Indian Journal of Chemistry
Vol. 47B, February 2008, pp. 259-271

Advances in Contemporary Research

Deoximation of keto- and aldoximes to carbonyl compounds

Sandhyamayee Sahu[a], Sagarika Sahu[a], Sabita Patel[a], Sukalyan Dash[b] & Bijay K. Mishra[a*]

[a] Centre of studies in Surface Science and Technology, Department of Chemistry, Sambalpur University, Jyoti Vihar 768 019, India

[b] Department of Chemistry, University College of Engineering, Burla- 768 018, India

Email: bijaym@hotmail.com

Received 18 July 2007; accepted (revised) 13 November 2007

Oxime is a protected form of carbonyl compound and is considered to be their equivalent. Various methods are adopted for the deoximation processes to effectively and suitably obtain the parent or new aldehydes and ketones. Deoximation can be achieved using various processes like oxidation, reduction, hydrolysis, hydrogenation etc. using organic and inorganic reagents. Besides, some surface templated processes and photochemical processes are also used to give products in a remarkably effective way.

Keywords: Oxime, deoximation, ketoximes, aldoximes, Surface templated process, photochemical process, carbonyl compound

Oximes, compounds with C=N-OH group, have provided a fruitful area of study over the past two decades. These are found to be the most important derivatives of carbonyl compounds and are utilized for the purification, characterization and protection of carbonyl compounds. Oximes derived from aldehydes are aldoximes and those from ketones are ketoximes. Unsymmetrical oximes, like acetaldoxime, occur as a mixture of (*E*) and (*Z*) isomers across the carbon-nitrogen double bond (**Figure 1**) and are referred to as *syn* and *anti* isomers, respectively. Configurations of oximes have been established by using ^{1}H NMR (ref. 1) and ^{13}C NMR (ref. 2) spectroscopy.

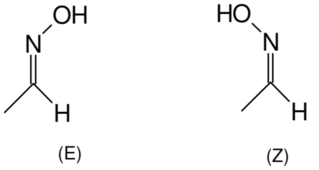


Figure 1

Oximes play an important role in various fields such as crystal engineering, pharmaceuticals, polymer sciences etc. Cyclohexanoneoxime is converted into its isomer ε-caprolactam, which is a precursor for nylon-6. Oximes are easily reduced to amines, which can be used in the manufacture of dyes, plastics, synthetic fibres, and pharmaceuticals. Christer *et al.*[3] have synthesized and studied the crystal structures of some new (pyridylmethylene) amino acetophenone-oxime ligands which are used as “Extended” building blocks for crystal engineering. Naturally occurring oximes are rare; a recent discovery of such type is lycoposerramine-B. Katakawa *et al.*[4] have reported the presence of an oxime alkaloid in Lycopodium, which produces structurally complex alkaloids and potent acetylcholine esterase inhibitors[5(a, b)].

Presence of active functionality like C=N-OH has made oxime useful compound having wide applications in various activities. Since oxime exists in *syn* and *anti* isomeric forms it undergoes various reactions like acetylation, α-alkylation, rearrangement reactions, 1, 3-dipolar addition, addition reactions, *ortho* functionalization, deoximation and many others.

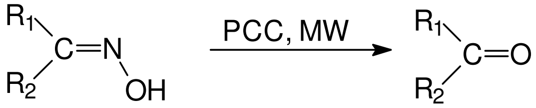
Deoximation Reactions

Since oximes have been employed as ketone or aldehyde functional group equivalents in organic synthesis[6-9], the conversion of oximes into their parent carbonyl compounds has received considerable attention[10]. Basing on the hydrolytic[11], reductive[12], and oxidative[13] reactions, a number of methods for deoximation have been developed to deprotect carbonyl compounds. The deoximation process can be undertaken in both homogeneous and heterogeneous conditions.

The classical method for the cleavage of oximes to aldehydes and ketones includes acid hydrolysis, which is not suitable for acid sensitive compounds[14]. Several methods have been developed for oxidative deoximation of carbonyl compounds having some advantages over the classical hydrolysis method. The hydrolytic stability of oximes leads to the development of several oxidative reagents, each having its own merits and limitations. Classical reagents of such type are manganese triacetate[15], dinitrogen tetroxide[16], trimethylsilyl chlorochromate[17], titanium silicate[18], pyridinium chlorochromate[19], bismuth trichloride[15], ammonium persulphate in silica gel[20], zirconium sulphophenyl phosphonate[21], N-halo-amides[22], triethylammonium chlorochromate[23], Dess-Martin periodinone (DMP)[24], quinolinium fluorochromate[25, 26] and Raney nickel[27] with certain limitations. In spite of many reagents available, there is still scope for newer reagents. Some of the reagents for deoximation are given in **Table I**.

Deoximation using microwave irradiation

Regeneration of carbonyl functions from oximes can be accomplished under microwave (MW) irradiation using several reagents within a short time with good yields. Growing interest in the application of MW irradiation in chemical reactions is due to the fact that the MW approach contributes to the much improved reaction rates, and formation of cleaner products. Chakraborty and Bordoloi[38] have reported a facile deoximation protocol using pyridinium chlorochromate under MW irradiation within a short time with yields of 90-97% (**Scheme I**).



Scheme I

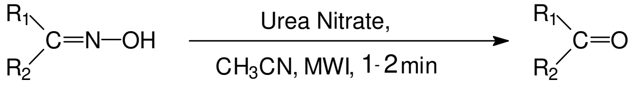
Heravi *et. al.*[39] have used zeofen, a mixture of $Fe(NO_3)_3.9H_2O$ and a weight equivalent of HZSM-5 zeolite, as a versatile oxidizing reagent for deoximation reactions. It has been used as a green chemical under microwave irradiation in solvent free condition[40]. Under green chemical approach, Bigdeli *et al.*[41] have used potassium peroxymonosulphate ($KHSO_5$), commercially known as Oxone, for deoximation reaction in the presence of alumina under microwave irradiation. The yield has been reported to be within 80-90% in a time period of seven minutes. In normal conditions, the reagent was used with glacial acetic acid in the range of 1-5 hr in good yields[42].

Perumal *et al.*[43] have reported a mild and efficient method for the cleavage of oximes to carbonyl compounds using readily available urea nitrate in acetonitrile-water (95:5) medium, under microwave irradiation, in 80-95% yield (**Scheme II**). Thermal decomposition of urea nitrate produces N_2O along

Table I — Oxidative reagents for deoximation reactions

Sl.No.	Reagents	Activity	Ref.
1	PCC (Pyridinium Chlorochromate)	Kinetics and mechanism of deoximation reaction	28
2	QFC (Quinolonium FluoroChromate)	Cleavage of C=N of oximes and hydrazones to corresponding carbonyl compounds.	29
3	QFC Supported over silica gel	Oxidation of alcohols and oximes to carbonyl compounds	30
4	DMCC/alumina (Trimethylammonium Chlorochromate)	Cleavage of C=N bond of oximes and *p*-nitrophenyl hydrazones	31
5	2, 6- DCPCC (2, 6-Dicarboxypyridinium Chlorochromate	Oxidative deprotection of oximes to carbonyl compounds	32
6	QDC (Quinolinium Dichromate)	Regeneration of carbonyl compounds from oximes, phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones	33
7	MCC/SiO_2 (Methyl ammonium Chlorochromate)	Regeneration of carbonyl compounds from their nitrogen containing derivatives	34
8	BAABCD(1-Benzyl-4-1-azoniabicyclo[2.2.2] Octane Dichromate)	Conversion of oximes and semicarbazones to corresponding carbonyl compounds	35
9	Dowex-50	Regeneration of carbonyl compounds from oximes and semicarbazones	36
10	Imidazolium Dichromate Adsorbed on Alumina	Convenient and Inexpensive Reagent for the Cleavage of C=N Functionalities	37

with CO_2 and water. This N_2O may be promoting the cleavage of oxime to corresponding carbonyl compounds. Electron-withdrawing groups such as nitro or carboxyl substituents result in the recovery of unchanged oximes and very low yields of corresponding aldehydes (5 and 10% respectively) under the same reaction conditions. Oximes of aliphatic aldehydes, cinnamaldehyde or phenylacetaldehyde, as well as semicarbazones or hydrazones of aliphatic and aromatic carbonyl compounds do not undergo the deprotection reaction.

