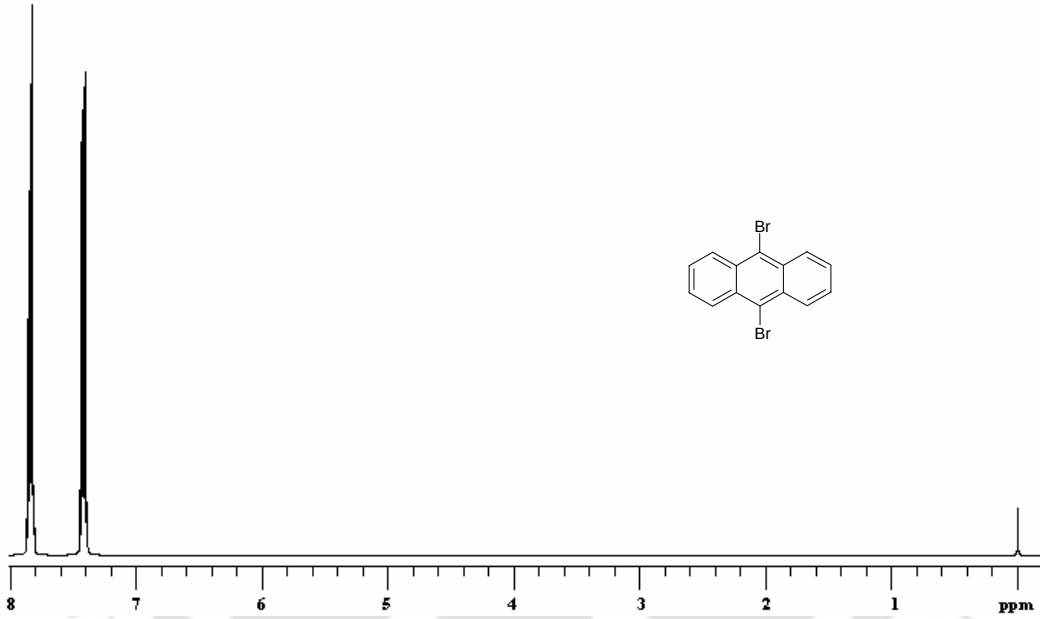


Figure 5.1 ^{1}H NMR Spectrum of 9,10-dibromoanthracene

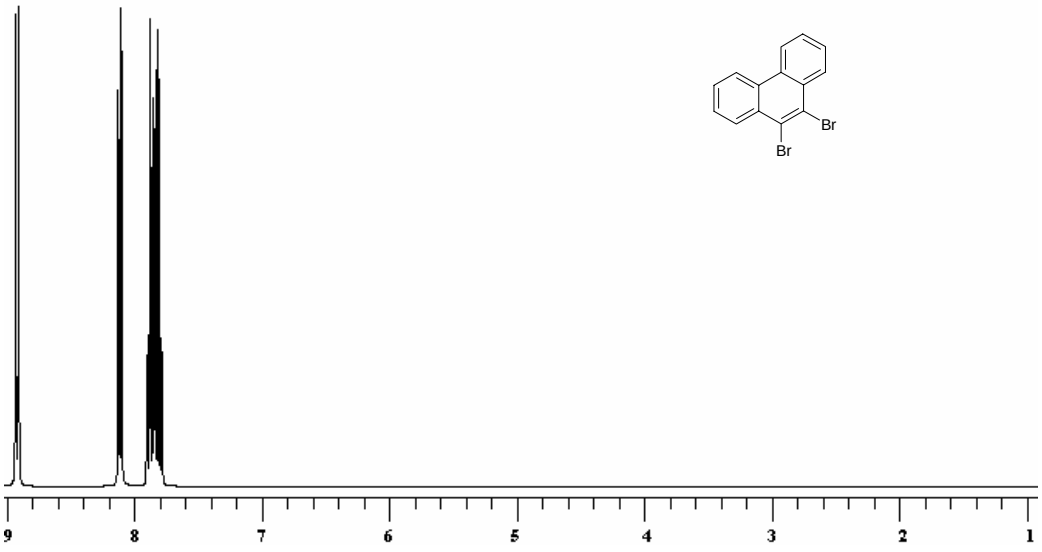


Figure 5.2 ^{1}H NMR Spectrum of 9,10-dibromophenanthrene

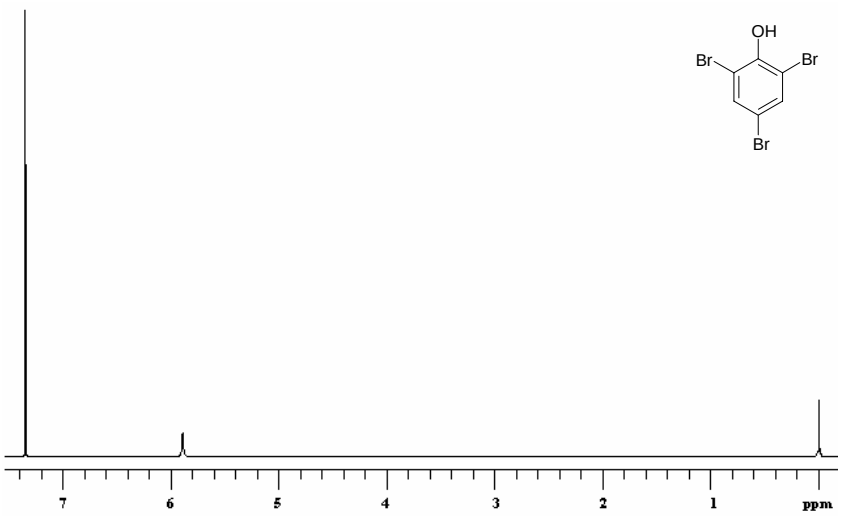


Figure 5.3 ^{1}H NMR Spectrum of 2,4,6-Tribromophenol

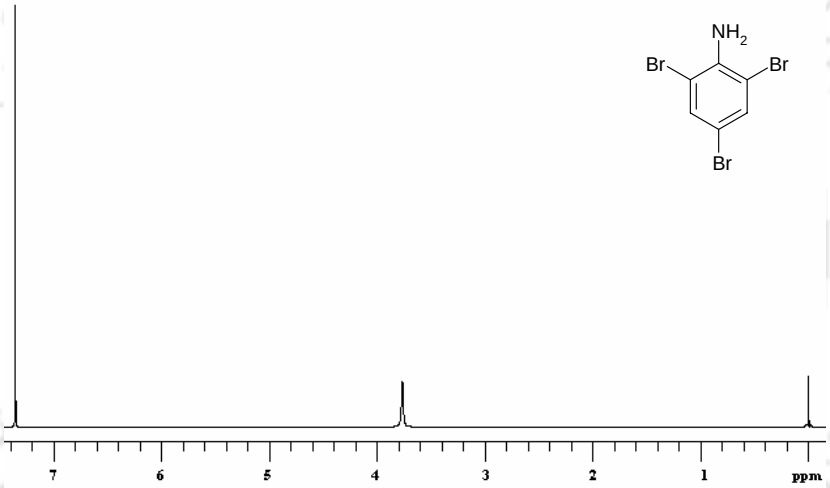


Figure 5.4 ^{1}H NMR Spectrum of 2,4,6-Tribromoaniline

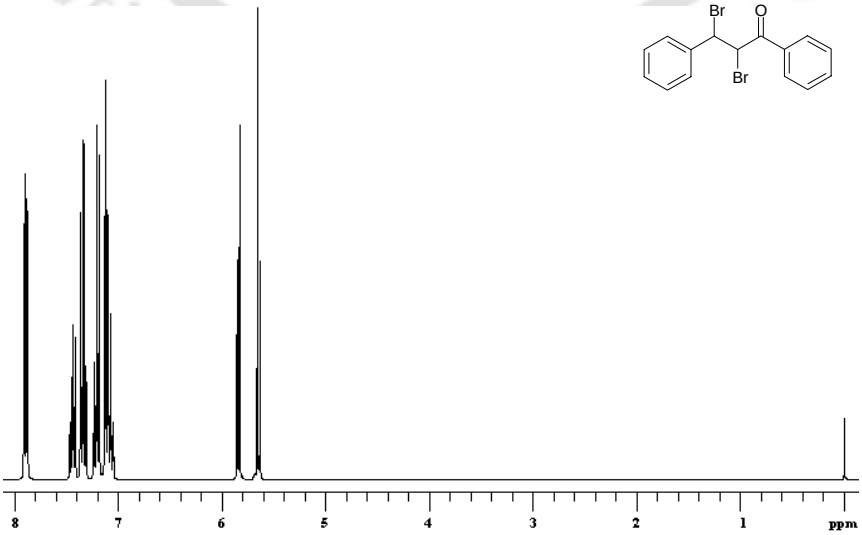
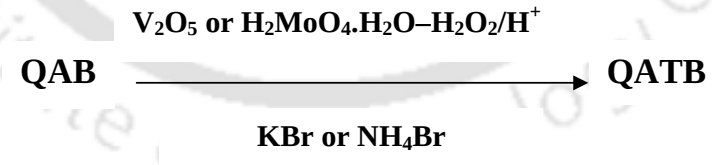


Figure 5.5 ^{1}H NMR Spectrum of 2,3-dibromo-1,3-diphenyl-propan-1- one

RESULTS AND DISCUSSION

Considering the acknowledged difficulties associated with the traditional brominating agents involving the use of hazardous molecular bromine or HBr or the combination of the two as mentioned in the preamble, it was one of our major concerns to improvise newer brominating agents and bromination protocols. Fortunately our research group has experience on the synthesis of peroxo compounds of metals such as Ti, V, Zr, and UO_2^{2+}, for instance.[9,10,34-56] The attention, in particular, was drawn a little more toward the peroxovanadium compounds leading to successful synthesis of a good number of simple and heteroligand di- and triperoxovanadates.[34-36] In order to explore the reactivity profiles of such compounds, oxidation of inorganic substrates including bromide[37] was investigated. What was observed was that, $[Ti(O_2)F_5]^{3-}$, $[VO(O_2)_2F]^{2-}$ and $[UO_2(O_2)F_2]^{2-}$, for instance, readily interacted with Br^- in an aqueous acidic medium to provide in each case an orange yellow solution with a characteristic electronic absorption at *ca.* 267 nm attributable to the formation of Br_3^- in solution.[57-59] Literature precedence[60] shows that peroxo-complexes of higher valent transition metals including peroxovanadium(V) are capable of bringing about bromide oxidation in an acidic condition leading to $OBr^- \leftrightarrows Br_2 \leftrightarrows Br_3^-$.

