CHAPTER 1
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1.1 GENERAL INTRODUCTION:

Oximes form a familiar class of compounds in chemistry and refer to compounds having C=NOH group. The name oxime is contraction of oxy-imine, and was first introduced by Meyer in 1878.

Oximes are important from synthetic and structural point of view. Several cobalt oxime complexes are used to mimic reactions analogous to vitamin B_{12}^{2a}. Because of the possibility of conversion of oximes to the relatively unstable nitrogen-oxygen bonded derivatives which can release slow energy, they attract attention. Thus, this class of compounds may serve precursor for combustion explosives and fuels^{2b}. Rust inhibiting materials can be prepared by addition of oxime derivatives to an oil^{3}. Polymeric nitriles in the form of fibre, films, filaments, or fabricated threads on derivatisation to their amido-oximes increase efficiency in properties like crease, flex-resistance, moisture regain and affinity towards...
acidic or basic vat and disperse dye. Polarographic estimation of hydroxylamine is done by indirect oximation reaction of cyclohexanone. Oximes are also of great importance in analytical chemistry. In addition to these, oxime functionality is found in biologically active compound such as I. Oxime II is a key reactant in the synthesis of antibiotic like dicloxacillin (III).

Out of several methods for preparation of oximes, two commonly used methods are (a) condensation of hydroxylamine with a carbonyl compound (Equation 1.1) and (b) reaction of nitrous acid or nitrous acid ester on an active methylene compound or a compound having a methylene group adjacent to carbonyl group (Equation 1.2).

\[
\begin{align*}
R' &+\text{C} = 0 + \text{H}_2\text{NOH} &\rightarrow &\text{C} = \text{NOH} + \text{H}_2\text{O} \\
\end{align*}
\]

Equation 1.1
Where $R = \text{t-Bu}$ or 

![Chemical Structure I](image1)

![Chemical Structure II](image2)

![Chemical Structure III](image3)
The first known oxime namely oximino-acetone was prepared by the second method (Equation 1.2). Recently a catalytic method for selective synthesis of oximes from primary aliphatic amines by the action of hydrogen peroxide in the presence of titanium silicate-molecular sieve as catalyst has been developed. Photochemical synthesis of oximes from reaction of \( \text{Bu}_3\text{SnNO}_3 \) with benzylic bromide has yielded oximes in good yield.

1.2 STRUCTURAL FEATURES OF OXIMES:

Oximes are basically represented by structures IV and V.

\[
\begin{align*}
\text{IV} & : R^1 \text{C} = \text{N} - \text{O} - \text{H} \\
\text{V} & : R^1 \text{C} = \text{N} - \text{O} - \text{H}
\end{align*}
\]
Where $R^1$ and $R^2$ may be hydrogen, alkyl or aryl group. The lone pair on the nitrogen atom of the oxime in an unsymmetrical oxime ($R^1 \neq R^2$) makes it possible to have two different stereo-isomers namely syn and anti. However, steric requirements allow trans form to be more stable among the two forms.

An alternative nitrone structure VI for oximes can be thought of. However, neutron diffraction studies on dimethylglyoxime suggest the presence of O-H bond (bond length $1.02 \pm 0.04 \, \text{Å}$). Thus, structure IV and V are the general structures of oximes. In solid state O-H...N via intermolecular hydrogen bonding is observed. The C=N and N-O bond distances calculated from covalent radii and electronegativity data are $1.27 \, \text{Å}$ and $1.44 \, \text{Å}$ respectively. Experimental values for C=N distances lie within the range of $\pm 0.02 \, \text{Å}$. However, the experimental N-O bond lengths are generally lower, and are in the range of $1.40 \pm 0.02 \, \text{Å}$. Structural complicacy in oximes arises on the sequential increase of the number of oxime functionality in a molecule. Thus, vicinal dioxime of symmetrical 1,2-diketone can exhibit three
geometrical isomers viz syn-syn (VII), anti-anti(VIII) and syn-anti(IX).

