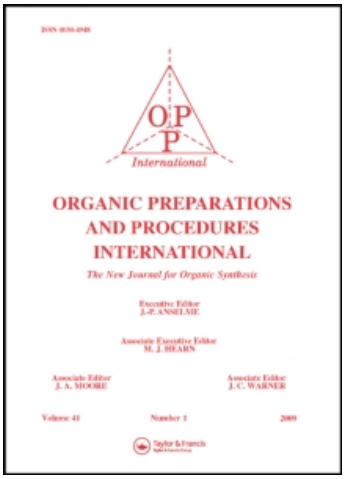

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

RECENT ADVANCES IN THE CHEMISTRY OF OXIMES

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To cite this Article Ãbele, Edgars and Lukevics, Edmunds(2000) 'RECENT ADVANCES IN THE CHEMISTRY OF OXIMES', Organic Preparations and Procedures International, 32: 3, 235 — 264
To link to this Article: DOI: 10.1080/00304940009355921
URL: http://dx.doi.org/10.1080/00304940009355921

ORGANIC PREPARATIONS AND PROCEDURES INT., 32 (3), 235-264 (2000)

RECENT ADVANCES IN THE CHEMISTRY OF OXIMES

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INTRODUCTION

Oximes and their derivatives are important intermediates in organic synthesis.[1] These compounds are also of interest as biologically active compounds. Some of recent reviews are devoted to the biological activity of oxime derivatives.[2,3] Although a number of reviews[4] appeared regarding to oximes, not so much general reviews about recent advances in the chemistry of oximes, oxime ethers and esters have been published.

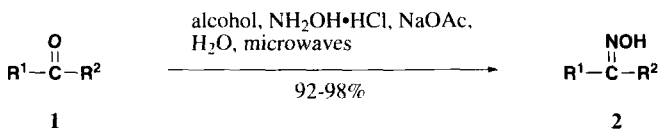
The aim of the present work is to describe modern methodologies of synthesis of oximes, oxime O-ethers and esters. The literature data published between January of 1990 and December of 1999 are included in this review. The advances in the synthesis of heterocyclic compounds from oximes are not included in this review and will be published separately. The reduction[5-8], dehydration (nitrile synthesis)[9], and deoximation[10] reactions of oxime derivatives are well reviewed and therefore are not included in this work.

I. SYNTHESIS OF OXIMES

1. Synthesis of Aldoximes and Ketoximes

Aldoximes and ketoximes usually are obtained by oximation reaction of corresponding carbonyl compounds with hydroxylamine salts in the presence of a base in alcohols.[11] The reaction of carbonyl compounds with hydroxylamine hydrochloride is accelerated by using of phase transfer catalyst such as polyethylene glycol-600 [12] or alkyl phenol (nonylphenol or dodecylphenol).[13]

Formation of oximes **2** is dramatically enhanced by microwave heating.[14-16] For example, ketones **1** are easily oximated by NH_2OH•HCl in the presence of sodium acetate in alcohol/water medium under microwave irradiation (*Eq. 1*).[15]

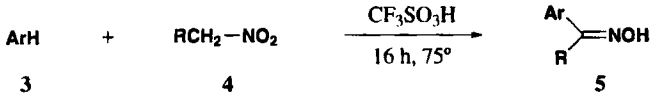


1 **2** (1)

R^1, R^2 = alkyl, aryl

Oxime formation is also accelerated when aldehyde or ketone is reacted with NH_2OH or its salts in the presence of organotin (IV) compounds (R'_nSnX_{4-n})[17] or Amberlyst A-21.[18] Solid phase oximation of carbonyl compounds with hydroxylamine hydrochloride was also described.[19] In this case the products were obtained in nearly quantitative yields.