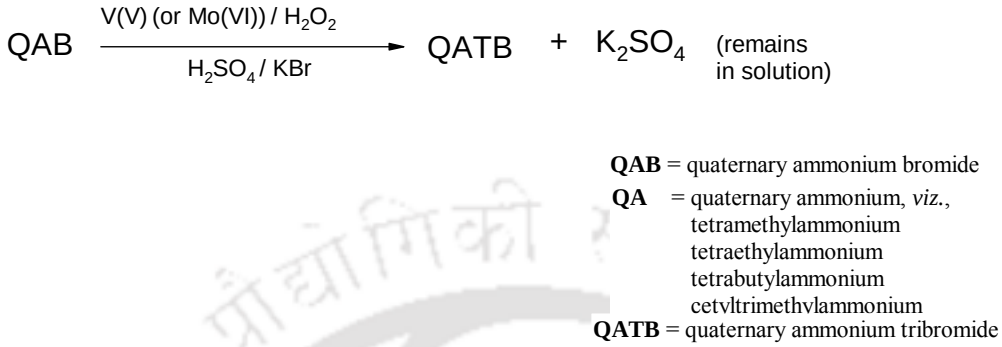
Intrigued by the above results, we sought to isolate the oxidized bromide species and accordingly, the reaction of a series of quaternaryammonium bromides were separately conducted with V_2O_5–H_2O_2, or $H_2MoO_4.H_2O$–H_2O_2 in the presence of a catalytic amount of acid at ca. 5 °C leading to the synthesis of yellow to orange–yellow quaternaryammonium tribromides (**QATB**s) in very high yields. The use of KBr or NH_4Br increases the yield of the product (**Scheme 5.2**).[13]



Scheme 5.2 Peroxo-Metal Catalyzed Synthesis of **QATB**s

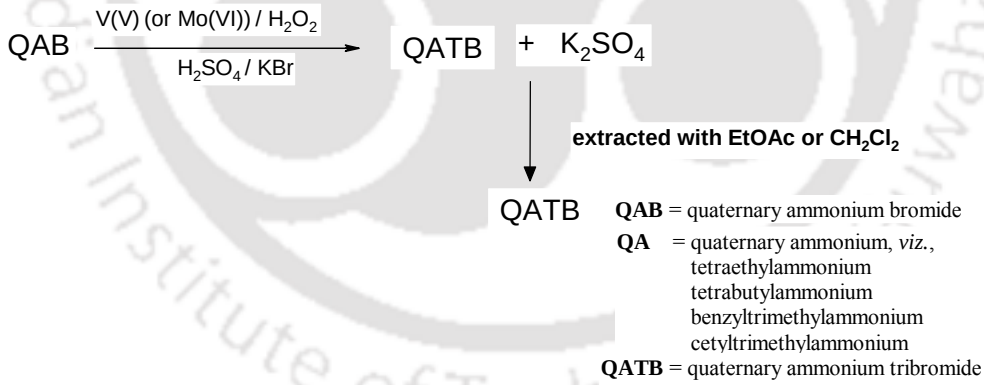
However, the method first developed in this laboratory[11] involved the use of higher amounts of H_2O_2 and H_2SO_4 i.e. 4 mole equivalent of H_2O_2 and 2 mole equivalent of H_2SO_4, for the oxidation of each mole equivalent of Br^-. Where as for oxidation of one mole equivalent of Br^-, 1 mole equivalent of each of H_2O_2 and H_2SO_4 are required. Thus, economic synthesis of **QATB**s was a major concern. Additionally, the excess of H_2O_2 on interaction with the oxidized bromine species may lead to the formation of Br^- and molecular O_2. Taking all such points into

consideration we have developed the economic synthesis of **QATB**s, such as **TMATB**, **TEATB**, **TBATB** and **CTMATB**, using 1 mole equivalent of H_2O_2 and 1 mole equivalent of H_2SO_4 for oxidation of each mole equivalent of Br^- (**Scheme 5.3)**.



Scheme 5.3 Economic Synthesis of **QATB**s

Having succeeded in the economic synthesis of the tribromides, it was thought that the synthesis could as well be achieved in a 'solid-phase' reaction if the effective volume of the acid solution is drastically reduced by increasing its strength. The proposition is, however, somewhat dicey because a very strong acid is expected to be detrimental to the process. This is all the more so since H_2O_2 is the oxidant of choice. Accordingly, we looked in to the possibility of solid-phase synthesis of **QATB**s (**Scheme 5.4**).



Scheme 5.4 Solid-Phase Synthesis of **QATB**s

In a typical reaction, molybdic acid monohydrate, potassium bromide, and quaternaryammonium bromide, were powdered separately, mixed together smoothly and thoroughly. The whole was transferred to a boat kept on ice-water bath and 30% hydrogen peroxide was added drop wise with continuous grinding for 15 min, followed by drop wise addition of 10M H_2SO_4 leading to the formation of a yellow colored mass. It was stirred smoothly with glass rod for 10 min and then at room temperature for 30 min. An exothermic reaction set in to form orange-yellow crystalline quaternaryammonium tribromide, **QATB**. The

compound was dried over fused $CaCl_2$ and extracted with ethyl acetate or dichloromethane by dissolving in minimum amount of solvent followed by filtration through Whatman No.42 filter paper. Aqueous phase, if formed, was removed using anhydrous sodium sulphate. The organic layer was concentrated to get yellow-orange quaternaryammonium tribromide, **QATB** (such as **TEATB**, **TBATB**, **BTMATB** and **CTMATB**), which was recrystallized from acetonitrile.

The compounds **TMATB**, **TEATB**, **TBATB**, **BTMATB** and **CTMATB** are all bright yellow to orange in color and crystalline in nature. Recrystallization from acetonitrile gives deep orange crystals. Each compound has a sharp melting point as reported herein, and all of them have a moderate to high solubility in the common organic solvents. Acetonitrile can be the solvent for reaction studies because of environmental acceptability. The tribromides synthesized by the present protocol have all a very long shelf life. Stored in sample vials, they stay stable for

Table 5.1 Melting Points and Analytical Data of **QATB**s

Compound (QATB)	m.p. (°C)	% Found (% Calcd)			
		C	H	N	Br
TMATB ($C_4H_{12}NBr_3$)	117 or 118	15.29 (15.31)	3.86 (3.85)	4.45 (4.46)	76.4 (76.38)
TEATB ($C_8H_{20}NBr_3$)	85 or 86	25.99 (25.97)	5.82 (5.45)	3.67 (3.79)	64.52 (64.79)
TBATB ($C_{16}H_{36}NBr_3$)	75	39.41 (39.86)	8.28 (7.52)	2.78 (2.90)	49.53 (49.71)
BTMATB ($C_{10}H_{16}NBr_3$)	98-101	30.7 (30.8)	4.18 (4.14)	3.62 (3.59)	61.53 (61.47)
CTMATB ($C_{19}H_{42}NBr_3$)	87 or 88	40.99 (43.53)	7.91 (8.07)	2.74 (2.67)	48.36 (45.72)

months.Their stability can be ascertained by the determination of bromine contents periodically and recording melting points from time to time.

The solution electrical conductance (Λ_M) of the four tribromides recorded at room temperature in 10^{-3} M acetonitrile solutions lie in the range 115-165 ($\Omega^{-1}cm^2mol^{-1}$). The conductance values (**Table 5.2**) are in order suggesting that the compounds are all 1 : 1 electrolytic in nature, in total agreement with their formulae.[61] Importantly, recording of (Λ_M values against time over a period of several days did not show any significant change thereby attesting to their stability in solution.

Table 5.2 Molar Conductance Values of **QATB**s

Compound (QATB)	Conductance (10^{-3} M) ($\Omega^{-1}cm^2mol^{-1}$)
TMATB ($C_4H_{12}NBr_3$)	162
TEATB ($C_8H_{20}NBr_3$)	118
TBATB ($C_{16}H_{36}NBr_3$)	151
BTMATB ($C_{10}H_{16}NBr_3$)	158
CTMATB ($C_{19}H_{42}NBr_3$)	166

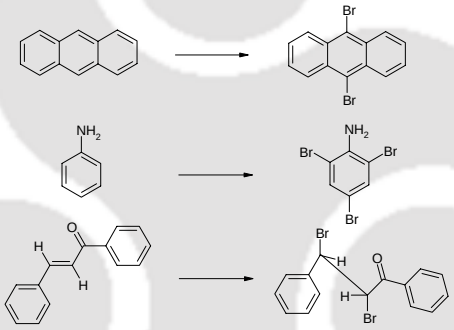
Solution electronic spectroscopy seems to be an extremely important technique for characterization of tribromides as Br_3^- in solution bears characteristic signatures at *ca.* 265 nm with a shoulder at *ca.* 385 nm due to the transitions $\sigma - \sigma^*$ and $\pi - \pi^*$, respectively.[39-40] The $\sigma - \sigma^*$ and $\pi - \pi^*$ transitions for the tribromides under discussion gave values in the range 267–269 nm and 380 – 400 nm, respectively, (**Table 5.3**) thereby conforming to the identity of the compounds as tribromides.

Table 5.3 Electronic Spectral Bands of **QATB**s

compound (QATB)	Uv-vis	
	λ (nm) (ε, $M^{-1}cm^{-1}$)	assignment
TMATB ($C_4H_{12}NBr_3$)	269 (51000) 380 (149)	$\sigma - \sigma^*$ $\pi - \pi^*$
TEATB ($C_8H_{20}NBr_3$)	269 (49500) 390 (152)	$\sigma - \sigma^*$ $\pi - \pi^*$
TBATB ($C_{16}H_{36}NBr_3$)	267 (52000) 400 (150)	$\sigma - \sigma^*$ $\pi - \pi^*_3$
BTMATB ($C_{10}H_{16}NBr_3$)	269 (50500) 390 (151)	$\sigma - \sigma^*$ $\pi - \pi^*$
CTMATB ($C_{19}H_{42}NBr_3$)	269 (49000) 385 (150)	$\sigma - \sigma^*$ $\pi - \pi^*$

Solvent-Free and Water-Assisted Bromine-Less Bromination of Organic Substrates by QATBs

In order to ascertain the versatility of **QATB**s bromination of a variety of substrates was carried out with cetyltrimethylammonium tribromide (**CTMATB**), as a representative example, under solvent-free conditions. The reactions were carried out by agitating the mixture of stoichiometric amounts of the substrate (**1-5**) and the reagent in an agate mortar or in a silica boat with an agate pestle, either at ambient temperature or at relatively higher temperatures between 60 and 70 ^{o}C in a hot air oven for the time period as shown against the entry in **Table 5.4**. The solid substrates (**1, 2** and **5**) and **CTMATB** were powdered separately before mixing together. The progress has been monitored with TLC. The reactions were worked up by adding 20 mL of water to the reaction mixture followed by separation of the product by simple filtration. In all cases the reactions proceeded with great alacrity affording the corresponding brominated products with high yield.