Vicinal dioxime of unsymmetrical 1,2-diketone (i.e R\textsuperscript{R'/R''}) can have one more stereoisomer because of the possibility of two syn-anti forms which are represented by structure X and XI. Detailed structural reports on oximes are available in literature\textsuperscript{18}.

1.3 CLASSIFICATION OF OXIMES:

On the basis of the original carbonyl compound from which an oxime is derived, oximes are classified into two broad classes, viz. aldoximes and ketoximes. Further sub-divisions, on the basis of the alkyl or aryl group(s) or functional group(s) attached are also widely used.

1.4 CO-ORDINATION MODES OF OXIMES WITH METAL IONS:

Presence of the nitrogen having lone pair and the hydroxyl group makes the oxime group a potentially important ambidentate ligand\textsuperscript{17,18}. The various modes of co-ordination with metal ions are shown below (XII - XV).
In majority of the transition metal complexes of oximes, the complexation occurs through the nitrogen atom; however, there are complexes where the co-ordination through oxygen does occur. Such studies draw attention due to complicacy arising from various modes of co-ordination to the transition metal ions. Depending on the number of oxime group on the ligand the structural complicacy increases and discussion on different co-ordinated complexes of oximes is available\textsuperscript{18}.

An oxime can form complex of the type $ML_nX_2$ (where $L$ = oxime, $n$ = 2 or 4 and $X$ = halogen) with copper(II), nickel(II) and cobalt(II) salts\textsuperscript{19}. Planar platinum complexes with mixed ligands such as
[PtL₂L′₂]Cl₂ (where L = acetoxime, L′ = NH₃) as well as simple acetoxime (L) complex of the type [PtL₄]Cl₂ are reported. Monoxime can serve as bridging ligand by binding through nitrogen and oxygen atom simultaneously. For example [PtL(OAc)]³ (where OAc = acetate, L = acetoxime) has a cyclic structure with bridging acetato as well as acetoxime group. Complexes containing neutral as well as anion of the oximes, for example [Pt(LH)₂L₂] (where LH = acetoxime, L = acetoxime anion) are known.

Organometallic complexes [cpM(CO)₂(ONCRR′)] where M = Mo, W; R = Me; R′ = Me, CH=CH₂ etc; cp = cyclopentadienyl anion) have monomeric structure having oxime as bidentate ligand (XVI). Sequential increase of oxime functionality increases the structural complicacy in oxime complexes. Structural variation is observed on changing the metal ion too. In the case of dimethylglyoxime (dmg) as ligand the copper complex [Cu(dmg)₂]²⁺ is dimeric (XVII) whereas analogous nickel complex is monomeric (XVIII). Dimethylglyoxime also forms mixed ligand multinuclear complex such as [Cu₃(dmg)₂(bpy)₂]Br₂ (XIX) (where bpy = bipyridyl).
Although \([\text{Cu(dmgH)}_2]_2\) is dimeric, dimethylglyoxime complex having monomeric structure \((\text{XX})^{25}\) is also known. Slight variation in the ligand\(^{24}\) also makes it possible to synthesise mixed metal complex \((\text{XXI})\). In a recent work magnetically coupled Cu(II)M types of complex \((\text{XXII})\) have been synthesised and characterised\(^{26}\).

\[
\begin{array}{c}
\text{Where } M = \text{Cr(III)}, \text{Mn(III)}, \text{Mn(II)}, \text{Co(III)}, \\
\text{Co(II)} \text{ etc.} \\
X = \text{Cl, OMe}
\end{array}
\]

\text{XXII}
It is also possible to design multimetal complexes of oximes by choosing appropriate oxime ligand\textsuperscript{27} having additional co-ordinating site. Thus [Cu\textsubscript{3}(\mu\textsuperscript{3}-OH)L\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2} H\textsubscript{2}O] (XXIII) [ Where L = 3-(benzylimino)butanone-2-oxime ] having a trihydroxy bridged [Cu\textsubscript{3}(\mu\textsuperscript{3}-OH)] core capped by triply co-ordinated perchlorate anion is reported. In basic medium this compound (XXIII) gets converted to hexanuclear complex [Cu\textsubscript{6}(\mu\textsuperscript{4}-O)\textsubscript{2}L\textsubscript{6}(H\textsubscript{2}O)](ClO\textsubscript{4})\textsubscript{2} 0.5H\textsubscript{2}O (XXIV), and these have been characterised by crystallography.

