Summary

Chapter 1: Introduction

Section A: Oxidative halogenations

This section deals with the basic introduction of halogens, naturally occurring organo halogen compounds, methods used for the halogenation of organic compounds, introduction about oxidative halogenation, how oxidative halogenations occurs in nature, reagents used for the oxidative bromination, applications of brominated organic compounds, introduction about oxone, applications of oxone and organic transformations using oxone in the present work.

Section B: Zeolites

This section deals with the basic introduction of zeolite molecular sieves, nomenclature of zeolite molecular sieves, classification of zeolite molecular sieves, structural details of zeolite molecular sieves, characteristic properties of zeolites, concepts of zeolite synthesis, mesoporous molecular sieves and applications of zeolite molecular sieves.

Chapter 2: Experimental and instrumental methods

Chapter 2 embodies the experimental methods used in the work. Procedure for modification of Zeolite beta by impregnation method with Ni, Cu, Pb, La, Ce, Cr, Fe, W, Zn, Co, Mo, Zr and Sn metal ions using their corresponding precursors is discussed. Synthesis of MCM-41 has been discussed. Salient features of different instruments like In Situ ESI-MS, In Situ $^{13}$C NMR, Computational study, X-ray powder diffractometer (XRD), FTIR and EDX are discussed. Techniques used for identification of products have been briefly discussed.
Chapter 3: Characterization of zeolite catalysts

Low and wide angle XRD and FT-IR were used to characterize the physico-chemical properties of the catalysts. Energy Dispersive X-ray Analysis (EDX) was used to determine the percentage of elements present in the modified zeolites.

Chapter 4: Oxybrominations using oxone

Section A: Oxybromination of aromatic compounds

In this section of the chapter, a mild and efficient method for the bromination of various aromatic compounds, including hydroxy, methoxy and alkyl arenes in high yields using NH$_4$Br as a bromine source and oxone as an oxidant in H$_2$O or MeOH at room temperature has been discussed (Scheme 7).

This study included activated and inactivated aromatics as well as compounds of moderate activity. The reactions typically proceeded via selective monobromination, preferentially at the para position. Interesting results were obtained with alkyl substituted aromatic compounds which gave ring-brominated products both in methanol and water. Bromination of alkyl benzenes required longer reaction times compared to those of the hydroxy benzene derivatives. Different results were obtained in the case of isobutylbenzene depending on the solvent. The ring-brominated product was obtained in methanol whilst the α-brominated derivative, (1-bromo-2-methylpropyl)benzene, was formed in water.
Section B: Oxybromination of carbonyl compounds

In this section of the chapter, bromination of various ketones such as aralkyl, cyclic, acyclic, 1,3-diketones and β-keto esters at room temperature (or reflux temperature) has been discussed (Scheme 8).

A variety of aralkyl ketones (acetophenone, substituted acetophenones, acetonaphthone and substituted acetonaphthones) were subjected to the bromination reaction and gave good to excellent yields. Interesting results were observed when unsymmetrical acyclic ketones subjected to the bromination with this reagent system. On contrary to the earlier reports, bromination took place at less substituted α-position predominantly. A variety of α-unsubstituted 1,3-diketones and β-keto esters were α-mono brominated and α,α-dibrominated with excellent yields. Different results were observed in case of tetralone depending on the solvent. The α-brominated product was obtained in MeOH, whilst the corresponding dehydrogenated product, i.e. 1-naphthol was formed in DCM.

Section C: Oxybromination of olefins

In this section of the chapter, a very simple, mild and efficient method for direct synthesis of bromohydrins, bromo ethers and dibromides from olefins using NH₄Br as a bromine source
and oxone as an oxidant without catalyst in a highly regio- and stereo selective fashion in short reaction time has been discussed (Scheme 9).

Scheme 9

Various olefins such as activated, inactivated and moderately activated aromatic alkenes, asymmetric trans-alkenes, symmetric trans/cis alkenes, cyclic and linear alkenes are regio- and stereoselectively hydroxybrominated, dibrominated and alkoxy brominated with anti fashion, following Markonikov’s rule, using eco-friendly, non-toxic, and stable reagents in CH$_3$CN/H$_2$O (1:1), CH$_3$CN and MeOH/EtOH without employing catalyst in moderate to excellent yields. Bromohydrins are formed instantaneously. Regio- as well as stereoselective products were formed when trans/cis-alkenes were subjected to bromination, selectively erythro isomers were obtained with trans-alkenes and corresponding threo isomers were formed in case of cis-alkenes.