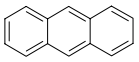
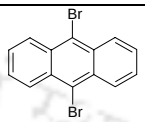
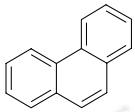
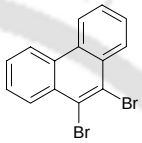
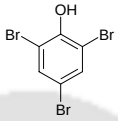
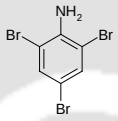
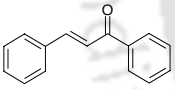
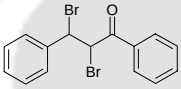


Panel 5.1 Solvent-Free Bromin-less Bromination by **CTMATB**

The solvent-less bromination of organic substrates may be explained in the following way: (i) in case of solid substrates, (**1, 2** and **5**), a eutectic mixture, with melting point lower than the ambient temperature, results and the reaction mixture is in fact a mutual solution of the compounds reacting together allowing uniform and close interactions of the interacting species to yield a solid product which separates from this solution as the reaction proceeds, and (ii) in case of liquid substrates, (**3** and **4**), the reaction proceeds owing to the interaction between substrate molecules in liquid phase and reagent molecule in the solid phase.

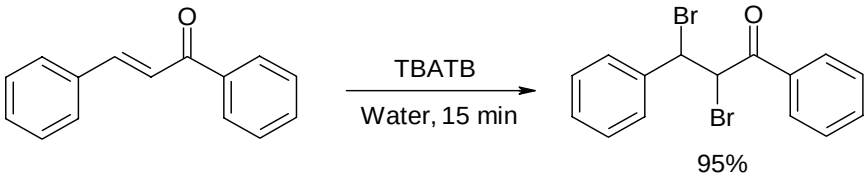
In order to gain further knowledge on the chosen reactions, bromination of chalcone was conducted using different **QATB**s such as **TMATB**, **TEATB**, **TBATB**, **BTMATB** and **CTMATB**. The results are summarized in **Table 5.5**. It is clear from the results that for bromination with **TMATB** and **BTMATB** the yields were rather low (54 and 62%, respectively), and **TBATB** was least effective affording the product in 25% yield even after

Table 5.4 Solvent-Free Bromination of Organic Subtrates with **CTMATB**

Substrate	Sub. / CTMATB Molar ratio	Temp. (^{o}C)	Time (min)	Product	Yield*
	1:2	**70**	**20**		**83**
	1:2	**70**	**20**		**92**
	**1:3**	**60**	**10**		**85**
	**1:3**	**60**	**10**		**90**
	**1:1**	**50**	**15**		**95**

grinding the reaction mixture for 36 h. Interestingly, **TEATB** and **CTMATB** were found to be far more effective in solvent-free bromination affording the products with very high yields (92-95 %) (**Table 5.5**). The results caused us to state that either **TEATB** or **CTMATB** may serve as an efficient brominating agent at least under solvent-free reaction conditions. Between the two reagents, **CTMATB** may be preferred over **TEATB** owing to its cost-effectiveness and ease of handling.

Significantly, what was observed in a separate experiment was that addition of a very small amount of water (**Scheme 5.5**) in the reaction between the chosen substrate and **TBATB**



Scheme 5.5 Water-Assisted Bromine-less Bromination of Chalcone by **TBATB**

Table 5. 5 Solvent-Free Bromine-less Bromination of (*E*)-Chalcone With **QATB**s

Ex. No	QATB	Time (h)	Yields(%)
1	**TMATB**	**1**	**54**
2	**TEATB**	**2**	**92**
3	**TBATB**	**36**	**25**
4	**BTMATB**	**4**	**62**
5	**CTMATB**	**0.25**	**95**

enhanced the reaction in terms of both time as well as yield. As much as 95% of the product was obtained from the water assisted reaction as opposed to 25% without the addition of a trace amount of water in 36 h. This implies that a trace of ionizing liquid (*c.f.* water) facilitates Br_3^- ions interact more efficiently with the organic substrate leading to a relatively easy formation of the product, as desired.

It is pertinent to mention that the first environmentally benign synthesis **TBATB** along with its efficiency as an oxidant in solution phase was reported in 1998.[11] It was shown therein that the reaction of chalcone with **TBATB** in CH_3Cl gave a 35:65 mixture of erytho- and threo-dibromochalcone.[11] Remarkable here is that the bromination reaction of chalcone appears to be highly stereocontrolled when carried out under solvent-free condition irrespective of whether **TBATB** or any of the other tribrimides *viz.*, **TMATB**, **TEATB**, **BTMATB** or **CTMATB** is used as the reagent. The water assisted bromination also proceeds with high selectivity (**Table 5.6**).

Table 5.6 Comparison of In-Solution, Solvent-Free and Water-Assisted Bromination of (*E*)-chalcone with **TBATB**

Conditions	Chalcone: TBATB Molar Stoichiometry	Time (h)	Yield (%)	*erythro*-dibromochalcone: *threo*-dibromochalcone
$CHCl_3$	1:2	3	85	65:35
Solvent-free	1:1	36	25	100:0
Water-assisted	1:1	0.25	95	100:0

In conclusion, we have demonstrated that quaternaryammonium tribromides QATBs such as tetramethylammonium tribromide (**TMATB**), tetraethylammonium tribromide (**TEATB**), tetrabutylammonium tribromide (**TBATB**), benzyltrimethylammonium tribromide (**BTMATB**), and cetyltrimethylammonium tribromide (**CTMATB**) are capable of being synthesized in a very economic manner as well as under solid-phase conditions. They have been very efficiently used for solvent-free bromine-less bromination of organic substrates and the protocol is found to be versatile for a variety of substrates. Further, in presence of a few drops of water the reaction proceeds with much alacrity. Stereoselectivity of chalcone bromination is yet another notable feature of the newly described reactions.

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Monoperoxo(citrato)vanadates(V) as Probable Catalysts: Synthesis, Structural Assessment and Studies of a few Reactions

Chapter 6

Studies involving interaction of vanadium with citric acid is relevant in understanding the possible interaction with in biological system. Citric acid, a trihydroxy tricarboxylic acid of the formula $HOOCCH_2C(OH)(COOH)CH_2COOH$, and citrate ions are the omnipresent small molecular weight species in most plant and animal tissue. Citrates appear at about 0.1 mM in blood plasma[1,2] and occur 0.3% by weight in teeth and bone.[3,4] They regulate fundamental physiological processes and are intermediates in carbohydrate metabolism, e.g. in the Krebs cycle[5,6] and nitrogen fixation.[7,8] The combination of citrato and peroxo ligands on vanadium, a bioessential metal ion of scanty known biological function,[9] is of interest to the biochemistry for several reasons. For example, the recently discovered vanadium enzymes, the bromoperoxidases, VBrPOs contains V(V).[10] In the process of purification and characterization of these enzymes, two operations are directly related to the properties of the peroxo(citrate)vanadates(V), the first of which is the formation of a product with a λmax of 420 nm, which gradually converts in slightly acidic solution into a different species with increasing the absorption at 460 nm.[11] In monoperoxovanadate(V) the LMCT bands occur typically between 415 and 430 nm and in more acidic solution they gradually develop the absorption at 450-460 nm due to the formation of $VO(O_2)^+$ cation.[12,13] Second, a citrate/phosphate buffer is used and consequently bonding of some citrate to vanadium is likely.

In addition, studies of vanadium inhibition of the activity of specific enzymes[9,14] of the glucose metabolism[15, 16] and of the bonding to the proteins[17] all demonstrate the importance of oxidation of the vanadium for a specific function in living cell. Vanadium(V) toxicity and moderate antitumer activity in mice have also been found to depend upon peroxo group presence and the type of peroxo complex formed, including oxoperoxocitratovanadates(V).[18] Also coordination of citrate to vanadium has interesting stereochemical alternatives. Citrates have been found to act as monodentate or polydentate (di- or tridentate) ligands involving generally the central hydroxyl and carboxyl groups.[3] Of the four ionizable protons, three or four dissociates usually upon coordination[3] and a citrate with charge -2 is very less common.[19]

Further there has been biochemical relevance of peroxo(hetroligand)vanadates(V) owing mainly to two recent events in vanadium chemistry. First, vanadium enzymes were discovered recently, the bromoperoxidase[20-22] and nitrogenase,[23] and somewhat earlier it had been found that peroxovanadates(V) act as selective oxidation catalysts. It has been confirmed that bromoperoxidase involve vanadium in oxidation state V,[11] and peroxovanadates known so far contain vanadium only in this highest possible, d^0, V(V) oxidation state in many instances. The biological activity of vanadium obviously depends upon the oxidation state[9] and for V(V) to exist in the enzymes, a ligand environment must be present that stabilizes the d^0 configuration of

vanadium ion. Peroxide, which can enter into the ligand sphere of vanadium, mostly requires V(V). peroxoheteroligandvanadate(V) thus represent an appropriate and useful model system to study property and stereochemistry of vanadium for surroundings likely to exist in biochemical interactions involving V(V).

Vanadium citrate complexes are of interest from yet another point of view regarding the interaction of vanadium with transferrin. Citrate ligands are supposed to compete in the cell with transferrin for the iron and aluminum ions,[2] which form stable complexes with citrates. Experiments have shown that vanadium binds to transferrin,[17, 24, 25] an iron–transfer protein, which may also transport vanadium.[26] Analogue ligand competation between citrates and transferrin proposed for iron may well operate for vanadium and the character of the vanadium-citrate bond is of great interest in this respect. One of the very rational follow up is the aqueous as well as solid state structural speciation of vanadium in the presence of citrate ligand. Consequently, efforts were undertaken for solution speciation studies[27-32] of citrate complexes of vanadium in parallel with synthetic effort for dinuclear vanadium-citrate species.[33-39]

Incidentally, our group has a long association with the chemistry of peroxonavadates(V), especially in terms of syntesis, characterization and studies of reactivity.[40-59] Nevertheless, in so far as the synthesis is concerned, we focused attention more on the di and triperoxo-vanadates(V) with a very little emphasis on monoperoxovanadates(V). As a logical sequel, endeavor is to be made for the synthesis and catalytic activity of the citrato complexes of monoperoxovanadates(V). Finally, the vanadium-peroxo species containing citrate once isolated has to be examined if it could demonstrate insulin mimetic activity.

Thus, as a part of the present Ph.D research, a few peroxo(heteroligand)vanadate(V) complexes were synthesized having citrate ion as the heteroligand of choice and isolated as NH_4^+, Na^+, K^+, Rb^+ or Cs^+ salts. The compounds that were thus synthesized were $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$ (**1**), $Na[VO(O_2)(C_6H_6O_7)].H_2O$ (**2**), $K[VO(O_2)(C_6H_6O_7)].H_2O$ (**3**), $Rb[VO(O_2)(C_6H_6O_7)].H_2O$ (**4**) and $Cs[VO(O_2)(C_6H_6O_7)].H_2O$ (**5**). Characterization of the complexes was made on the basis of elemental analyses and a variety of spectroscopic studies. It may be mentioned that the compounds reported in this chapter exhibit a rather typical electronic spectral pattern and may provide an excellent scope for study of the peroxo-metal interactions in solution. One of the important concerns was to investigate the catalytic (oxidation) properties of such compounds, as a part of our on going programme.