Acetoxime complex with oxo-molybdate core has revealed complicated binding pattern\textsuperscript{28}. In [Mo\textsubscript{4}O\textsubscript{12}(Me\textsubscript{2}CNO)\textsubscript{2}]\textsuperscript{2-} (XXV) having n-Bu\textsubscript{4}N\textsuperscript{+} as cation, the nitrogen and oxygen atoms of oxime serve as bridging bidentate ligand.

1.5 REACTIONS OF OXIMES:

Organic transformation on oxime functionality has been a center of study in organic chemistry. Depending on the reagent and the reaction conditions, the oxime group undergoes a number of transformations (Scheme I).
In addition to these, transition metal complexes of oximes can get transformed or serve as template for organic transformations. Each type of reactions of oxime are discussed under separate headings.
1.5.1 DEOXIMATION REACTION:

Regeneration of the parent carbonyl compound (Equation 1.3) from its oxime derivative is known as deoximation reaction. Deoximation reaction is used for purification and isolation of carbonyl compounds\(^{29}\). Deoximation reaction is successfully used for 1,2-transposition of carbonyl group (Equation 1.4)\(^{30}\).

\[
\begin{align*}
R >& C = NOH & \rightarrow & R >& C = O \\
\text{Equation 1.3}
\end{align*}
\]

Wide varieties of methods are available which may be broadly classified into biochemical, hydrolysis, oxidative deoximation, reductive deoximation and disproportionation reaction.

Biochemical methods are convenient as they
are performed under mild condition and can be specific. Backer yeast is recently used for conversion of oxime to ketone\textsuperscript{31}.

Commonly used reagents for hydrolytic cleavage are hydrochloric acid/formaldehyde\textsuperscript{32}, hydrochloric acid/levulinic acid\textsuperscript{33}, pyruvic acid in the presence of a strong acid\textsuperscript{34}, sodium hydrogen sulphide\textsuperscript{35} etc.

In reductive cleavage, reagents like titanium(III) chloride\textsuperscript{36}, chromium(II) acetate\textsuperscript{30}, iron pentacarbonyl\textsuperscript{37}, Raney nickel\textsuperscript{38}, zinc and acetic acid\textsuperscript{39}, aluminium isopropoxide\textsuperscript{40} are used.

Oxidative deoximation by ceric ammonium nitrate\textsuperscript{41}, lead tetraacetate\textsuperscript{42}, thallium(III) nitrate\textsuperscript{43}, chromium(IV) oxide\textsuperscript{44}, periodic acid\textsuperscript{44}, ozone\textsuperscript{45}, bis(triphenylphosphine)palladium\textsuperscript{46} and various nitronium\textsuperscript{47} and nitrosonium salts\textsuperscript{48} are known. The mechanism of such reactions varies from reagent to reagent. A second order kinetic dependence between aliphatic oxime and thallium(III) acetate\textsuperscript{49} is reported to describe a mechanistic sequence shown below (Scheme II).
SCHEME II

In most of the oxidative deoximation reaction
gem-nitroso alkanol (XXVI) is proposed as the intermediate. The intermediate (XXVI) has been isolated or observed as transient species having blue green colour. Kinetic study of deoximation reaction by
Mn(OAc)$_3$ also supports similar intermediate$^{50}$. An alkaline Raney nickel solution can effectively cause deoximation reaction. Such process is explained on the basis of an equilibrium shown in equation 1.5 and in these reactions the subsequent consumption of hydroxylamine produced by an irreversible degradation process takes place.