The second group of methods for the synthesis of oximes is based on reduction of corresponding nitro compounds. Thus, primary nitroalkanes **4** react with aromatics **3** in triflic acid to yield arylated oximes **5** in yields up to 96% (*Eq. 2*).[20]

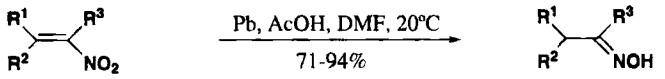


(2)

3 **4** **5**

Ar = Ph, subst. Ph; R = alkyl

The reduction of 1-nitro-1-alkenes **6** with lead/acetic acid in DMF affords corressponding aldoximes **7** in excellent yields (*Eq. 3*). For example, *trans*-PhCH=CHNO$_2$ gives *E*-PhCH$_2$CH=NOH in 94% yield.[21]



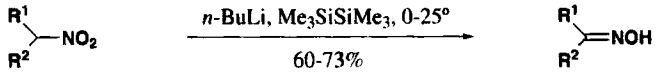
(3)

6 **7**

R^1, R^2, R^3 = H, alkyl, aryl

Nitroalkenes can be easily converted to corresponding oximes also by reduction with zinc borohydride [22] or CS_2/K_2CO_3 under PTC conditions.[23] Electroreduction of α-nitrobenzylic compounds in a mixture of acetic buffer (65%) and EtOH (35%) readily afforded oximes and hydroxylamine.[24,25]

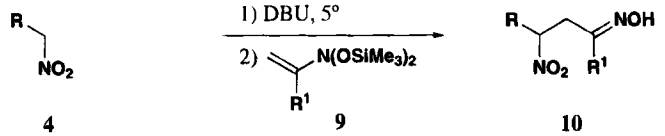
Nitroalkanes **8** and nitrones undergo mono-deoxygenation by hexamethyldisilane and *n*-BuLi through 1,2-elimination to give corresponding oximes **2** in good yields (*Eq. 4*).[26]



(4)

8 **2**

Terminal *N,N-bis*(siloxy)enamines **9** smoothly undergo C,C-cross-coupling reaction with anions of aliphatic nitro compounds affording β-nitro oximes **10** in good yields (*Eq. 5*).[27] Conjugated nitroso alkenes generated from *N,N-bis*(siloxy)enamines by means of nucleophiles are considered to be the key intermediates in the reaction pathway.

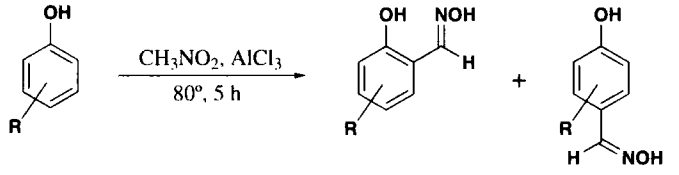


(5)

4 **9** **10**

R, R^1 = H, alkyl

Mild synthesis of phenolic oximes **12** and/or **13** has been performed by heating of suitable phenol **11** with $AlCl_3$ in nitromethane (*Eq. 6*). The *ortho*-oxime **12** (yields up to 80%) is produced as a single *E*-isomer whereas the *para*-oxime **13** (yields up to 85%) is obtained as a mixture of *E* and *Z* isomers.[28]

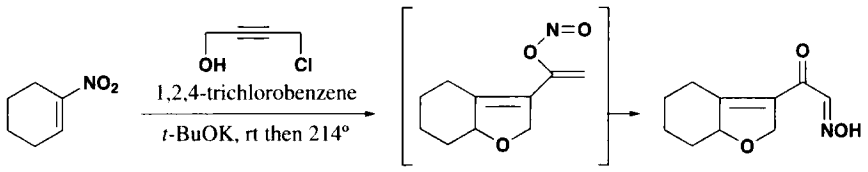


(6)

11 **12** **13**

R = alkyl

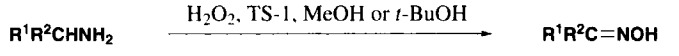
Cyclic nitroalkene **14** in the presence of chlorobutynol and *t*-BuOK afforded dihydrofuran derived keto oxime **16**. The formation of **16** proceeds *via* novel [1,3]-sigmatropic rearrangement of intermediate vinyl nitrite **15** (*Eq. 7*).[29]



(7)