EXPERIMENTAL SECTION

The sources of chemicals and solvents, methods for quantitative determination of elements, and the details of all the equipment used for physico-chemical studies are described in **Chapter 2**.

Preparation of $K[VO(O_2)(C_6H_6O_7)].H_2O$

To an aqueous suspension of V_2O_5 (5 g, 27.5 mmol) in 20 mL water in a 250 mL beaker kept on an ice-water bath, 30% H_2O_2 (25 mL, 220 mmol) was added and the mixture stirred for 30 min to obtain a clear dark red solution. Citric acid (11.56 g, 55 mmol) dissolved in 50mL water was added drop wise with constant stirring to the ice-cooled solution, which turned red-orange. It was followed by drop wise addition of 20% KOH solution (30.9 mL, 110 mmol) (pH ~ 3).Cold ethanol (95%) was added dropwise until turbidity persisted. The reaction mixture was allowed to stay overnight in a refrigerator. Orange crystals that were formed were filtered and washed in turn with 50% and 95% ethanol and dried *in vacuo* over fused $CaCl_2$. Yield:16.24 g (85%)

Preparation of $Na[VO(O_2)(C_6H_6O_7)].H_2O$

To an aqueous suspension of V_2O_5 (5 g, 27.5 mmol) in 20 mL water in a 250 mL beaker kept on an ice-water bath, 30% H_2O_2 (25 mL, 220 mmol) was added and the mixture stirred for 30 min to obtain a clear dark red solution. Citric acid (11.56 g, 55 mmol) dissolved in 50 mL water was added drop wise with constant stirring to the ice-cooled solution, which turned red-orange. It was followed by drop wise addition of 20% NaOH solution (22mL, 110 mmol) (pH ~ 4).Cold ethanol (95%) was added dropwise until turbidity persisted. The reaction mixture was allowed to stay overnight in a refrigerator. Orange crystals that were formed were filtered and washed in turn with 50% and 95% ethanol and dried *in vacuo* over fused $CaCl_2$. Yield: 15.79 g (87%)

Preparation of $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$

To an aqueous suspension of V_2O_5 (5 g, 27.5 mmol) in 20 mL water in a 250 mL beaker kept on an ice-water bath, 30% H_2O_2 (25 mL, 220 mmol) was added and the mixture stirred for 30 min to obtain a clear dark red solution. Citric acid (11.56 g, 55 mmol) dissolved in 50 mL water was added drop wise with constant stirring to the ice-cooled solution, which turned red-orange. It was followed by drop wise addition of 25% ammonia solution (7.48 mL, 110 mmol) (pH ~ 3).Cold ethanol (95%) was added dropwise until turbidity persisted. The reaction mixture was allowed to stay overnight in a refrigerator. Orange crystals that were formed were filtered and washed in turn with 50% and 95% ethanol and dried *in vacuo* over fused $CaCl_2$. Yield: 14.96 g (81%)

Preparation of $Rb[VO(O_2)(C_6H_6O_7)].H_2O$

To an aqueous suspension of V_2O_5 (0.5 g, 2.75 mmol) in 20 mL water in a 250 mL beaker kept on an ice-water bath, 30% H_2O_2 (2.5 mL, 22 mmol) was added and the mixture stirred for 30 min to obtain a clear dark red solution. Citric acid (1.156 g, 5.5 mmol) dissolved in 50 mL water was added drop wise with constant stirring to the ice-cooled solution, which turned red-orange. It was followed by drop wise addition of 20% Rb_2CO_3 solution (6.4 mL, 5.5 mmol) (pH ~ 3). Cold ethanol (95%) was added drop wise until turbidity persisted. The reaction mixture was allowed to stay overnight in a refrigerator. Orange crystals that were formed were filtered and washed in turn with 50% and 95% ethanol and dried *in vacuo* over fused $CaCl_2$. Yield: 1.68 g (78%)

Preparation of $Cs[VO(O_2)(C_6H_6O_7)].H_2O$

To an aqueous suspension of V_2O_5 (0.5 g, 2.75 mmol) in 20 mL water in a 250 mL beaker kept on an ice-water bath, 30% H_2O_2 (2.5 mL, 22 mmol) was added and the mixture stirred for 30 min to obtain a clear dark red solution. Citric acid (1.156 g, 5.5 mmol) dissolved in 50mL water was added drop wise with constant stirring to the ice-cooled solution, which turned red-orange. It was followed by drop wise addition of 20% Cs_2CO_3 solution (9 mL, 5.5 mmol) (pH ~ 3). Cold ethanol (95%) was added drop wise until turbidity persisted. The reaction mixture was allowed to stay overnight in a refrigerator. Orange crystals that were formed were filtered and washed in turn with 50% and 95% ethanol and dried *in vacuo* over fused $CaCl_2$. Yield: 1.82 g (75%)

Oxidation of Cetyltrimethylammonium Bromide

A sample of potassium oxoperoxo(citrato)vanadate(V), $K[VO(O_2)(C_6H_6O_7].H_2O$ (0.14 mmol, 0.049 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (13.76 mmol, 1.56 mL) was added to it. The mixture was stirred for 30 min. at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept in the ice-water bath. A solution of cetyltrimethylammonium bromide (**CTMAB**) (13.72 mmol, 5 g) and potassium bromide (KBr) (27.48 mmol, 3.27 g) dissolved in H_2SO_4 (0.3M) (13.72 mmol, 45.73 mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was stirred in ice-water bath for another ~1 h and then kept standing in ice-water bath for 2 h to get orange yellow cetyltrimethylammonium tribromide, CTMATB. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused $CaCl_2$ and was recrystallized from acetonitrile.

Yield: 6.44 g (89.5%)

Mp: 76 or 77 ^{0}C.

Analytical data: The compound analyzed correctly $C_{16}H_{36}NBr_3$:

Calc. C, 39.86; H, 7.52; N, 2.90; Br, 49.71 %.

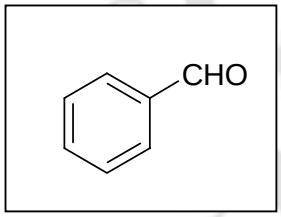
Found. C, 39.41; H, 8.28; N, 2.78; Br, 49.53 %.

Oxidation of Organic Substrates

An acetonitrile (20 mL) solution of the organic substrate was mixed with an aqueous solution of (30 mL) $K[VO(O_2)(C_6H_6O_7].H_2O$ and 30% H_2O_2 maintaining the appropriate stoichiometry as reported (**Table 6.5**). The mixture was stirred at the given temperature for the time period shown against each entry in **Table 6.5**. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. The reaction mixture was then kept at room temperature and the organic layer was extracted with dichloromethane (3X30 mL).It was concentrated and purified by column chromatography (hexane /ethyl acetate, 95/5, v/v) to afford pure product in good yields (**Table 6.5**).

CHARACTERIZATION OF THE PRODUCTS

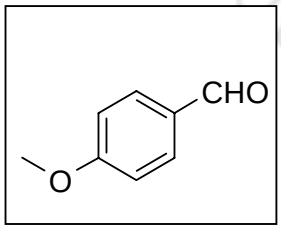
The compounds were characterized by IR and ^{1}H NMR and data are summarized below:



Name Benzaldehyde

IR (cm^{-1}) 1716

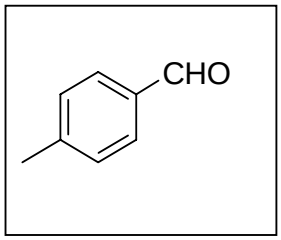
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 9.87 (s, 1H, COH), 7.85 (d, J=8.4, 2H, ArH), 7.57 (t, J=8.2, 1H, ArH), 7.43 (m, 2H, ArH)



Name 4-methoxybenzaldehyde

IR (cm^{-1}) 1688

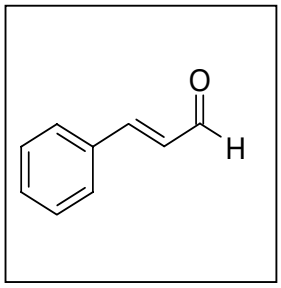
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 9.92 (s, 1H, -CHO), 7.81 (d, J=8.6, 2H, ArH), 6.98 (d, J=8.1, 2H, ArH), 3.84 (s, 3H, -OCH_3)



Name p-Tolualdehyde

IR (cm^{-1}) 1692

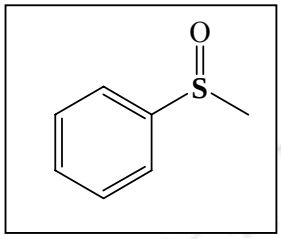
^{1}H NMR ($CDCl_3$, 300MHz, ppm) δ 9.94 (s, 1H, -CHO) 7.72 (d, J=8.1, 2H, ArH), 7.25 (d, J=8.6, 2H, ArH), 2.25 (s, 3H, -CH_3).