Chapter 5: Iodine-catalysed tandem synthesis of cyclic acetals and esters from olefins using oxone

Section A: Synthesis of cyclic acetals from olefins

In this section of the chapter, a novel and efficient metal-free protocol for the synthesis of terminal acetals from olefins using oxone as an oxidising agent in presence of catalytic amount of iodine in tandem synthetic manner has been discussed (Scheme 10).
A variety of activated, inactivated and moderately activated aromatic olefins was subjected to the acetalization reaction and gave good to excellent yields. Asymmetric and symmetric olefins also underwent oxidative rearrangement and afforded good yields of the corresponding acetals. It is worth mentioning that in the case of cyclic olefin, the ring-contraction product was observed.

Initial support for the proposed mechanism was obtained by acetalization of styrene-β,β-d2, which gives a benzylic deuterated product. In situ ESI-MS and $^{13}$C NMR experimental data also support the proposed mechanism. Further, computational studies at the B3LYP/6-31G* level, clearly demonstrate the propensity for O$^-\$ attack on α-C rather than on β-C in the phenonium ion intermediate.

**Section B: Synthesis of esters from olefins**

In this section of the chapter, a one-pot procedure for the preparation of glycol mono esters from olefins is presented for the first time using oxone as an oxidizing agent in presence of catalytic amount of iodine in tandem synthetic manner (Scheme 11).
symmetric olefins also underwent oxidative rearrangement and afforded good yields of the corresponding esters. It is worth mentioning that in the case of cyclic olefin, the ring-contraction product was observed.

**Chapter 6: Selective organic transformations over modified zeolites**

**Section A: Vapour phase synthesis of annelated pyridines over modified zeolite Beta**

In this section of the chapter, a novel environment-friendly vapour phase synthesis of annelated pyridines was developed using non-hazardous, commercially available and low cost feeds over zeolites has been discussed (Scheme 12).

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\begin{align*}
\text{Scheme 12} \\
\text{A simple and selective single step synthesis of 1,2,3,4,5,6,7,8-octahydroacridine using simple cyclohexanone, formaldehyde and ammonia in vapor phase conditions over zeolites has been studied. To get the good yield of 1,2,3,4,5,6,7,8-octahydroacridine, different reaction conditions like catalyst variation, metal cation variation, temperature variation, molar ratio variation, Weight Hourly Space Velocity (W.H.S.V) variation and Metal Weight Percent variation has been studied. Highest yield of 1,2,3,4,5,6,7,8-octahydroacridine was observed with Hβ catalyst at 350°C temperature, 0.5 h\(^{-1}\) WHSV, 1:1:5 molar ratio of cyclohexanone, formaldehyde and ammonia. The Hβ catalyst modified with various transition metal cations (Fe,}
\end{align*}
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Cu, Pb, Mo, Zn, Ni, Co, Ce, W and Sn) and 5wt% Pbβ furnished highest yield of 1,2,3,4,5,6,7,8-octahydroacridine under similar conditions.

Encouraged by these results, synthesis of 1,2,3,5,6,7-hexahydrodicyclopenta\[b,e\]pyridine was carried out with same reaction conditions by taking cyclopentanone, formaldehyde and ammonia and provided the good yield of desired product.

**Section B: Tetrahydropyranylation of alcohols over modified zeolite Beta**

In this section of the chapter, tetrahydropyranylation of alcohols and phenols using zeolites has been discussed (Scheme 13).

![Scheme 13](image)

To get the good yield of tetrahydropyranylated product, different reaction conditions like catalyst, solvent, amount of catalyst and metal cation variation has been studied by taking equimolar amounts of benzyl alcohol and 3,4-dihydro-2H-pyran. Highest yield of tetrahydropyranylated product was observed with Hβ catalyst in acetic acid solvent with 10 mg of catalyst. To get the highest yield at short reaction time, Hβ zeolite modified with various transition metal cations (Fe, Cr, Mo, Zr, W, Co, Pb, Cu, Ni, Zn and Ce) and reaction with 5wt%Moβ exhibits much higher activity than that with other metals.

This novel method for tetrahydropyranylation is applied to a variety of alcohols including primary, secondary, benzylic, heterocyclic and allylic alcohols as well as phenols and naphthol and provided the corresponding tetrahydropyranylated products in moderate to excellent yields.