$$\begin{align*}
R\text{C}=\text{NOH} + \text{H}_2\text{O} & \rightleftharpoons \text{Raney Ni} \xrightarrow{\text{OH}} R\text{C}=\text{O} + \text{NH}_2\text{OH} \\
\text{Equation 1.5}
\end{align*}$$

Similar equilibrium is also proposed by Okac et al. to explain the formation of dimethylglyoxime from diacetylmonoxime$^{51}$ (Equation 1.6).

$$\begin{align*}
\text{C}=\text{NOH} & \rightleftharpoons \text{Ni}^{2+} \xrightarrow{\text{Ni}^{2+}} \text{C}=\text{O} + \text{CH}_2\text{C}=\text{NOH} \\
\text{Equation 1.6}
\end{align*}$$
Electrochemical oxidation of oximes to give carbonyl compounds via intense deep blue intermediate (presumably a nitroso intermediate) is reported\(^2\) (Equation 1.7).

\[
\begin{align*}
\text{R}_2\text{C}=\text{NOH} & \quad \xrightarrow{e^-} \quad \text{R}_2\text{C} \quad \text{OCOCH}_3 \\
& \quad \xrightarrow{\text{H}_2\text{O}^+} \quad \text{R}_2\text{CO}
\end{align*}
\]

Equation 1.7

In a more recent study on thermal deoximation by \(\text{Fe}_2(\text{CO})_9\) an initial co-ordination of nitrogen with a \(\text{Fe}(\text{CO})_4\) fragment in the course of the reaction is demonstrated.\(^5\)

1.5.2 NITRILES FROM OXIMES:

The dehydration of aldoximes is an important reaction to prepare nitrile functional group\(^5\)-\(^6\) (Equation 1.8).

\[
\begin{align*}
\text{R} \quad \text{C} = \text{NOH} & \quad \xrightarrow{} \quad \text{R} \quad \text{C} \equiv \text{N}
\end{align*}
\]

Equation 1.8
A number of methods involving reagents like triphenylphosphine / carbon tetrachloride\textsuperscript{57}, triflic anhydride\textsuperscript{58}, 1-diethylaminopropyne\textsuperscript{59}, phosphorus tris [dimethylamide]\textsuperscript{60}, potassium cyanide/phase transfer catalyst\textsuperscript{61}, trimethylamine/sulphur dioxide complex\textsuperscript{62}, selenium dioxide\textsuperscript{63}, diphosphorus tetraiodide/pyridine\textsuperscript{64} trifluoroacetic anhydride/pyridine\textsuperscript{65}, N,N-dimethylchloromethaniminium chloride\textsuperscript{66}, N-trifluoroacetyl-imidazole\textsuperscript{67}, trichloroacetyl chloride / triethylamine\textsuperscript{68}, aluminium iodide /acetonitrile\textsuperscript{69} cause dehydration of oximes. One pot conversion of aldehydes into nitriles via aldoximes\textsuperscript{70,71} is also known. Some of these methods require the use of strong bases, acids or oxidizing agents under conditions which may be incompatible with sensitive substrates and thus may lead to the undesired products. Catalytic method for the conversion of aldoximes into nitriles consisting of heating the aldoximes in boiling acetonitrile in the presence of copper(II) acetate is known\textsuperscript{73}.

Some ketoximes also yield nitriles; in such reactions the carbon chain attached to oxime group gets shortened (Equation 1.9 and 1.10).
\[
\text{NOH} \\
\text{Me}_2\text{CH} - \text{C} - \text{CHMe}_2 \rightarrow \text{Me}_2\text{CH} - \text{CN} + \text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{O}
\]

Equation 1.9

\[
\text{NOH} \\
\text{R} - \text{C} - \text{COOH} \rightarrow \text{R} - \text{CN} + \text{CO}_2 + \text{H}_2\text{O}
\]

Equation 1.10

Usually oximes substituted at an \(\alpha\)-carbon by groups capable of stabilising positive charge undergo such fragmentations. Palladium bis(phosphine) complex also causes such fragmentation.\(^\text{74}\).