Name Cinnamaldehyde

IR (cm^{-1}) 1682

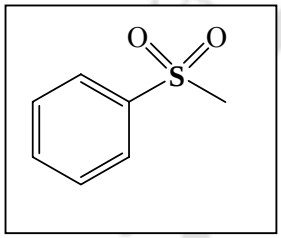
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 9.68 (d, 1H, OCH), 7.55 (d, J=15.1, 2H, ArH), 7.51 (d, 1H, ArCH), 7.45 (m, 3H, ArH), 6.70 (dd, J=7.1, 6.3, 1H, -CHCO)



Name Methylsulfinylbenzene

IR (cm^{-1}) 1047

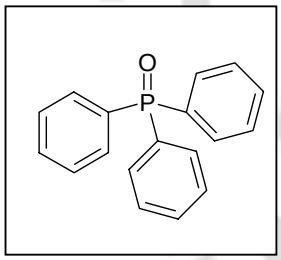
^1H NMR ($CDCl_3$, 300MHz, ppm) δ 2.78 (3H, s, Me), 7.44–7.66 (m, 5H, Ph)



Name Methylsulfonylbenzene

IR (cm^{-1}) 1320, 1164

^1H NMR ($CDCl_3$, 300MHz, ppm) δ 3.0 (3H, s, Me), 7.44–7.64 (m, 3H, Ph), 7.84–7.95 (2H, d, Ph–H, *J* = 8.1 Hz)



Name Triphenylphosphine oxide

IR (cm^{-1}) 452, 500, 542, 696, 722, 752, 996, 1071, 1118, 1189, 1437, 3052,

^1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.35-7.55 (m, 9H, ArH), 7.61-7.75 (m, 6H, ArH),

RESULTS AND DISCUSSION

Oxomonoperoxocitrato complexes of vanadium(V) of the formula $M[VO(O_2)(C_6H_6O_7].H_2O$ (M= NH_4, Na, K, Rb or Cs) (**1-5**)have been prepared from aqueous solutions (**Scheme 6.1**). It has been demonstrated that V(V) is stabilized by peroxide in a citrate

$$V_2O_5 \xrightarrow[\text{MOH or } M_2(CO_3)]{C_6H_8O_7,\ 30\%\ H_2O_2} M[VO(O)_2(C_6H_6O_7)].H_2O$$

$$\text{pH} \sim 2\text{-}4$$

$$\text{Where M} = NH_4^+, K^+, Na^+, Rb^+ \text{ or } Cs^+$$

Scheme 6. 1 Preparation of Monoperoxo(citrato)vanadates(VI)

ligand sphere. The orange crystalline compounds are insoluble in organic solvents and slightly soluble in water. These solutions are stable at pH > 2 and show absorption at λmax = 450 nm, characteristic of the $VO(O)_2^+$ ion. The stability of the compounds is temperature dependant, and thus $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$ (**1**), $Na[VO(O_2)(C_6H_6O_7)].H_2O$ (**2**), $K[VO(O_2)(C_6H_6O_7)].H_2O$ (**3**), $Rb[VO(O_2)(C_6H_6O_7)].H_2O$ (**4**) and $Cs[VO(O_2)(C_6H_6O_7)].H_2O$ (**5**) are stable at *ca.* 4 °C. One of the most dependable ways of monitoring the stability is by the estimation of active oxygen content periodically. The compounds all analyzed very well.

Table 6.1 Analytical Data of $M[VO(O_2)(C_6H_6O_7)].H_2Os$

Compound	Found %(Calcd.%)			
	V	O_A	C	H
$NH_4[VO(O_2)(C_6H_6O_7)].H_2O$	15.51 (15.67)	9.67 (9.84)	22.01 (22.17)	3.43 (3.72)
$Na[VO(O_2)(C_6H_6O_7)].H_2O$	15.21 (15.43)	9.42 (9.69)	21.34 (21.83)	2.05 (2.44)
$K[VO(O_2)(C_6H_6O_7)].H_2O$	14.15 (14.72)	9.02 (9.24)	20.36 (20.82)	2.31 (2.33)
$Rb[VO(O_2)(C_6H_6O_7)].H_2O$	12.54 (12.98)	5.02 (5.16)	18.12 (18.36)	2.01 (2.05)
$Cs[VO(O_2)(C_6H_6O_7)].H_2O$	11.23 (11.58)	7.02 (7.27)	16.32 (16.38)	1.56 (1.83)

The peroxide contents were estimated by redox titrations involving potassium permanganate in an acidic medium. Boric acid was used to prevent any loss of active oxygen. Yet another important point to be noted is that the observed stoichiometry between V(V) and O_2^{2-} is 1 : 1, as evidenced by the chemical analyses. A consistent occurrence V(V) : O_2^{2-} as 1 : 1 supports the contention that the complexes are all monoperoxo species (**Table 6.1**).

The molar conductances (10^{-3} M, aq. soln) of the newly synthesized compounds were found to lie in the range 100-130 $\Omega^{-1}cm^2mol^{-1}$ suggesting a 1:1 electrolytic nature of each of them, which was in agreement with their formulae. The results of conductance measurements have been set out in **Table 6.2**.

UV-Vis spectra of peroxocitrato complexes in aqueous solutions show a weak broad peroxo LMCT band around 450 nm (ε= 480-520 M^{-1} cm^{-1}) is observed, as expected due to $VO(O_2)^+$ present in solutions. The band at 450 nm is characteristic of a peroxo to vanadium

Table 6.2 Solution Electrical Conductance Values

Compound	Solution electrical conductance (10^{-3} M) ($\Omega^{-1}cm^2mol^{-1}$)
$NH_4[VO(O_2)(C_6H_6O_7)].H_2O$	106
$Na[VO(O_2)(C_6H_6O_7)].H_2O$	128
$K[VO(O_2)(C_6H_6O_7)].H_2O$	115
$Rb[VO(O_2)(C_6H_6O_7)].H_2O$	110
$Cs[VO(O_2)(C_6H_6O_7)].H_2O$	102

ligand to metal charge transfer (LMCT) and it would be rational to assign as π_v-d transition. An additional LMCT band appears at around 220-230 nm (ε = 3500-4500 M^{-1} cm^{-1}) owing to the π_h-d transition (**Table 6.3**).[36]

Table 6.3 Electronic Spectral Data

Compound	uv-vis λ (nm) (ε, $M^{-1}cm^{-1}$)
$NH_4[VO(O_2)(C_6H_6O_7)].H_2O$	464(482), 222(3856)
$Na[VO(O_2)(C_6H_6O_7)].H_2O$	451(522), 229(3945)
$K[VO(O_2)(C_6H_6O_7)].H_2O$	441(512), 221(4123)
$Rb[VO(O_2)(C_6H_6O_7)].H_2O$	453(491), 231(4315)
$Cs[VO(O_2)(C_6H_6O_7)].H_2O$	456(502), 225(4524)

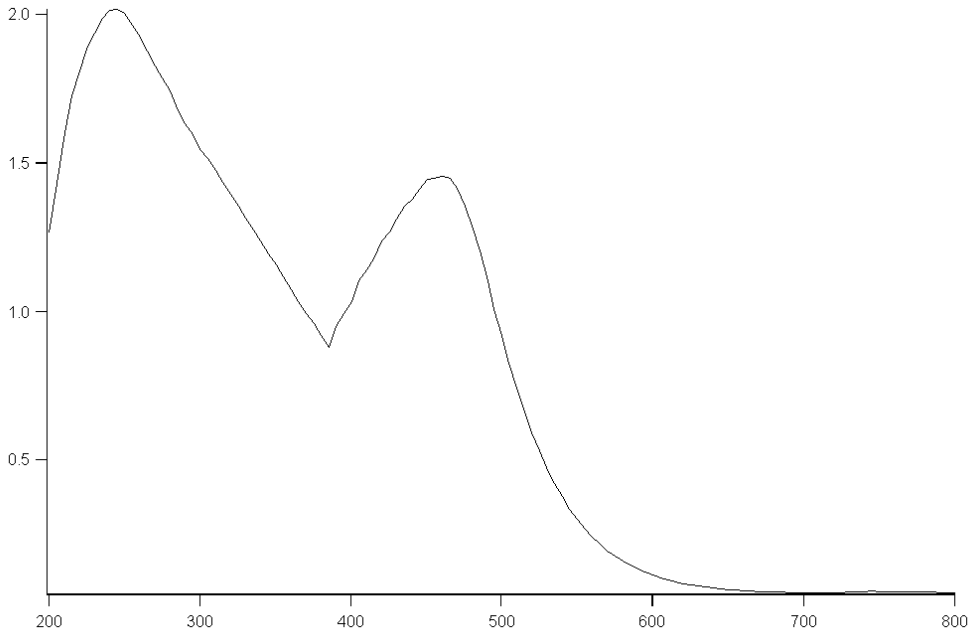


Fig 6.1 Electronic Spectrum of $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$

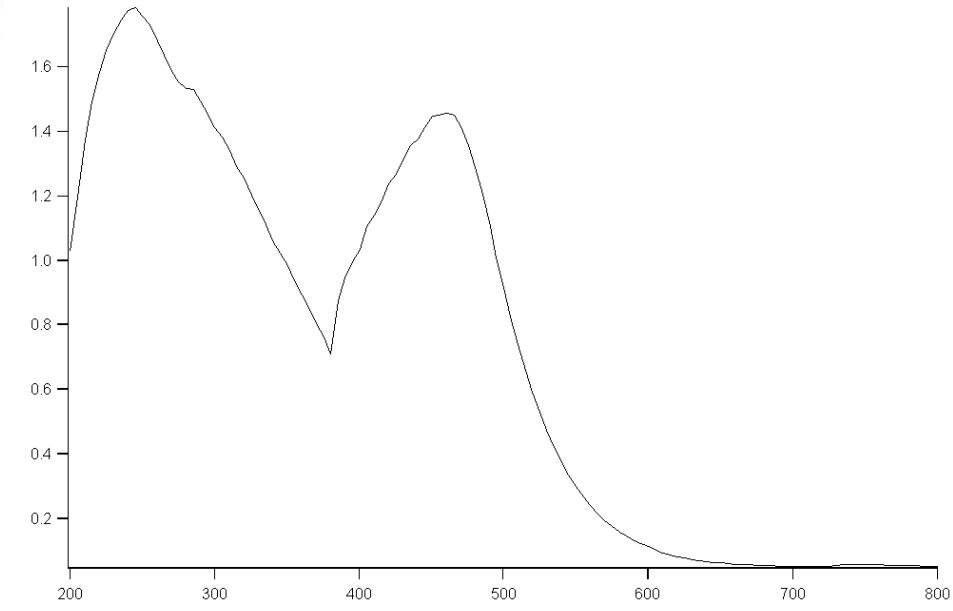


Fig 6.2 Electronic Spectrum of $Na[VO(O_2)(C_6H_6O_7)].H_2O$

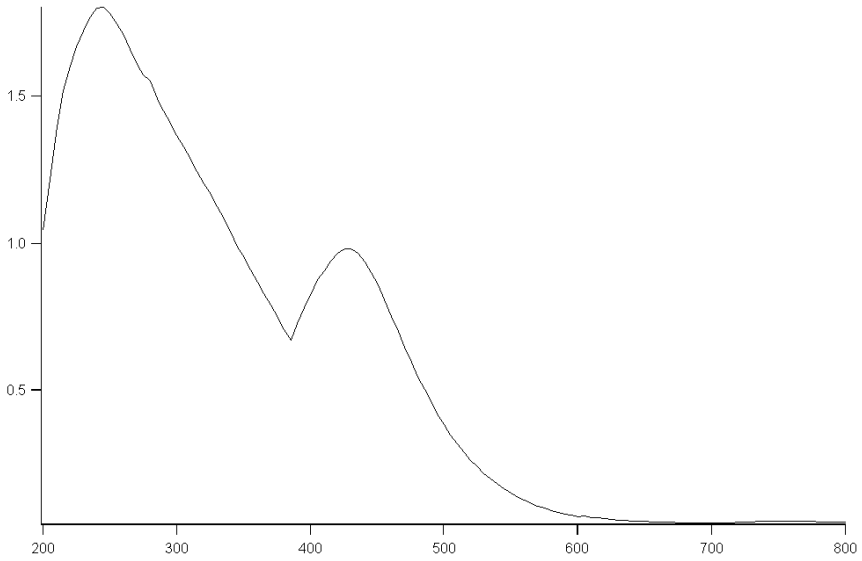


Fig 6.3 Electronic Spectrum of $K[VO(O_2)(C_6H_6O_7)].H_2O$

In order to make a rather unambiguous assignment of ν(O-O), the non peroxo citratovanadium(V), $K[VO_2(C_6H_6O_7]$ (**6**), was synthesized and its IR spectum recorded for comparision. Structurally significant bands of citric acid, the newly synthesized oxomonoperoxo(citrato)vanadates(V) **1-5**, and the non peroxo complex 6 are set out in **Table 6.4**.