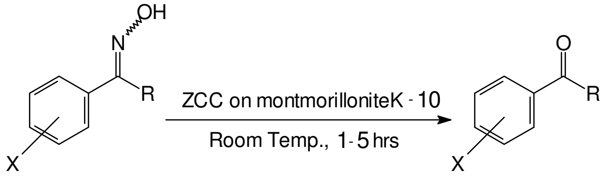


Scheme II

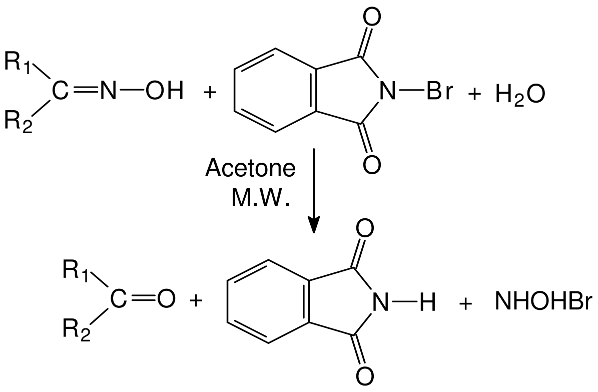
Deprotection of nitrogenous derivatives of carbonyl compounds such as oximes, hydrazones, and semicarbazones was performed under heterogeneous conditions by oxidation, reduction, or hydrolysis in the presence of another carbonyl compound. In fact, usually the reactions are performed by mixing the nitrogenous derivative with the oxidizing or reducing reagent (frequently utilized in a large excess) in the presence of a heterogeneous material to simplify the workup by absorbing tar materials. Sartori *et al.*[44] have summarized these methods on the basis of the nature of the support/catalyst. Various ammonium and metal nitrates mixed with clays were reported to regenerate carbonyl compounds from oximes and semicarbazones[45-50]. In some cases the reaction occurs simply by grinding all the reagents in a mortar. Meshram *et al.*[51] have obtained the deprotected carbonyl compounds by grinding the corresponding oximes in the presence of zinc chlorochromate (ZCC) on montmorilloniteK-10 in a mortar (**Scheme III**). The same reactions can be performed in shorter time by microwave irradiation[52-55].

Khazaei and Manesh[56] have developed a selective method for the cleavage of oximes. The deprotection has been achieved by a simple reaction of a ketoxime or an aldoxime with N-bromophthalimide (NBPI) in acetone under microwave irradiations with a yield of 88-96% (**Scheme IV**). The reaction also precedes chemoselectively. In the presence of benzyl alcohol, benzaldoxime is oxidized to the corresponding benzaldehyde (**Scheme V**) and oxime of benzophenone is oxidized to the ketone in the presence of styrene (**Scheme VI**).

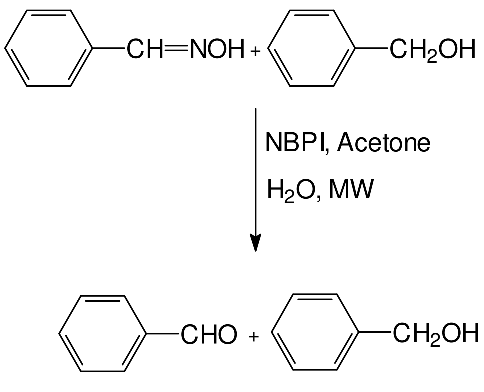
Narsaiah and Nagaiah[57] have used lanthanum chloride and sodium dihydrogen phosphate doped in



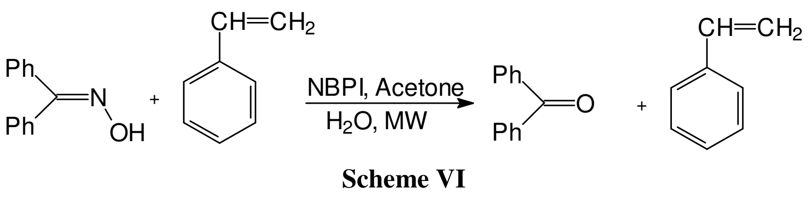
Scheme III



Scheme IV



Scheme V

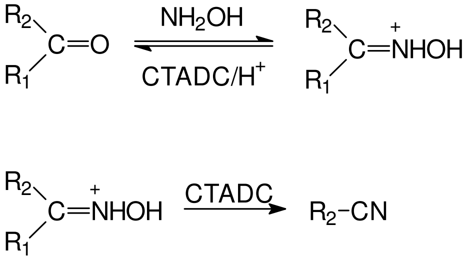


Scheme VI

neutral alumina with various oximes for deoximation under microwave irradiation. The microwave method was found to be highly efficient with respect to consumption of time when compared to reaction in homogeneous medium.

Deoximation using chromates and dichromates

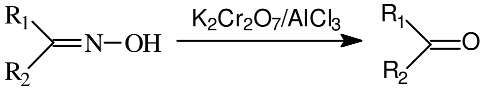
The metallic oxidants like Mn(VII) and Cr(VI) becomes mild with quaternary ammonium ion as the carrier[58-64]. These oxidants have been used for the oxidation of various organic substrates including oximes in organic solvents. Chromium (VI) is an established oxidant that can be inducted in the deoximation processes through various compound forms. Among the phase transferring reagents, cetyltrimethylammonium dichromate (CTADC) is found to be a new, selective, and mild phase transferring oxidant. When treated with CTADC in the presence of trace of acetic acid in dichloromethane medium, oximes give corresponding carbonyl compounds with good yield (**Table II**), whereas without acid, nitriles are obtained as the only product for arylaldoxime substrates[64] (**Scheme VII**).



R_2 = aryl group, R_1 = H, Me

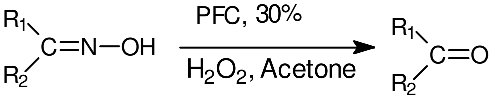
Scheme VII

A reagent pyridinium fluorochromate (PFC)[65], obtained as orange crystals by a 1:1:1 in stoichiometric reaction among CrO_3, aqueous HF and pyridine in 99.2% yield, readily converts cyclohexanoneoxime to cyclohexanone under solvent-free conditions. Potassium dichromate in the presence of Lewis acids under solid phase conditions has immense synthetic utility[66]. This reagent efficiently oxidizes oximes to their corresponding carbonyl compounds with a yield of 85-95% (**Scheme VIII**). Potassium dichromate in the presence of aluminium chloride is used for this purpose.



Scheme VIII

Pyridinium fluorochromate (PFC) in combination with 30% hydrogen peroxide is an excellent reagent for oxidative deoximation[67] (**Scheme IX**). The deoximation method has been found to be effective for a wide range of aliphatic and aromatic oximes, and may be used for selective cleavage of aldoximes in the presence of ketoximes. Conjugated or unconjugated carbon-carbon double bonds, ester, and methylenedioxy functions were not affected under these conditions.



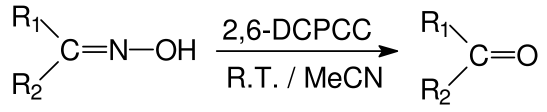
Scheme IX

2, 6-Dicarboxypyridinium chlorochromate (2, 6-

Table II — Oxidation of oximes to the corresponding aldehydes and ketones by CTADC and acid[64].