1.5.3 REDUCTION OF OXIMES:

Reduction of oximes is an useful general method for the preparation of primary amines.\(^\text{31(11)}\),\(^\text{75}\). A variety of reagents can reduce oximes via imines as the intermediate (Equation 1.11).
\[ \text{Equation 1.11} \]

Number of reagents for selective reduction of oximes are being sought for the reduction of acid or ester having oxime functionality as it leads to the formation of amino acids\textsuperscript{76} (Equation 1.12).

\[ \text{Equation 1.12} \]

Catalytic hydrogenation over Raney nickel, rhodium on alumina, palladised carbon, platinum(IV)
oxides, dissolving metals such as zinc and formic acid or acetic acid, nickel-aluminium alloy in alkali and lithium aluminium hydride are some of the reagents which convert oximes to primary amines.\textsuperscript{3,75,77,78} Reduction of oxime not necessarily pass through intermediacy of an alkyl hydroxylamine as hydroxylamines are usually inert towards hydrogenation. Study on the reduction of 2-inanoneoxime shows that hydrogenolysis of N-O bond is the first step in it, in the absence of an acid.\textsuperscript{77,79} However, reduction of oximes, O-acyloximes and O-alkyloximes by pyridine-borane complex in acidic medium to the corresponding hydroxylamine suggests that only the C=N bond can be reduced by choosing appropriate reagent and reduction condition.\textsuperscript{80} Catalytic hydrogenation over a platinum catalyst in the presence of acid is successful for reduction of few oximes to hydroxylamine derivatives. Diborane, however, appears to be a generally acceptable reducing agent for this purpose and gives good yields.\textsuperscript{81}

Phosphate oximes can be selectively reduced by the use of trimethylsilyl chloride (TMSCl) in the presence of lithium borohydride (Equation 1.13).
reaction proceeds via generation of two reducing species namely trimethylsilane and borane-tetrahydrofuran complex\(^{82}\) (Equation 1.14).

\[
\text{Me}_3\text{SiCl} + \text{LiBH}_4 \xrightarrow{\text{THF}} \text{Me}_3\text{SiH} + \text{BH}_3\text{THF} + \text{LiCl}
\]

Equation 1.14

Catalytic oxidation of carbon monoxide to carbon dioxide can be achieved by the use of ruthenium-carbonyl cluster, namely \(\text{Ru}_3(\text{CO})_{12}\)^{83} (Equation 1.15).

\[
\begin{align*}
\text{R}^1\text{C} = \text{NOH} + \text{CO} & \xrightarrow{\text{Ru}_3(\text{CO})_{12}} \text{R}^1\text{C} = \text{NH} + \text{CO}_2 \\
\end{align*}
\]

Equation 1.15
Asymmetric reduction of oxime to corresponding amine in enantiomeric excess is done by catalytic reaction of \([-(-)\text{DIOP}]\text{Rh}(S)\text{Cl}\) with diphenyl silane where \(S\) is solvent and DIOP is diphosphine ligand (XXVII).

\[
\text{XXVII}
\]

1.5.4 Rearrangement Reactions:

Oximes are structural isomer of amides and conversion of oxime to amide is synthetically important. Both aldoximes and ketoximes can be converted to N-substituted amides in acidic medium (Equation 1.16) and is known as Beckmann rearrangement. Use of various catalysts such as \(\text{PCl}_5\), \(\text{H}_2\text{SO}_4\), \(\text{P}_2\text{O}_5\), \(\text{SO}_2\text{Cl}_2\) are
worth mentioning\textsuperscript{85,86}. Aldoximes can also be converted to amides under neutral condition using reagents like silica gel\textsuperscript{87} and nickel acetate\textsuperscript{88}. Such process may also occur under weakly acidic condition, e.g., boron trifluoride in acetic acid\textsuperscript{89}. A modified Beckmann rearrangement of O-acyl derivatives of oximes under very mild and weakly acidic condition by a system consisting of triphenylphosphine-diethyl azodiformate (TPP-DAF) with carboxylic acids or alcohols\textsuperscript{90} is (Equation 1.17) reported.