Table 6.4 Structurally Significant IR (cm^{-1}) Spectral Data

Citric acid	**1**	**2**	**3**	**4**	**5**	**6**	Assigments
3495 vs 34489 w 3298 s, br	3595 s 3442 s, br	3605 s, vs 3498 s, br	3601 s, vs 3493 s, br	3603 s, vs 3490 s, br	3607 s, vs 3499 s, br		ν(OH)
	3275 vs,br 3056 vs, br						ν(NH)
1750 vs 1704 vs, br	1731 vs 1670 vs 1619 vs	1710 vs 1679 vs 1600 vs	1716 vs 1672 vs 1609 vs	1711 vs 1679 vs 1603 vs	1719 vs 1670 vs 1604 vs	1692 s, br	ν_{as}(COO)
1430 s 1390 s 1359 s	1404 vs, br 1390s 1332 m	1414 vs 1392 sh 1310 m	1419 vs 1393 sh 1316 m	1412 vs 1391 sh 1315 m	1414 vs 1398 sh 1312 m	1395 m 1330 m	ν_{s}(COO)
	999 vs	988 vs	990 vs	991 vs	985 vs		ν(V=O)
						956 s	$\nu_{s}(VO_2)$
						890 m	$\nu_{as}(VO_2)$
	933 s, vs	931 s, vs	934 s, vs	930s, vs	933 s, vs		ν(O-O)

Additional medium to strong bands appear in the region between 2850-2510 cm^{-1}, originating from the hydrogen–bonded protonated carboxylato groups. Typical of the spectra of the oxoperoxo(citrato)vanadate(V) are the three resolved strong bands between 1730 and 1600 cm^{-1}, assigned to ν_{as} (COO). The ν_s(COO) bands were found to lie between 1415 and 1310. Notable is that they are shifted to lower frequencies with respect to free citric acid. The difference between asymmetric and symmetric **COO** stretchings, $d(\nu_{as}-\nu_s)$ is of the order 300 cm^{-1}, implying the presence of free or unidentate coordinated carboxylate groups. This observation demonstrates that the $d(\nu_{as}-\nu_s)$ relationship with the carboxylate group coordination, thoroughly studied in acetate complexes, holds also for a polycarboxylate such as citrate. The V=O stretchings occur as very strong sharp bands at *ca.* 988 cm^{-1} in the oxomonoperoxo(citrate) complexes. The values are relatively lower frequency in the dioxocitrato complexes. The $\nu_{(O-O)}$ stretchings are easily detected as strong additional bands near 933 cm^{-1}. This region is not interfered by the citrato bands thereby rendering it rather easy to ascertain its identity.