Sl.No	Oxime	Product	Reflux time (h)	M.P.(s)/B.P. (l) in °C	% Yield
1	*o*-$OMeC_6H_4CH=NOH$	*o*-$OMeC_6H_4CHO$	6.0	238(l)	84
2	*p*-$OMeC_6H_4CH=NOH$	*p*-$OMeC_6H_4CHO$	5.0	249 (l)	90
3	*o*-$NO_2C_6H_4CH=NOH$	*o*-$NO_2C_6H_4CHO$	3.0	45 (s)	80
4	*p*-$NO_2C_6H_4CH=NOH$	*p*-$NO_2C_6H_4CHO$	2.5	105(s)	95
5	*m*-$NO_2C_6H_4CH=NOH$	*m*-$NO_2C_6H_4CHO$	4.5	57(s)	90
6	*o*-$ClC_6H_4CH=NOH$	*o*-ClC_6H_4CHO	2.5	215(l)	82
7	*p*-$ClC_6H_4CH=NOH$	*p*-ClC_6H_4CHO	1.5	46(s)	94
8	*o*-$OHC_6H_4CH=NOH$	*o*-OHC_6H_4CHO	1.0	198(l)	82
9	*p*-$OHC_6H_4CH=NOH$	*p*-OHC_6H_4CHO	1.5	114(s)	90
10	$C_6H_{10}NOH$	$C_6H_{10}O$	4.0	47(s)	88
11	$C_6H_5C(CH_3)=NOH$	$C_6H_5C(CH_3)=O$	2.0	203(l)	85
12	$C_6H_5C(=NOH)CH(OH)C_6H_5$	$C_6H_5C(=O)C(=O)C_6H_5$	0.5	93 (s)	91

DCPCC)[32] has been used as a rapid, efficient and selective reagent for the oxidative deprotection of oximes to their corresponding carbonyl compounds in acetonitrile at ambient temperature (**Scheme X**).



R_1=R_2= alkyl, aryl or H

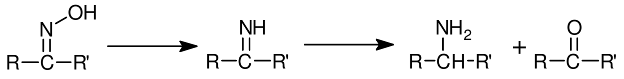
Scheme X

Poly[N-(4-pyridiniumdichromate)-p-styrenesulphonamide] (PPDSS)[68] was found to be an efficient oxidant for the conversion of C=N of oximes to their corresponding carbonyl compounds with a yield of 89-95% (**Scheme XI**). Important advantage of this reagent is that the polymeric reagent can be stored for months without loss in its activity.

Pyrazine-based polymeric complex of oxodiperoxochromium (VI) compound was prepared and was characterized as stable, mild, efficient and versatile oxidant by Tamami *et al.*[69]. It was used as a stoichiometric oxidizing agent for the deprotection of oximes. It was also used for the oxidation of alcohols, thiols, sulfides, phosphines, amines and polycyclic compounds and also for the oxidative deprotection of silylethers.

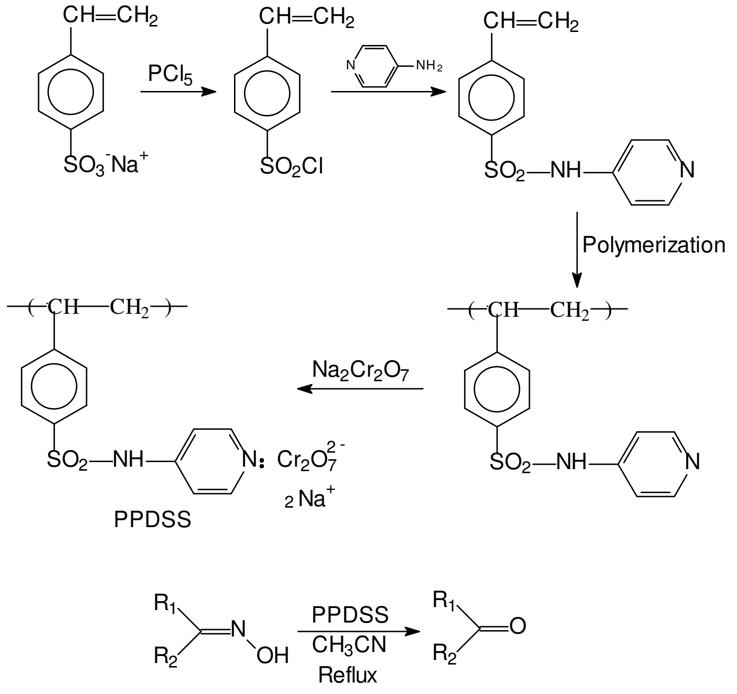
Deoximation using metal salts and metal catalysts

There has been growing interest in the use of metals in neat as well as in salt or complex forms in synthetic organic chemistry. Reduction of oximes by standard metal catalysts to amines and carbonyl compounds as side products is an important method in many organic synthetic processes. According to the proposition suggested by Rylander *et al.*[70], the metal catalyzed deoximation proceeds through initial N-O bond cleavage giving rise to the formation of an imine, which on hydrogenation yields amine. Some imines are hydrolyzed to yield carbonyl group (**Scheme XII**).



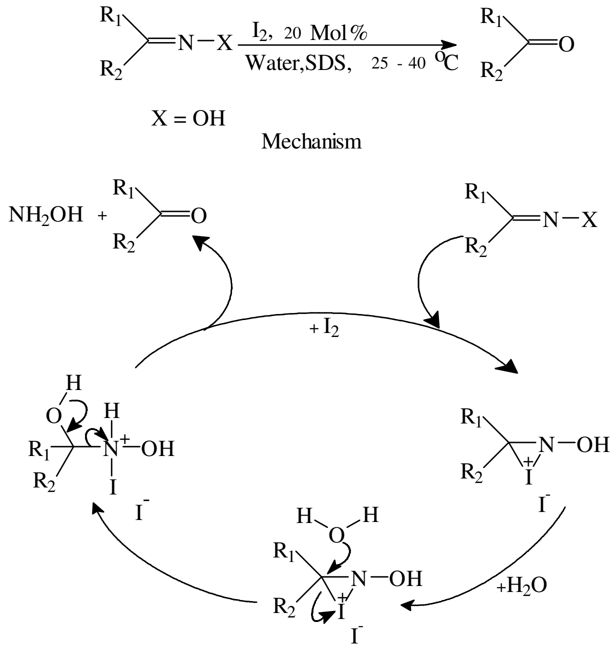
Scheme XII

Successful attempts have been made by Curran *et al.*[27] to make the carbonyl compound as the major product from oxime by using the reagents, Raney Ni, boric acid, in aqueous methanol and hydrogen gas. Acetophenoneoxime, when treated with these reagents, generates acetophenone as the major product. The side products, such as amine and alcohol, were further eliminated by using acetone in



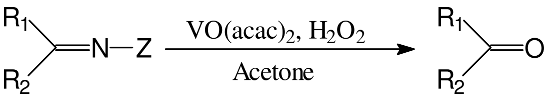
Scheme XI

the medium, which is generally used to reduce the over-reduction of Raney Nickel[71]. Gogoi *et al.*[72] have used an environment-friendly method by applying "I_2/surfactant/water" system for the deprotection of oximes and imines to the corresponding carbonyl compounds under neutral conditions in water at 25-40°C with an yield of 60 - 90%. Albeit the reaction of oximes/imines with a catalytic amount of I_2 in water did not proceed at all, the addition of surfactant (sodium dodecyl sulfate, SDS) to the reaction mixture led to the formation of carbonyl compounds. Iodine is poorly soluble in water but the addition of SDS to the reaction mixture helps in solubilizing iodine. The surfactant promotes micelle formation from iodine and the oxime/imine in water, in which the electrophilic iodine activates hydration of the C-N double bond, possibly via an iodonium ion, that suffers attack by water to form carbonyl compounds and iodine in the reaction mixture (**Scheme XIII**).