14 **15** **16**

Primary amines **17** with α-hydrogens are oxidized with hydrogen peroxide in the presence of catalytic quantities of titanium silicalite molecular sieves (TS-1) to give corresponding oximes **2** as main products. The latter formed with good substrate selectivity (up to 88%) and peroxide efficiency (*Eq. 8*).[30,31]



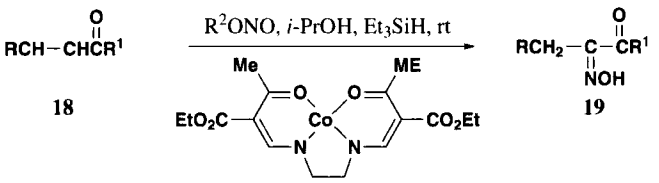
(8)

17 **2**

R^1, R^2 = H, alkyl, aryl

The oxidation of secondary amines with H_2O_2 in the presence of methyltrioxorhenium afforded nitrones in good yield. Benzylamines in the same conditions are selectively oxidized to corresponding oximes, while primary alkylamines possessing α-CH bond gave a mixture of oximes, nitroso dimers and azoxy compounds.[32] Aliphatic and cycloaliphatic oximes are also prepared by reaction of corresponding imines with O_2 in the presence of titanium catalysts[33] or by interaction of alkanones with NH_3/hydroperoxide/$VO(OCHMe_2)_3$.[34]

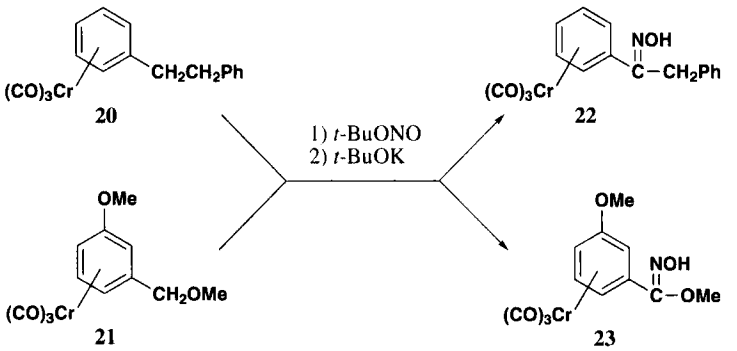
Oximes are successfully prepared by nitrosation of various activated C-H bonds. Thus, α-ketooximes **19** are prepared by reaction of alkenes **18** with nitrites in the presence of Et_3SiH and cobalt complex catalyst (*Eq. 9*).[35]



(9)

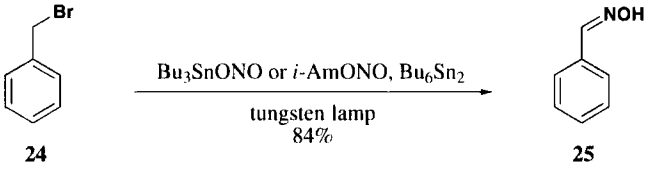
R = H, alkyl; R^1 = OH, alkoxy, siloxy

Chromium tricarbonyl benzene complexes **20** and **21** are nitrosated by *t*-BuONO in the presence of *t*-BuOK at benzylic position to obtain a mixture of E and Z isomers of correspoding oximes **22** and **23** in good yields (*Eq. 10*). Using as substrates m-xylene and isochroman it is possible to obtain dinitrosation products.[36]



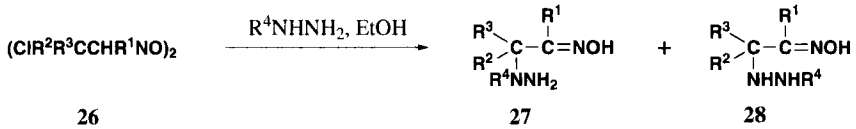
(10)

Exposure of benzyl bromide **24,** isoamyl nitrite and hexabutylditin under a tungsten lamp for 5 h afforded 84% of benzaldoxime **25**. The formation of product occurs *via* radical process (*Eq. 11*).[37,38]



(11)