\[
\begin{align*}
\text{Ph} &- \overset{\text{TPP-DAF}}{\text{Ph}} \overset{\text{Ph}}{\text{N=O}} \overset{\text{ArCO}_2\text{H}}{\text{Ph}} \overset{\text{SPONTANEOUS}}{\text{Ph}} \overset{\text{N=O}}{\text{Ar}} \\
\text{Ph} &- \overset{\text{SPONTANEOUS}}{\text{N=Ph}} \overset{\text{O \quad O}}{\text{Ar}} \overset{\text{SPONTANEOUS}}{\text{Ph}} \overset{\text{N=O}}{\text{Ar}} \overset{\text{O \quad O}}{\text{Ar}}
\end{align*}
\]

Equation 1.17
Beckmann rearrangement under photochemical condition is also observed. In such rearrangement hydrolysis of N-O bond in excited oxime occurs as the primary step.  

1.5.5 CONVERSION OF OXIMES to -NO and -NO₂ GROUP:

Oximes are tautomeric with nitroso alkanes (Equation 1.18). Although, such equilibria are not common, isolation of tautomeric quinone monoxime (Equation 1.19) has been reported.

\[ R_2C=NOH \rightleftharpoons R_2CH-NO \]

Equation 1.18

\[ \begin{array}{c}
  \text{O} \\
  \text{NOH} \\
  \text{H} \\
\end{array} \rightleftharpoons \begin{array}{c}
  \text{O} \\
  \text{OH} \\
  \text{NO} \\
\end{array} \]

Equation 1.19

Similar form for other \( \alpha,\beta \)-unsaturated oximes such as cinnamaldoxime is unknown.  

Possibility of such tautomerism leaves scope for alkylation or functionalisation of oximes at carbon.
atom bearing the \( =\text{NOH} \) group. Ring expansion and ring contraction of six membered modified oximes usually pass through such tautomeric process\(^94\). Such phenomena are illustrated in equation 1.20 and equation 1.21.

\[
\begin{align*}
\text{Equation 1.20} \\
\text{Equation 1.21}
\end{align*}
\]

Tautomerisation process is important from the point of view of nitrosyl radical which finds application as radical trap. First iminoxy radical \( \text{RR}^1\text{C}=\text{NO}^- \) derived from oxime was reported by Thomas in 1964\(^95\). The iminoxy radicals are characterised by their e.p.r. spectra and have characteristic blue colour. They are
usually distinguished from NO\textsubscript{2} derivatives by their visible spectra. Nitrosyl radical has absorbance in the range 530-800 nm whereas -NO\textsubscript{2} has their absorbance maximum at about 400 nm.

Oximes can be oxidised to nitrate group by the action of trifluoroperacetic acid\textsuperscript{96} (Equation 1.22). This reaction is widely used for oxidation of carbohydrate oximes.

\[
\text{NOH} \xrightarrow{F_3CCOOH} \text{NO}_2
\]

Equation 1.22

1.5.6 CYCLISATION REACTION OF OXIMES:

Cyclisation of oximes can occur via intramolecular or intermolecular process. Intramolecular process occurs usually in the oxime having additional functionality where the addition can take place. Simple example of such cyclisation is the catalytic cyclisation in \(\alpha,\beta\)-unsaturated oximes by PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}\textsuperscript{97} (Equation 1.23).
More complicated products are observed in the cyclisation by PhSeSePh\(^9\) (Equation 1.24).