Scheme XIII

De[73] has developed a method, where oximes undergo facile deprotection in the presence of a catalytic amount of vanadyl acetylacetonate and hydrogen peroxide in acetone at room temperature (**Scheme XIV**). He observed a higher order of yield of carbonyl compounds from ketone derivatives than aldehyde derivatives and attributed it to over-oxidation of regenerated aldehydes to the corresponding acids (although only 5-10%). This method was also applied for the deprotection of hydrazones and semicarbazones.

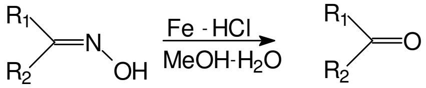


Z = -OH, -NH.Ph, -NH.CO.NH_2

Scheme XIV

The advantages of this method include (a) operational simplicity, (b) inexpensive reagents, (c) no need for any additive to promote the reaction, (d) the use of relatively nontoxic reagents and solvents, and (e) compatibility of other protecting groups.

Fe-HCl mixture[74] was found to deprotect the oximes to carbonyl compounds with an yield of 80-94% (**Table III**). As reduction of nitro groups to the amines takes place through the intermediacy of the nitroso derivatives of the oximes, in the cases of nitroalkenes and nitroalkanes containing a methyl group α to the NO_2 functionality, oximes are generated that subsequently undergo oxidative hydrolysis to their respective ketones. This is a simple, efficient and facile method for deprotection of oximes (**Scheme XV**).



Scheme XV

Deprotection of oximes, phenylhydrazones, *p*-nitrophenylhydrazones, semicarbazones and tosylhydrazones to their parent aldehydes and ketones was efficiently achieved by using sodium nitrite[75] in the presence of Amberlyst-15. The reactions were performed in dioxane at 70°C resulting in high yields. Addition of a few drops of water was found to enhance the reaction rate considerably.

Photosensitization induced deoximation

The photochemistry of oximes and its use as a method for the regeneration of carbonyl compounds has been explored[76-80] in addition to the numerous classical methods. Both aromatic aldoximes and ketoximes were found to undergo photohydrolysis via their lowest excited singlet state; however, the quantum yields for these processes were generally low (ϕ=0.01-0.15), and certuain substituents (e.g., nitro) prevented the photohydrolysis reactions taking

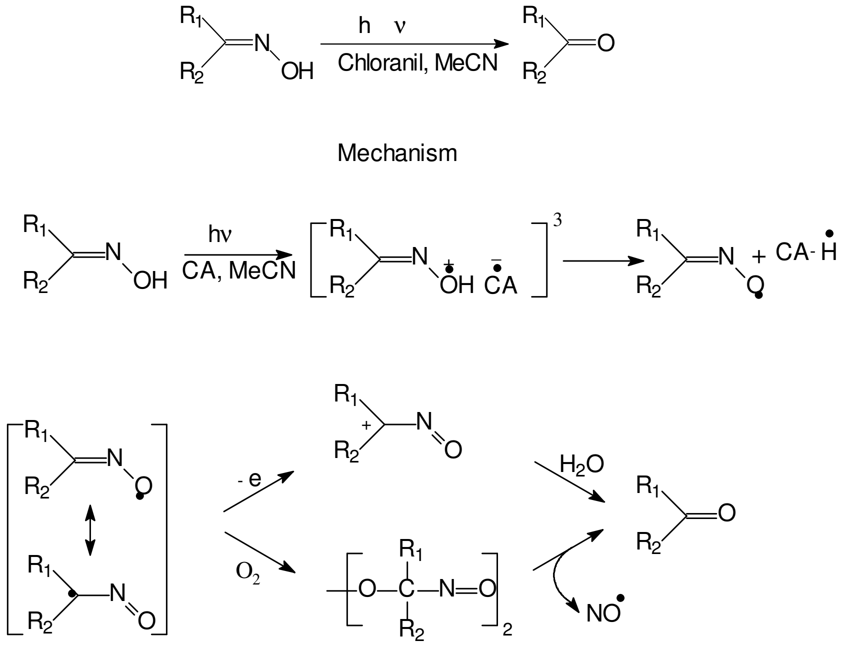
Table III — Conversion of oximes to the corresponding carbonyl compounds[74]

Oximes	Carbonyl compounds	Yield %
Benzaldehyde oxime	Benzaldehyde	94
Benzo(1, 3)dioxole-5-carbaldehyde oxime	Benzo(1, 3)dioxole-5-carbaldehyde	85
Chroman-4-one-oxime	Chroman-4-one	80
6-(2-Hydroxyamino-propyl)-4H-benzo(1, 4)oxazine-3-one	6-(2-Oxo-propyl)-4H-benzo(1, 4)oxazine-3-one	82
Furan-2-carbaldehyde oxime	Furan-2-aldehyde	81
4-Nitro-benzaldehyde oxime	4-Amino-benzaldehyde	90
1-(4-Hydroxy-3-methoxyphenyl)-propan-2-one oxime	1-(4-Hydroxy-3-methoxyphenyl)-propan-2-one	82
1-Phenyl-ethanone oxime	1-Phenyl-ethanone	84
Diphenyl-methanone oxime	Diphenyl-methanone	81
4-Methoxy benzaldehyde oxime	4-Methoxy benzaldehyde	90

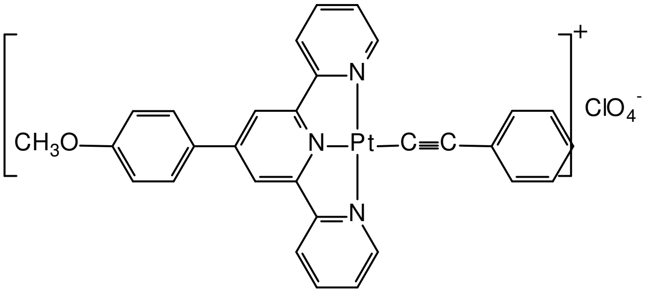
place[80]. The photolysis reactions generally involve an oxaziridine intermediate.

Because of the low quantum yields and the poor reactivity, photosensitized electron transfer (PET) has been focused as a method for the deprotection of oximes by Lijser *et al.*[81]. They reported the deprotection of oximes to their corresponding carbonyl compounds through the use of PET, which proceeds in reasonable yield of 71-99%. Better yields are obtained in nonpolar solvents and when triplet sensitizers like chloranil (CA) are used. Preliminary mechanistic studies suggest the involvement of an iminoxyl radical (**Scheme XVI**).

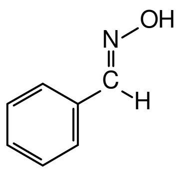
Yang *et al.*[82] have suggested a method, where platinum(II) terpyridyl acetylide complex **1** photosensitizes the oxidation of aldoximes **2**-**4**, aliphatic acyclic and cyclic ketoximes **5**-**7**, and aromatic ketoximes **8-10** into their corresponding carbonyl compounds with yields of 10-94% in acetonitrile solution. This deprotection of oximes proceeds via a mechanism involving singlet oxygen ($^1O_2$) (**Scheme XVII**). The photosensitizer can be easily separated from the product and unreacted starting material by extraction with ethyl acetate and reused for photo-oxidation without loss of $^1O_2$ -generation capacity.