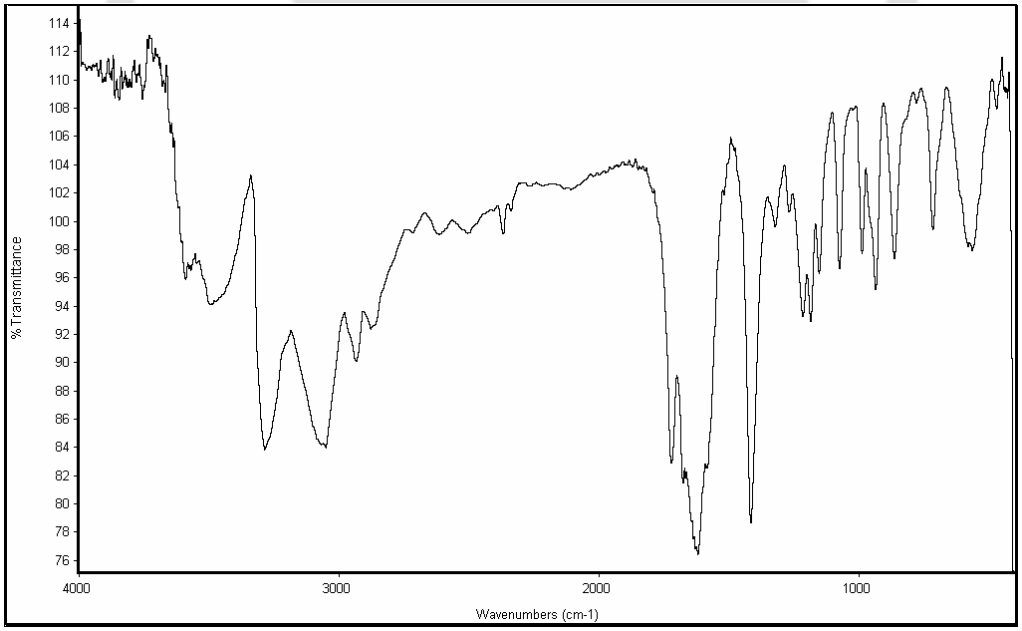


Fig 6.4 IR Spectrum of $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$

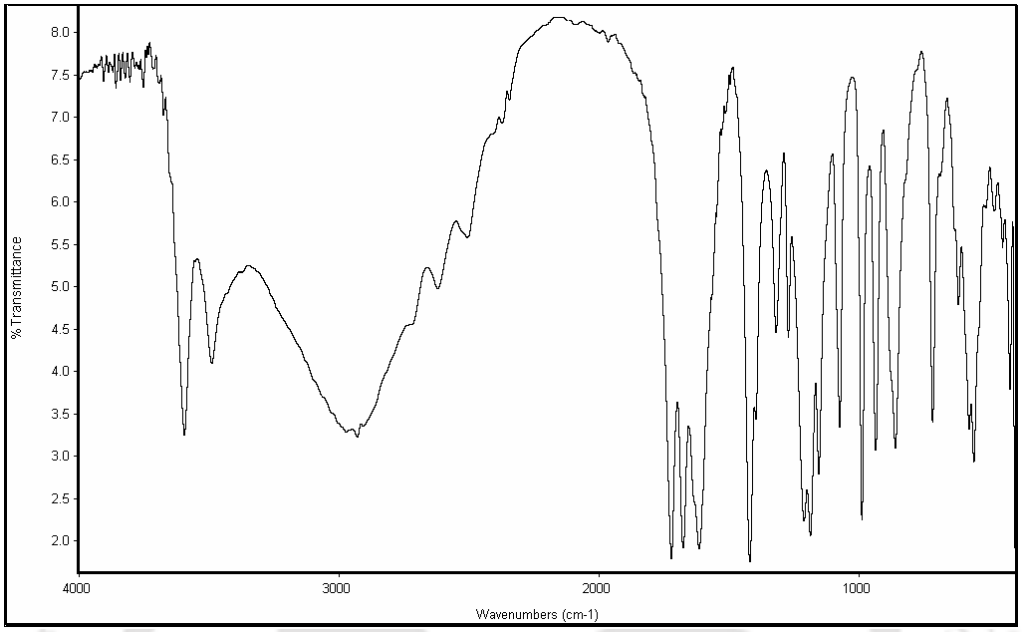


Fig 6.5 IR Spectrum of $Na[VO(O_2)(C_6H_6O_7)].H_2O$

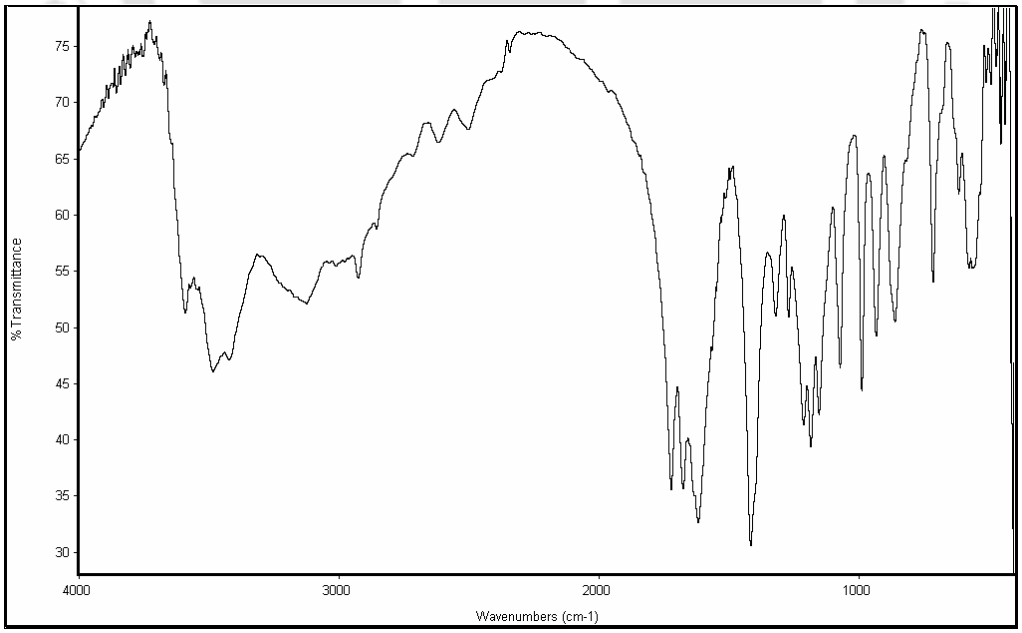


Fig 6.6 IR Spectrum of $K[VO(O_2)(C_6H_6O_7)].H_2O$

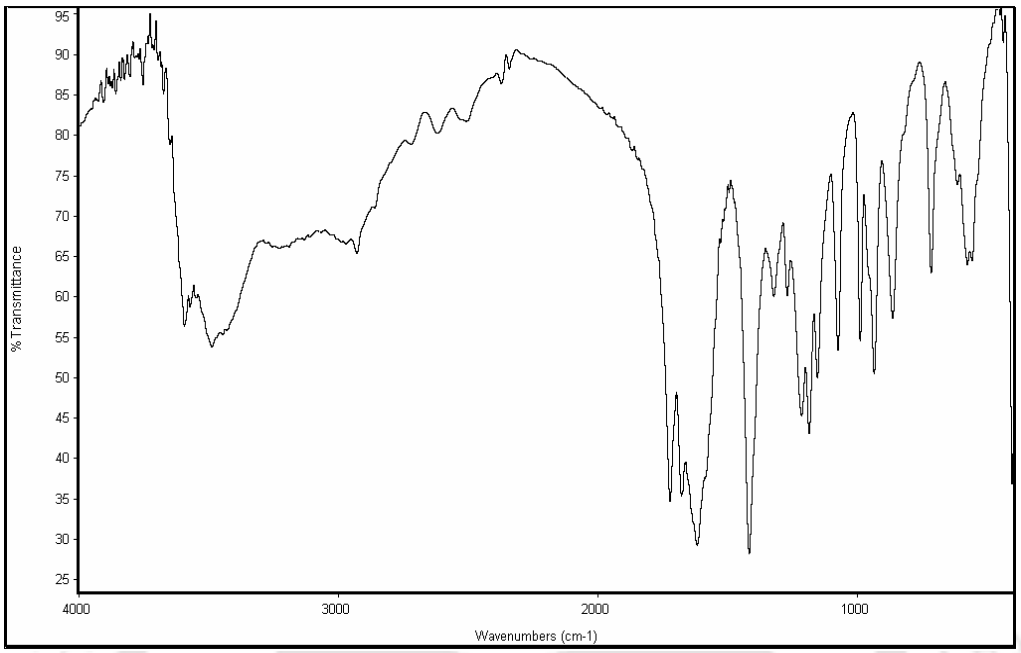


Fig 6.7 IR Spectrum of $Rb[VO(O_2)(C_6H_6O_7)].H_2O$

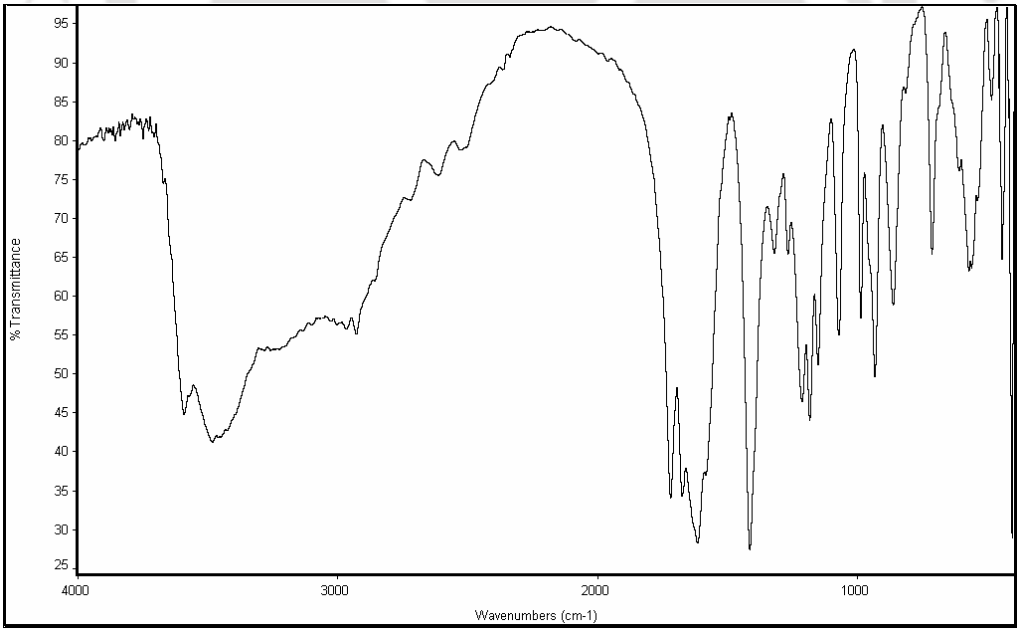


Fig 6.8 IR Spectrum of $Cs[VO(O_2)(C_6H_6O_7)].H_2O$

In order to understand the thermal behavior and decomposition pattern, the compounds were subjected to thermo gravimetric analysis over a temperature range of 25-800 ^{0}C. It is evident from the themograms that all the compounds (2-5), except the NH_4^+ salt, are stable up to a temperature of 100^{0}C and then shows weight losses at 100-250 ^{0}C, 250-450 ^{0}C and 450-800 ^{0}C. The weight loss in the first stage corresponds to the loss of three molecules of carbon dioxide. While in the second step the weight loss is due to loss of an acetone molecule followed by the loss of a water molecule in the third step to finally afford a white compound leading to the formation of the corresponding metavanadates (MVO_3). Where as in case of the ammonium salt (**1**), the decomposition started right from room temperature till a temperature of 80^{0}C with loss of an ammonia molecule. It was followed by weight losses in the ranges of 150 -500 ^{0}C and 500-800 ^{0}C. The weight losses correspond to loss of three molecules of carbon dioxide and one molecule of acetone in the first step and one molecule of water in the second step, finally affording a brownish yellow compound of V_2O_5.