Intramolecular cyclisation are also effected by cations like Cu(II), Mn(II) in the presence of oxygen\(^9\) (Equation 1.25).
This reaction is different from the process described in equation 1.23 as an additional OH group gets incorporated in the final product. Intermolecular condensation reactions are used for production of nitroso phenol derivatives (Equation 1.26).

\[
\begin{align*}
\text{R}^1\text{CH} & \rightarrow \text{OH} \\
\text{NO} & \text{CH}_3 \\
\text{R}^2 & \text{CH}_2\text{CCH}_3
\end{align*}
\]

Equation 1.26

Other cyclisation reactions includes thermal 1,3-dipolar addition reaction. One such reaction is represented in equation 1.27.

Cyclisation reaction of oximes has been developed to a general route to synthesise 3-substituted 1,5-diacyl-2,4-pentanediones and 4-methoxy-2-pentanone (Equation 1.28). Oximes serve as precursor for macrocyclic ligand (XXVIII) via oligomerisation reaction. Specific synthesis of macrocycles are of great value in synthetic chemistry.
Ph

\[ \text{Equation 1.28} \]

\[ \text{Equation 1.27} \]

\[ \text{Equation 1.28} \]
1.5.7 REACTIONS OF CO-ORDINATED OXIMES:

Co-ordinated oxime group can be converted to another functional group by reaction on the co-ordinated ligand. Salicylaldoximato complex of vanadate reacts with acetonitrile to result in complex XXIX\(^1\)\(^{103}\). Study on reactions of co-ordinated oxime revealed the route for transformation of varieties of oxonitrosyl species\(^2\)\(^8\). For example \([\text{Mo}(\text{NO})(\text{OMe})(\text{Me}_2\text{CNO})_2]\) reacts with \([\text{n-Bu}_4\text{N}]_2(\text{Mo}_2\text{O}_7)\) to yield \([\text{n-Bu}_4\text{N}]_2(\text{Mo}_4\text{O}_{10}(\text{NO})(\text{OMe})(\text{Me}_2\text{CNO})_2]\).

Cobaloxime (abbreviation of \([\text{Co(dmgH)}_2]\)) is a complex which can effectively cause hydrogenation, carbon-carbon bond formation\(^1\)\(^{104}\). In a recent work\(^1\)\(^{105}\), on photochemical reaction \(\text{RCH}_2\text{Co(dmgH)}_2(\text{Py})\) (Where \(\text{Py} = \text{pyridine}\)) in the presence of oxygen shows formation of alcohol and aldehyde of the alkyl group attached to cobalt (Equation 1.29).

\[
\text{RCH}_2\text{Co(dmgH)}_2\text{Py} \\
\text{O}_2 + \text{hv} \\
\text{RCH}_2-\text{O}-\text{O}-\text{Co(dmgH)}_2\text{Py} \\
\text{reduction} \\
\text{RCH}_2\text{OH} \\
\text{RCHO} + \text{RCH}_2\text{OH}
\]

Equation 1.29
1.6 SCOPE OF THE PRESENT STUDY:

In the foregoing discussion different types of reactivities of oximes are highlighted. Broadly two types of reactivities are observed with transition metal complexes. Firstly, complex formation and secondly, transformation of oxime functional group to another functional group. Due to the co-ordination effect the oxidation and reduction reactions are important in the presence of transition metal complexes as it enhances the product selectivity and continuous processing.

From the limited report on copper(II) catalysed/promoted reactions of oximes, the mechanism
of such reactions are not clearly understood. A few studies have suggested involvement of radicals in copper(II) catalysed reactions. Hence, a study on the reactions of oxime functionality in the presence of radical generating species such as benzoyl peroxide would diversify the scope in studying mechanistic and synthetic utilities.

Protection and deprotection of oximes are an important reactions in organic chemistry; hence, an attempt to develop mild reagent for deoximation reaction is important.

Furthermore, a comparative study on the oxidation as well as reduction reaction of C=N bond with C=C bond would be helpful in generalising such a reaction. This is particularly important in case of oxime as analogous vinyl alcohol exists in keto form rather than the enol form.

Thus, keeping these scope in mind along with anticipation of selective synthetic methods in redox reaction of oximes in the presence of copper and nickel complexes are studied.