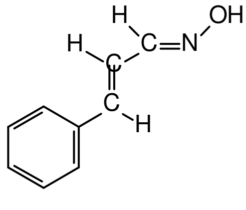
Scheme XVI



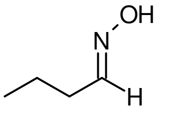
1



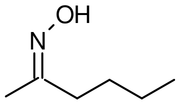
2



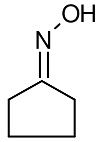
3



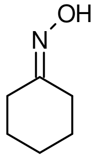
4



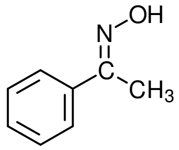
5



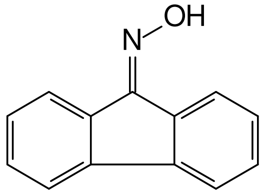
6



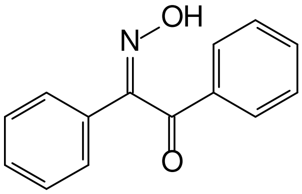
7



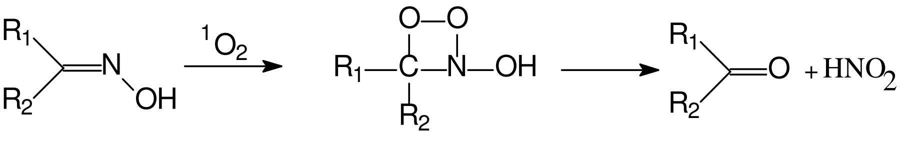
8



9

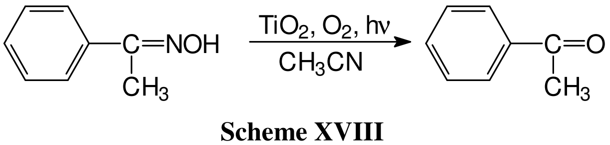


10



Scheme XVII

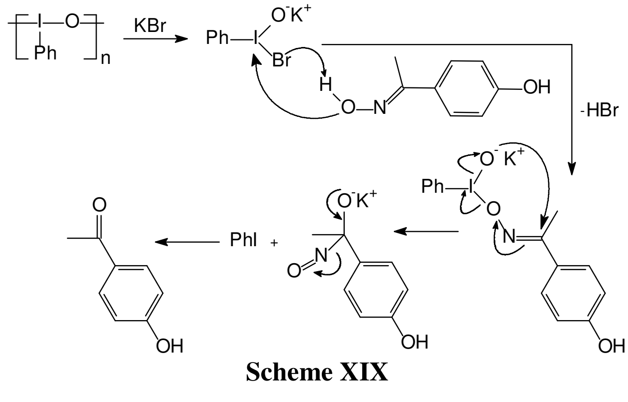
Saravanselvi *et al.*[83] have proposed that irradiation of solutions of oximes in acetonitrile in the presence of oxygen and suspended photocatalyst, TiO_2, effectively regenerates the ketone (**Scheme XVIII**).



Scheme XVIII

Deoximation with organic reagents

Various organic reagents have been used for the deoximation to carbonyl functionality. Narender *et al.*[84] have suggested a mild and efficient method for the regeneration of carbonyl compounds from oximes at room temperature with an yield of 84-90% using iodosobenzene(IOB)/KBr in the presence of β-cyclodextrin in water (**Scheme XIX**). As cyclodextrins are cyclic oligosaccharides, which exert a micro-environmental effect, a bio mimetic approach



Scheme XIX

has been reported involving β-cyclodextrins through supramolecular catalysis. Again, phenolic OH groups are known to undergo oxidation with IOB, but they could survive in the present reaction conditions under supramolecular catalysis without any oxidation. This indicates the complexation of IOB from the primary side of the β-cyclodextrin (**Figure 2**).

Vaghei *et al.*[85] have synthesized a novel and efficient reagent N-bromobis(p-toluenesulfonyl)amine (NBBTA) for the conversion of oximes to their corresponding carbonyl compounds with a yield of 89-95% under mild conditions and proposed a mechanism involving a bromonitronium ion for the deoximation (**Scheme XX**). The advantages of the reagent NBBTA are, (a) its easy preparation, (b) its stability for long period of time in atmospheric condition, and (c) sulphonamide can be recovered after reaction of NBBTA and can be reused several times without lowering the yield.

An efficient and convenient method of conversion of aldoximes and ketoximes to the corresponding carbonyl compounds with tetrameric DABCO-

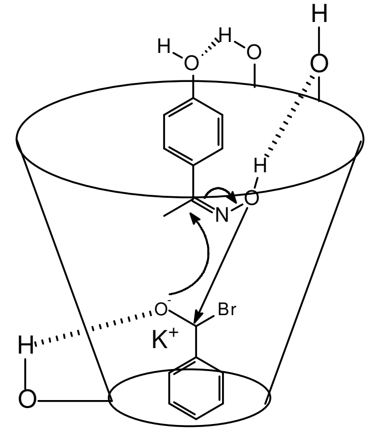
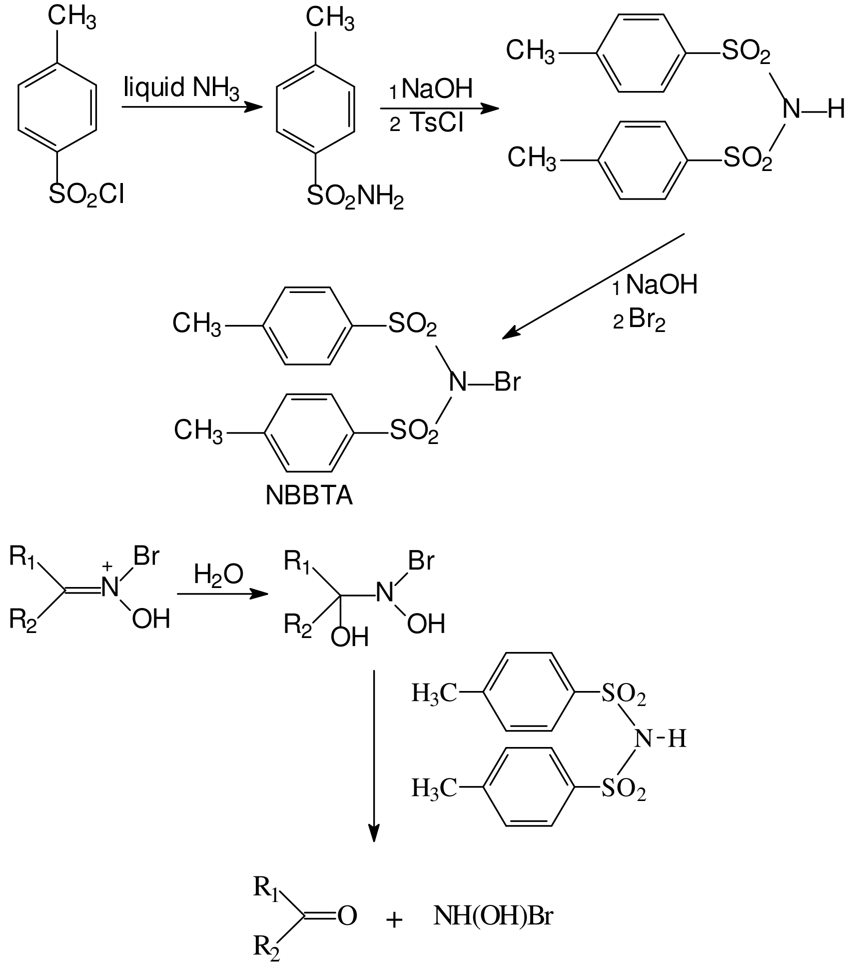
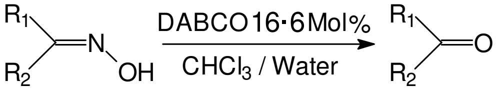


Figure 2 — Supramolecular catalysis of deprotection of oximes using IOB/KBr.



Scheme XX

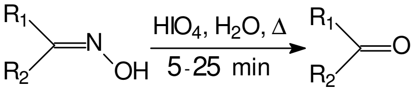
bromine complex[86] (**Scheme XXI**). TDB (tetrameric DABCO-bromine) is very stable at room temperature, is not affected by ordinary exposure to light, air, or water, and has no offensive odor of bromine or amine. Ease of workup and the stability of the reagent make it a safe and convenient source of active bromine.