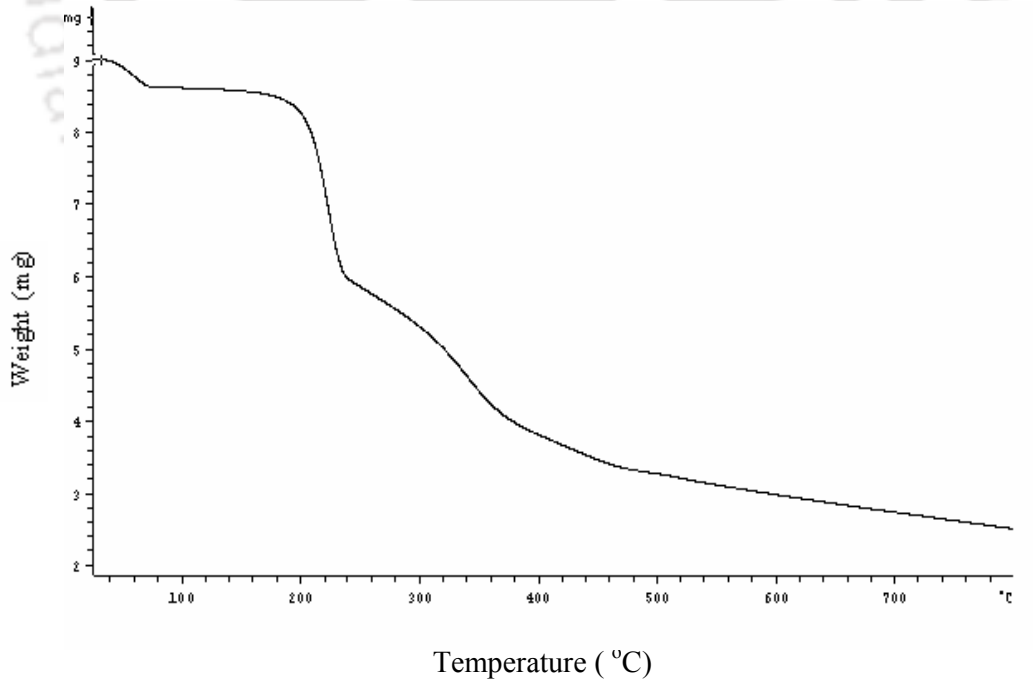


Fig 6.9 TGA Curve of $NH_4[VO(O_2)(C_6H_6O_7)].H_2O$

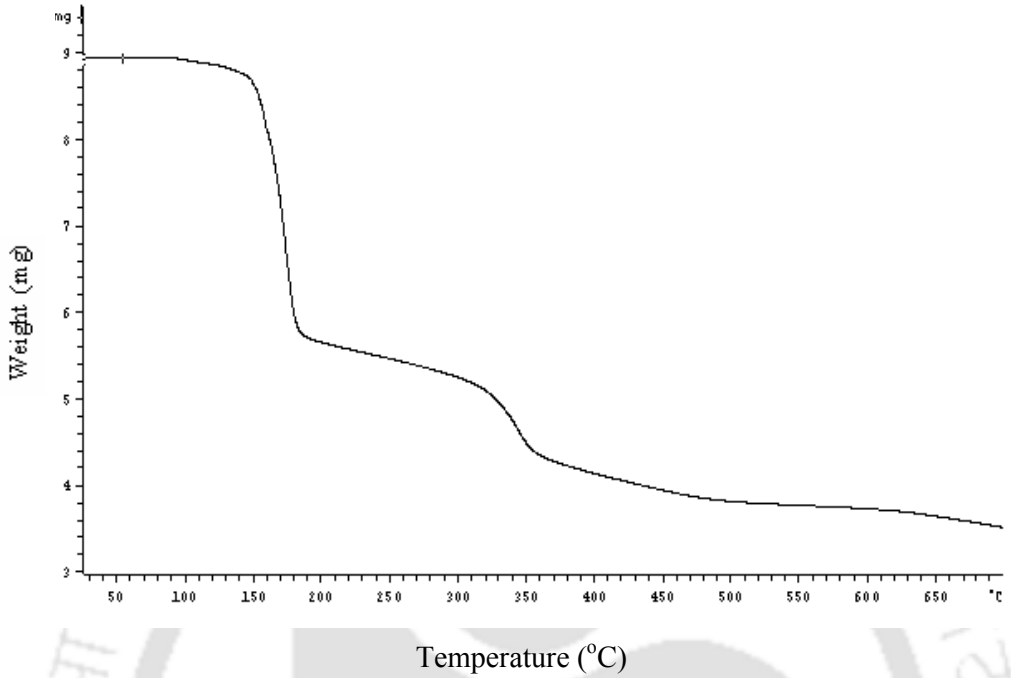


Fig 6.10 TGA Curve of $Na[VO(O_2)(C_6H_6O_7)].H_2O$

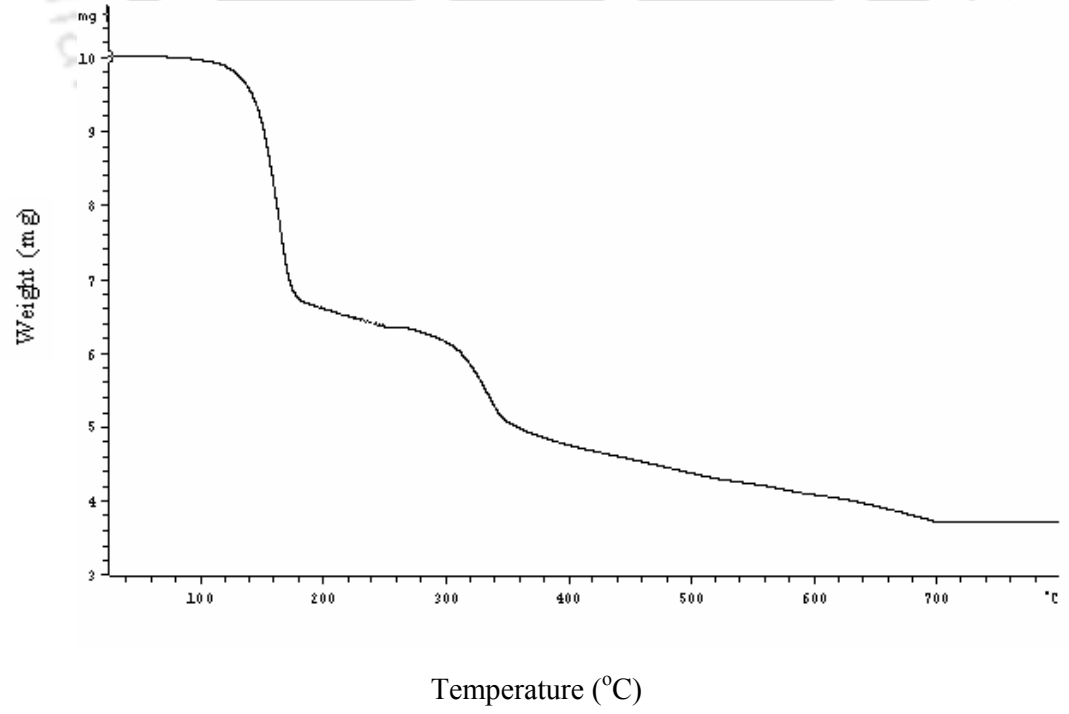
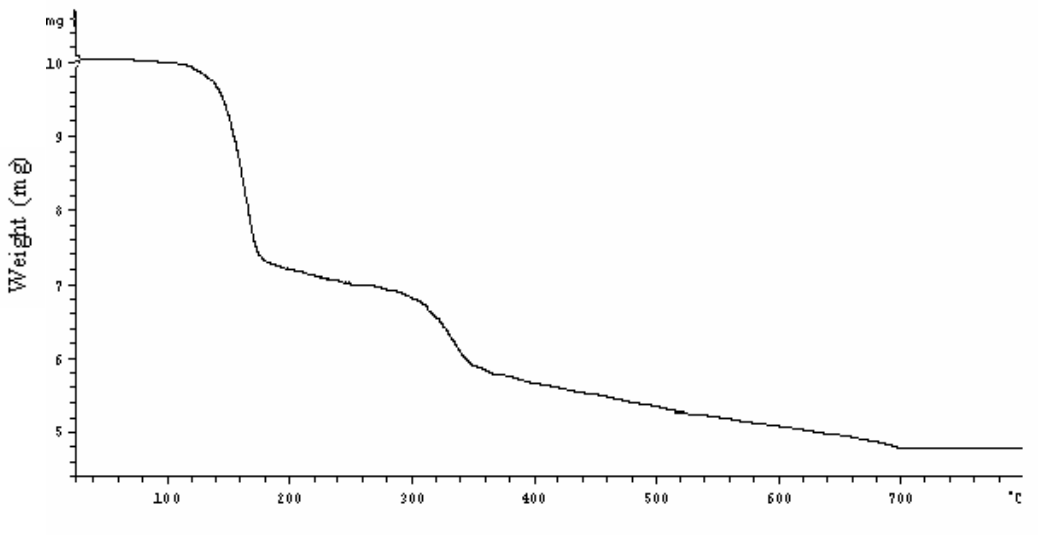
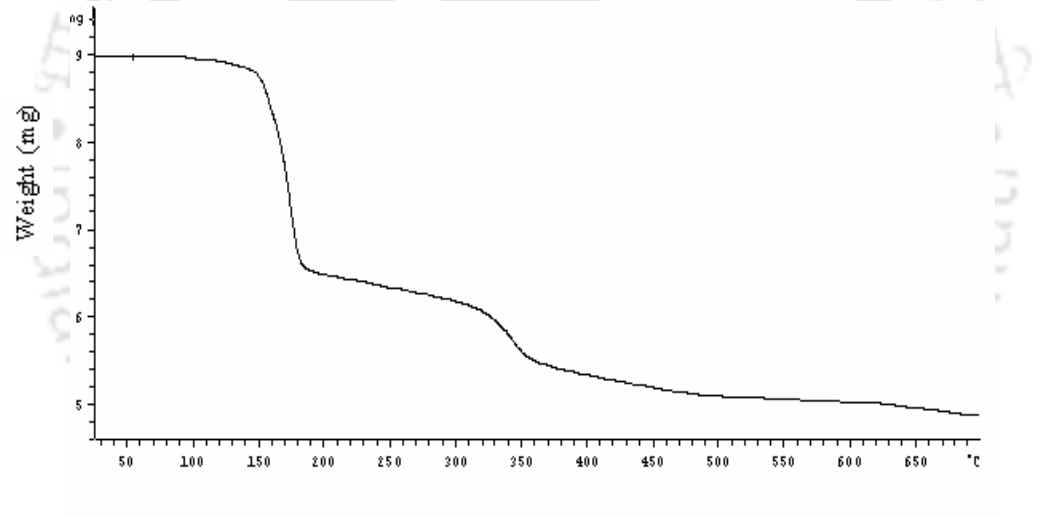


Fig 6.11 TGA Curve of $K[VO(O_2)(C_6H_6O_7)].H_2O$



Temperature (^{o}C)

Fig 6.12 TGA Curve of Rb[VO(O_2)($C_6H_6O_7$)].H_2O



Temperature (^{o}C)

Fig 6.13 TGA Curve of Cs[VO(O_2)($C_6H_6O_7$)].H_2O

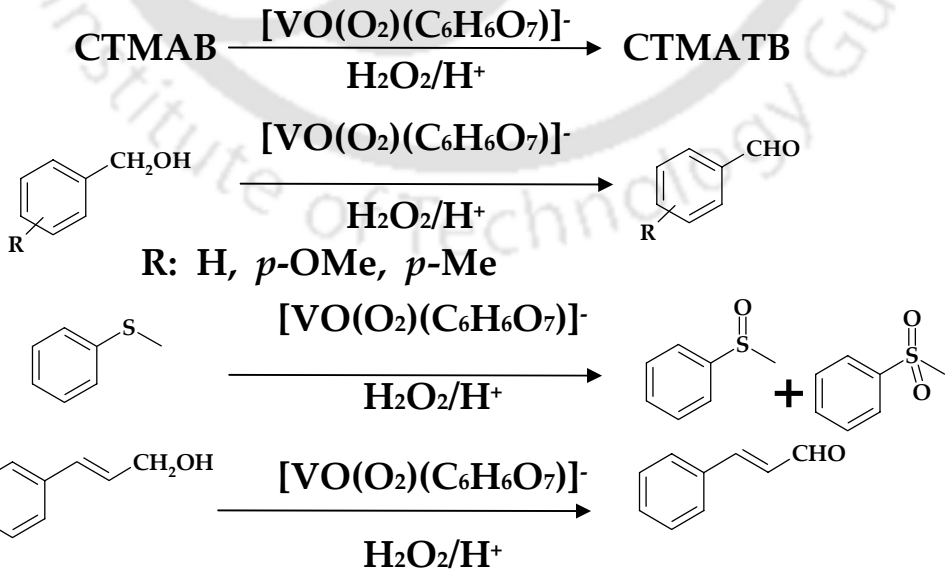
One of our major concerns was to develop newer oxidation catalysts based on vanadium(V), as mentioned earlier. Having characterized the compounds, we sought to investigate their reaction profile. The reactivity of peroxovanadium(V) complexes in terms of organic transformations are generally very encouraging. Many such transformations including vanadium catalyzed stoichiometric as well as catalytic oxidations of sulfides and alcohols were reported.

In line with one of our concerns to ascertain the profiles of oxomonoperoxo(citrato)vanadate(V) complexes as reagents or catalysts, we have carried out a

few oxidations with $K[VO(O_2)(C_6H_6O_7].H_2O$ as the representative example. The reactivity of the complex as oxidant has been first evaluated for oxo-transfer reaction involving triphenyl phosphine as the substrate (**Scheme 6.2**). An acetonitrile (10 mL) solution of triphenyl phosphene (0.79 g, 3 mmol) was mixed with an aqueous solution 25 mL of $K[VO(O_2)(C_6H_6O_7].H_2O$ (1.04 g, 4.5 mmol) and the mixture was refluxed for *ca.* 3 h. The reaction mixture after cooling to room temperature, was poured on to ice-cold water. The product was extracted with ethyl acetate and was purified by column chromatography (hexane/ethyl acetate, 95/5, v/v). Yield: 0.77 g (93%).

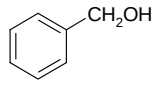
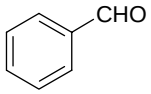
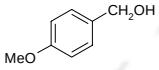
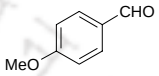
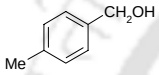
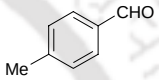
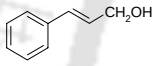
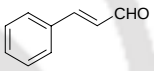
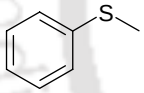
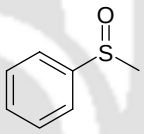
Scheme 6.2 Oxidation of Triphenylphosphine by $K[VO(O_2)(C_6H_6O_7].H_2O$

Further, in order to broaden the scope of reactivity, the versatility of $K[VO_2(C_6H_6O_7)(H_2O)]$ as catalyst was evaluated for oxidation of a variety of substrates including cetyltrimethylammonium bromide (**CTMAB**), bezylic (entry **1-3**, **Table 6.5**) and α, β-unsaturated alcohols (entry **4**, **Table 6.5**), and a organic sulfide (entry **5**, **Table 6.5**)using hydrogen peroxide as the oxidant (**Panel 6.1**). The desired products were obtained in high to very high yields as shown in **Table 6.5**. Oxidation of organic sulfide afforded a mixture sulfoxide and sulfone in the ratio of 75:25. The reaction runs conducted with the other members **1**, **2**, **4** and **5** went on similarly.



Panel 6.1 $K[VO(O_2)(C_6H_6O_7].H_2O$ Catalyzed Oxidations of Inorganic and Organic Substrates by H_2O_2

Table 6.5 $K[VO(O_2)(C_6H_6O_7].H_2O$ Catalyzed Oxidation of Organic Substrates by H_2O_2

Entry	Substrate	Sub.:H_2O_2: Cat. molar ratio	Temp(°C)/Time(h)	Product	Yield* (%)
1		1:2:0.01	rt/2		86
2		1:2:0.01	rt/2		91
3		1:2:0.01	rt/2		92
4		1:2:0.01	rt/0.5		94
5		1:2:0.01	10/1		70

*Isolated yields are reported

Notably, a comprehensive account of the catalytic and biocatalytic activities, e.g. insulin mimetic studies, of such compounds is underway. The present results, while unveiling synthesis, spectroscopic studies and structural assessment of oxoperoxovanadates(V), revealed some facets of the reactions of oxoperoxovanadates(V), $M[VO(O_2)(C_6H_6O_7].H_2O$ as oxidizing agents as well as catalysts.

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