Scheme XXI

Deoximation through acidic catalysts

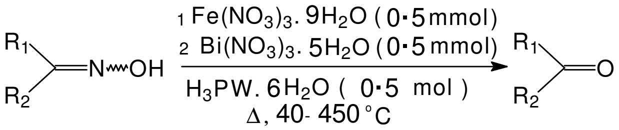
Acid catalyzed deoximation has gained much importance in synthetic organic processes. Li *et al.*[87] have developed a method, where ketone and aldehyde oximes can be readily converted to the corresponding carbonyl compounds with a yield of 89-98% under solvent-free conditions when treated with periodic acid (**Scheme XXII**). In this method, deoximation takes place very efficiently without rearrangement or cleavage of the aliphatic C=C bonds and the reaction is essentially chemoselective. The advantages of this process include a rapid reaction rate and a simple workup procedure. No volatile organic solvents are required in the reaction process. In addition, oximes, including heterocycles, did not have a great difference in rate and yield compared with other aromatic oximes, and no by-product formation was observed.



Scheme XXII

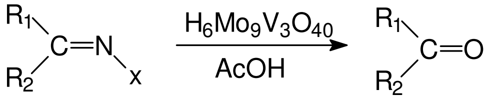
Tungstophosphoric acid ($H_3PW_{12}O_{40}$. $6H_2O$) has been used as a catalyst[88] for a simple, rapid, selective, and solvent-free cleavage of oximes to carbonyl compounds using iron (III) and bismuth (III) nitrates as oxidants with a yield of 45-95% (**Scheme XXIII**). However, this method is not suitable for the oxidation of benzoinoxime because of the extensive cleavage of carbon-carbon bonds. α, β-Unsaturated ketoxime is unreactive towards the oxidation process and the starting material is recovered unchanged after 60 minutes. The reagents are nontoxic, inexpensive, and are easily available.

An efficient and improved procedure for oxidative cleavage of C=N bond has been developed[89] using a green and reusable catalyst, $H_6PMo_9V_3O_{40}$ in refluxing acetic acid (**Scheme XXIV**).



R_1= Alkyl, Aryl; R_2= Alkyl, Aryl, H

Scheme XXIII



X= -NH- Ph, -NH.CS.NH_2, -OH

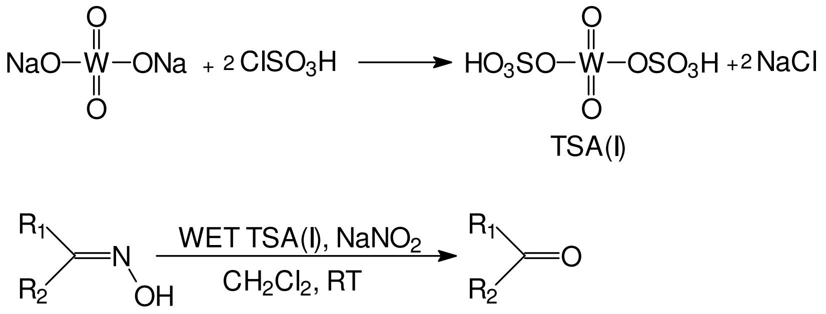
Scheme XXIV

In the presence of wet (10%w/w) tungstate sulphuric acid (TSA(I)) obtained from the reaction of anhydrous sodium tungstate with chlorosulfonic acid (1:2 mole) and $NaNO_2$ in dichloromethane, effective deprotection of oximes can take place[90] to produce the respective carbonyl compounds with a yield of 90-97% (**Scheme XXV**).

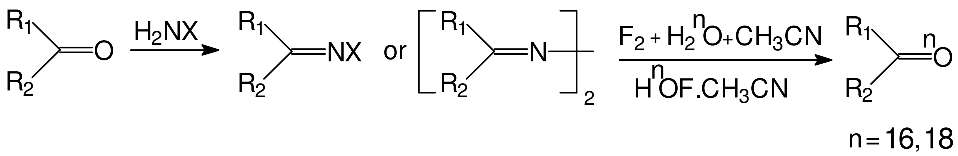
Carmeli and Rozen[91] have suggested that C=N derivatives of carbonyl compounds can be deprotected by HOF·CH_3CN instantaneously to the corresponding ketone or aldehyde in very good yields. This reaction also offers a very efficient route for replacing the oxygen atom of most carbonyls with any other oxygen isotope, for example, ^{18}O (**Scheme XXVI).**

Surface induced deoximation

Surface reactions are an important class with high efficiency in product formation. A variety of organic synthetic reactions have been carried out on suitable surfaces like silica, alumina, charcoal etc. with high yield and remarkable performances. Samajdar *et al.*[92] have used bismuth nitrate in wet silica gel for the regeneration of ketones from oximes with an yield of 85-97%. Shirini *et al.*[93] proposed a method where oximes, hydrazones and semicarbazones can be converted to their corresponding carbonyl compounds with a yield of 85-90% by a combination of silica chloride and wet SiO_2. Advantage of this method is the conversion of silica chloride to the silica gel during the reaction, which can be used for the regeneration of silica chloride for several times. De[94] suggested the use of mercuric nitrate in wet silica gel as an excellent reagent for the regeneration of carbonyl compounds from oximes with an yield of 83-94% (**Scheme XXVII**).

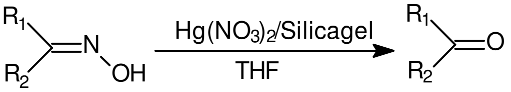


Scheme XXV



R_1 = alkyl, aryl; R_2 = alkyl, H; X = -NH_2, -NHPh, -$NHCONH_2$, -OMe

Scheme XXVI



$R_1 = R_2 = C_6H_5$; Me; *p*-$MeOC_6H_4$; *p*-BrC_6H_4; -$(CH_2)_5$-; -$(CH_2)_4$-; *p*-ClC_6H_4

Scheme XXVII

Y[95] and ZSM-5[96] zeolites, combined with potassium permanganate or iron nitrate respectively, have been efficiently utilized in the deoximation reactions of ketones. Lower yields were observed with aldehydes, probably due to the over-oxidation processes. Silica gel has been more extensively employed than clays and zeolites as heterogeneous support in performing oxidative deprotection of nitrogenous derivatives. A wide number of oxidizing reagents, namely nitrates[92, 97], chromates[34, 98-100], persulfates[101-102], iodates[103], chlorides/O_2[104] and perchlorates[105] were reported to be effective in performing the cleavage. In many cases, by using microwave irradiation, the deprotection reactions occurred faster and cleaner[21, 106-114]; in fact, it has been reported that silica gel, in contrast to other cheap solid materials, is a good microwave conductor[106]. Chlorochromates[31, 115-118], fluorochromates[119] and permanganates[120] in combination with alumina have been utilized for the regeneration of carbonyl compounds from semicarbazones, hydrazones and oximes. The reactions showed general applicability for both aldehyde and ketone derivatives, including camphor and benzophenone.

Conclusion

Oxime has been an intermediate during various chemical reactions on substrate with carbonyl group as the nonreacting functional group. The ease of oximation, relative inertness of oximes to various reagents and easy availability of reagents for deoximation have stemmed the use of oximes to protect carbonyl groups. The reagents cover a wide extent of activities i.e. from hydrolysis to redox reactions, in homogeneous as well as heterogeneous systems. Sometimes, photochemical energy is found to be sufficient for the deprotection process. Thus with the availability of a plethora of reagents, the deoximation process can be tuned according to the requirement of the substrate.

Acknowledgement

The authors thank UGC and DST, New Delhi for financial assistance through DRS and FIST programs respectively. SP thanks CSIR, New Delhi for Extended Senior Research Fellowship.

References

1 (a) Karabatsos G J & Taller R A, *Tetrahedron*, 24, **1968,** 3347; (b) Lichter R L, Dorman D E & Wasylishen R, *J Am Chem Soc*, 96, **1974**, 930.

2 Hawkes G E, Herwig K & Roberts J D, *J Org Chem*, 39, **1974,** 1017.

3 Christer B A, Alicia M B & Destin S L, *Crys Grow Design*, 1, **2001**, 47.

4 Katakawa K, Kitajima M, Aimi N, Seki H, Yamaguchi K, Furihata K, Harayama T & Takayama H, *J Org Chem*, 70, **2005,** 658.

5 (a) Ayer W A & Trifonov L S, *Lycopodium alkaloids*, *The Alkaloids*, edited by G A Cordell & A Brossi (Academic Press: San Diego, CA) Vol 45, Chapter 3, **1994**; (b)Ayer W A, *Nat Prod Rep*, 8, **1991,** 455.

6 Kiasat A R, Kazemi F & Nourbakhsh K, *Phosphorus Sulfur Silicon*, 179, **2004** 1809.

7 Polyakov V A, Nelen M I, Nazarpack K N, Ryabov A D & Eliseev A V, *J Phys Org Chem*, 12, **1999**, 357.

8 Swann P G, Casanova R A, Desai A, Frauenhoff M M, Urbanci M, Slomczynska U, Hopfinger A J, Le Breton G C & Venton D L, *Biopolymers*, 40, **1996**, 617.

9 (a) Eliseev A V & Nelen M I, *J Am Chem Soc,* 119, **1997**, 1147; (b) Eliseev A V & Nelen M I, *Chem Eur J*, 4, **1998**, 825.

10 (a) Corsaro A, Chiachio U & Pistara V, *Synthesis*, **2001**, 1153; (b) Hajipour A R, Khoee S & Ruoho A E, *Org Prep Proced Int*, 35, **2003**, 527.

11 Huc I & Lehn J M, *Proc Natl Acad Sci* USA, 94, **1997,** 2106.

12 (a) Rowan S J & Sanders J K M, *Chem Comm*, **1997,** 1407; (b)Brady P A & Sanders J K M, *J Chem Soc Perkin Trans 1*, **1997**, 3237; (c)Brady P A & Sanders J K M, *Chem Soc Rev*, 26, **1997**, 327.

13 Tennant G, *Comprehensive Organic Chemistry*, edited by I O Sutherland, D Barton & W D Ollis, (2 Pergamon Press, New York), **1979**, pp.392.

14 Friedman L & Kosower E, *Org Synth Coll*, 3, **1955**, 510.

15 Demir A S, Tanyeli C & Altinel E, *Tetrahedron Lett*, 38, **1997**, 7267.

16 Shim S B, Kim K & Kim Y H, *Tetrahedron Lett*, 28, **1987**, 645.

17 Aizpurua J M, Juaristi M, Lecea B & Palomo C, *Tetrahedron*, 41, **1985**, 2903.

18 Joseph R, Sudalai A & Ravindranathan T, *Tetrahedron Lett*, 35, **1994**, 5493.

19 Maloney J R, Lyle R E, Savendra J E & Lyle G G, *Synthesis*, **1978**, 212.

20 Baruah A, Baruah B, Prajapati D & Sandhu J S, *Tetrahedron Lett*, 38, **1997**, 4267.

21 Varma R S, Dahiya R & Saini R K, *Tetrahedron Lett*, 38, **1997**, 8819.

22 Curini M, Rosati D & Pisani E, *Synlett*, **1996**, 333.

23 Rao G C, Radhakrishna A S, Singh B B & Bhatnagar S P, *Synthesis*, **1983**, 808.

24 Bose D S & Narasaiah A V, *Synth Commun*, 29, **1999**, 937.

25 Bose D S & Narasaiah A V, *Synth Commun*, 30, **2000**, 1153.

26 Bose D S, Reddy A V N & Das A P R, *Synthesis*, 12, **2003**, 1883.

27 Curran D P, Brill J F & Rakiewicz D M, *J Org Chem*, 49, **1984**, 1654.

28 Bhandari A, Sharma P K & Banerji K K, *Indian J Chem,* 40A, **2001**, 470.

29 Rajkumar G A, Sivamurugan V, Arabindoo B & Murugesan V, *Synth Commun*, 30, **2000**, 1153.

30 Rajkumar G A, Sivamurugan V, Arabindoo B & Murugesan V, *Indian J Chem*, 39B, **2000**, 936.

31 Gui-Sheng Z, De-Hong Y & Mi F C, *Synth Commun,* 28, **1998**, 3721.

32 Hosseinzadeh R, Tajbakhsh M & Niaki M Y R, *Tetrahedron Lett*, 43, **2002**, 9413.

33 Sadeghi M M, Mohammadpour-Baltork I, Azarm M & Mazidi M R, *Synth Commun*, 31, **2001**, 435.

34 Gui-Sheng Z & Bing C, *Synth Commun*, 30, **2000**, 2507.

35 Hajipour A R, Mallakpour S E, Mohammadpour-Baltork I & Khoee S, *Synth Commun*, 31, **2001**, 1184.

36 Ranu B C & Sarkar D C, *J Org Chem*, 53, **1988**, 878.

37 De S K, *Let Org Chem,* 2, **2005**, 77.

38 Chakraborty V & Bordoloi M, *J Chem Res (S),* **1999**, 120.

39 Heravi M M, Ajami D, Aghapoor K & Ghassemzadeh M, *Chem Commun*, **1999**, 833.

40 Heravi M M, Ajami D, Mohajerani B, Tabar-Hydar K & Ghassemzadeh M, *Synth Commun*, 32, **2002**, 3325.

41 Bigdeli M A, Alavi Nikje M M & Heravi M M, *Phosphorous Sulfur Silicon,* 177, **2002**, 15.

42 Bose D S & Srinivas P, *Synth Commun,* 27, **1997**, 3835.

43 Perumal P T, Anniyappan M & Muralidharan D, *J Chem Sci,* 116, **2004**, 261.

44 Sartori G, Ballini R, Bigi F, Bosica G, Maggi R & Righi P, *Chem Rev,* 104, **2004**, 199.

45 Sanabria R, Miranda R, Lara V & Delgado F, *Synth Commun,* 24, **1994**, 2805.

46 Sanabria R, Castaneda P, Miranda R, Tobon A & Delgado F, *Org Prep Proc Int,* 27, **1995**, 480.

47 Meshram H M, Reddy G S, Srinivas D & Yadav J S, *Synth Commun,* 28, **1998**, 2593.

48 Meshram H M, Srinivas D, Reddy G S & Yadav J S, *Synth Commun,* 28, **1998**, 4401.

49 Hirano M, Kojima K & Yakabe S, *J Chem Res (S),* **2001**, 277.

50 Nattier B A, Eash K J & Mohan R S, *Synthesis,* **2001**, 1010.

51 Balalaie S, Salimi S H & Sharifi A, *Indian J Chem,* 40B, **2001**, 1251.

52 Heravi M M, Tajbakhsh M, Bakooie H & Ajami D, *Monatsh Chem,* 130, **1999**, 933.

53 Heravi M M, Beheshtiha Y S, Ghasemzadeh M, Hekmatshoar R & Sarmad N, *Monatsh Chem* 131, **2000**, 187.

54 Heravi M M, Ajami D, Mohajerani B, Tajbakhsh M, Ghassemzadeh M & Tabarhydar K, *Monatsh Chem,* 132, **2001**, 881.

55 Heravi M M, Tajbakhsh M, Habibzadeh S & Ghassemzadeh M, *Phosphorus, Sulfur Silicon,* 176, **2001**, 195.

56 Khazaei A & Manesh A A, *J Braz Chem Soc,* 16, **2005,** 874.

57 Narasaiiah A V & Nagiah K, *Indian J Chem*, 43B, **2003**, 2045.

58 Dash S & Mishra B K, *Bull Chem Soc Jpn*, 67, **1994**, 673.

59 Dash S & Mishra B K, *Int J Chem Kinet*, 27, **1995**, 627.

60 Mishra B K, Dash S & Nayak B B, *Indian J Chem*, 40A, **2001**, 159.

61 Mishra B K, Kuanar M, Sharma A & Nayak B B, *Indian J Chem*, 40B, **2001**, 724.

62 Patel S, Kuanar M, Nayak B B, Banichul H & Mishra B K, *Synth Commun*, 35, **2005**, 1033.

63 Patel S & Mishra B K, *Tetrahedron Lett*, 45, **2004**, 1371.

64 Sahu S, Patel S & Mishra BK, *Synth Commun*, 35, **2005**, 3123.

65 Chaudhuri M K, Dehury S K, Dhar S S & Sinha U B, *Synth Commun,* 34, **2004,** 4077.

66 Mohammadpoor-Baltork, I, Sadeghi M M & Adibi A H, *Molecules,* 6, **2001**, 900.

67 Ganguly N C, Sukai A K, De S & De P, *Synth Commun,* 31, **2001**, 1607.

68 Vaghei R G & Khazaei A, *Phosphorus, Sulfur, and Silicon,* 179, **2004**, 55.

69 Tamami B & Yeganeh H, *Tetrahedron*, 53, **1997**, 7889.

70 Rylander P N, (Academic Press, New York), **1979**, pp. 153-62.

71 Barkley L B, Farrar M W, Knowles W S & Raffelson H, *J Am Chem Soc*, 76, **1954**, 5017.

72 Gogoi P, Hazarika P & Konwar D, *J Org Chem*, 70, **2005**, 1934.

73 De S K, *Synth Commun,* 34, **2004**, 4409.

74 Pradhan P, Dey S, Jaisankar P & Giri V S, *Synth Commun,* 35, **2005**, 913.

75 Lakouraj M M, Noorian M & Mokhtary M, *Reactivity And Functional Polymers,* 66, **2006,** 910.

76 Amin J H & de Mayo P, *Tetrahedron Lett,* **1963**, 1585.

77 (a) Just G & Pace-Asciak C, *Tetrahedron*, 22, **1966**, 1069; (b) Taylor R T, Douek M & Just G, *Tetrahedron Lett,* **1966**, 4143; (c) Just G & Ng L S, *Can J Chem,* 46, **1968**, 3381; (d) Cunningham M, Ng Lim L S & Just G, *Can J Chem*, 49, **1971**, 2891; (e) Just G & Cunningham M, *Tetrahedron Lett,* **1972**, 1151.

78 Suginome H, Furukawa K & Orito K, *J Chem Soc*, *Perkin Trans 1*, **1991**, 917.

79 (a) Ogata Y, Takagi K & Mizuno K, *J Org Chem,* 47, **1982**, 3684. (b) Oine T & Mukai T, *Tetrahedron Lett*, **1969**, 157.

80 Haley M F & Yates K, *J Org Chem,* 52, **1987**, 1817.

81 Lijser H J P, Fardoun F H, Sawyer J R & Quant M, *Org Lett,* 4, **2002**, 2325.

82 Yang Y, Zhang D, Wu L, Chen B, Zhang L & Tung C, *J Org Chem,* 69, **2004**, 4788.

83 Saravanselvi C, Somasundaram N, Vijaikumar S & Srinivasan C, *Photochem Photobiol Sci*, 1, **2002**, 607.

84 Narender M, Reddy M S, Krishnaveni N, Surendra K, Nageswar Y V D & Rao K R, *Synth Commun,* 36, **2006**, 1463.

85 Vaghei R G & Khazaei A, *Phosphorus Sulfur Silicon,* 179, **2004**, 1169.

86 Heravi M, Derikvand F & Ghassemzadeh M, *Synth Commun,* 36, **2006**, 581.

87 Li Z, Ding R, Xing Y & Shi S, *Synth Commun,* 35, **2005**, 2515.

88 Firouzabadi H, Iranpoor N & Amani K, *Synth Commun,* 34, **2004**, 3587.

89 Heravi M M, Ranjbar L, Derikvand F, Oskooie H A & Bamoharram F F, *J Molecular Cat: Chemical,* 265, **2007**, 186.

90 Karami B, Montazerozohori M, Karimipour G R & Habibi M H, *Bull Korean Chem Soc*, 26, **2005**, 1431.

91 Carmeli M & Rozen S, *Tetrahedron Lett* 47, **2006**, 763.

92 Samajdar S, Basu M K, Becker F F & Banik B K, *Synth Commun,* 32, **2002**, 1917.

93 Shirini F, Zolfigol M A & Khaleghi M, *Synth Commun,* 33, **2003**, 1839.

94 De S K, *Synth Commun,* 34, **2004**, 2289.

95 Jadhav V K, Wadgaonkar P P, Joshi P L & Salunkhe M M, *Synth Commun,* 29, **1999**, 1989.

96 Heravi M M, Ajami D, Mohajerani B, Tabar-Hydar K & Ghassemzadeh M, *Synth Commun,* 32, **2002**, 3325.

97 Lee J G & Hwang J P, *Chem Lett,* **1995**, 507.

98 Bendale P M & Khadilkar B M, *Synth Commun,* 30, **2000**, 665.

99 Shirini F, Zolfigol M A & Pourhabib A, *Synth Commun,* 32, **2002**, 2837.

100 Ali M H, Greene S, Wiggin C & Khan S, *Synth Commun,* 36, **2006**, 1761

101 Bose D S, Narsaiah A V & Lakshminarayana V, *Synth Commun,* 30, **2000**, 3121.

102 Movassagh B, Lakouraj M M & Ghodrati K, *Synth Commun,* 30, **2000**, 4501.

103 Shirini F, Zolfigol M A & Azadbar M R, *Synth Commun,* 32, **2002**, 315.

104 Hashemi M M & Beni Y A, *Synth Commun,* 31**, 2001**, 295.

105 Parmar A, Goyal R, Kumar B & Kumar H, *Indian J Chem,* 37B, **1998**, 941.

106 Ghiaci M & Asghari J, *Synth Commun,* 30, **2000**, 3865.

107 Varma R S & Meshram H M, *Tetrahedron Lett,* 38, **1997**, 5427.

108 Bendale P M & Khadilkar B M, *Tetrahedron Lett,* 39, **1998**, 5867.

109 Mitra A K, De A & Karchaudhuri N, *Synlett,* **1998**, 1345.

110 Yadav J S, Reddy B V S, Reddy M S K & Sabitha G, *Synlett,* **2001**, 1134.

111 Bose D S, Narsaiah A V & Goud P R, *Indian J Chem,* 40B, **2001**, 719.

112 Zhou J F, Tu S J & Feng J C, *Synth Commun,* 32, **2002**, 959.

113 Nagarapu L, Ravirala N & Akkewar D, *Synth Commun,* 32, **2002**, 2195.

114 Tamami B & Kiasat A R, *Synth Commun,* 30, **2000**, 4129.

115 Gong H & Zhang G S, *Synth Commun*, 29, **1999**, 2591.

116 Zhang G S, Yang D H & Chen M F, *Org Prep Pro Int*, 30, **1998**, 713.

117 Zhang G S, Gong H, Yang D H & Chen M F, *Synth Commun*, 29, **1999**, 1165.

118 Zhang G S, Yang D H, Chen M F & Cai K, *Synth Commun*, 28, **1998**, 2221.

119 Ganguly N C, De P, Sukai A K & De S, *Synth Commun*, 32, **2002**, 1.

120 Chrisman W, Blankinship M J, Taylor B & Harris C E, *Tetrahedron Lett,* 42, **2001**, 4775.