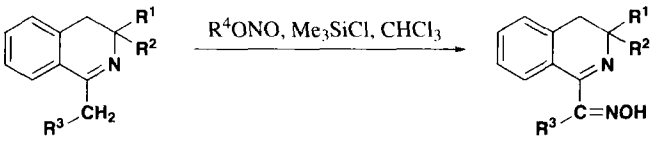
α-Hydrazino oximes **27** are easily obtained by treatment of dimeric nitrosochlorides **26** with monoalkylhydrazines in EtOH. Products **27** were isolated as E-isomers in 65-80% yield along with by-product **28** in ~ 4:1 ratio (*Eq.12*).[39]



(12)

R^1, R^2, R^3, R^4 = H, alkyl

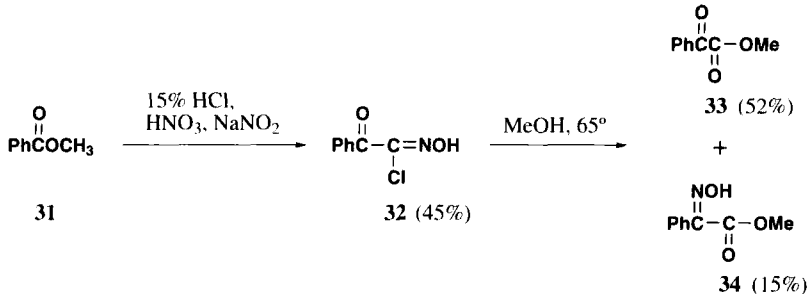
A novel synthesis of imino oximes from Schiff bases *via* nitrosation is described.[40] 1-Alkyl-3,4-dihydroisoquinolines **29** in the presence of reagent Me_3SiCl/alkyl nitrite in chloroform afforded imino oximes **30** in yields up to 98% (*Eq. 13*). The process of synthesis of 3,4-dihydroquinolines **30** probably includes *N*-nitrosation prior to subsequent NO migration to carbon.



29 **30** (13)

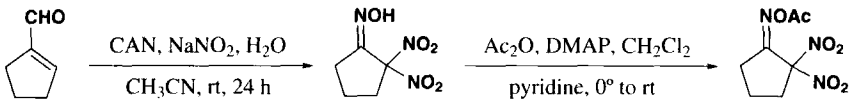
R^1, R^2, R^3, R^4 = H, alkyl, aryl

Interestingly, *N*-hydroxy-α-oxophenylethanimidoyl chloride (**32**), a 2-(hydroxyimino)-1-phenylethan-1-one derivative, is easily obtained in one step from acetophenone (**31**) by treatment with a mixture of $HCl/HNO_3/NaNO_2$. Acid catalyzed methanolysis of **32** leads to a mixture of α-oxophenylacetate (**33**) and methyl α-(hydroxyimino)phenylacetate (**34**) (*Eq. 14*).[41]



31 **32** (45%) **33** (52%) + **34** (15%) (14)

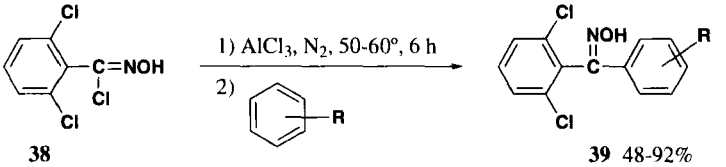
Unusual formation of 2,2-dinitrocyclopentanone oxime (**36**) during an attempted nitroacetamidation of cyclopentenecarboxaldehyde (**35**) using ceric ammonium nitrate (CAN) and sodium nitrite is described. The compound **36** is somewhat unstable, partially decomposing on standing at room temperature over several days. However, it is easily esterified using a mixture of acetic anhydride and 4-dimethylaminopyridine (DMAP) in pyridine/CH_2Cl_2 mixture to give dinitrooxime ester **37** in good yield (*Eq. 15*).[42]



35 **36** (21%) **37** (68%) (15)

Aromatic ketoximes are also obtained by Lewis acid promoted electrophilic aromatic substitution reaction of carbamoyl chlorides.[43,44] Thus, reaction of 2,6-dichlorobenzohydroxi-

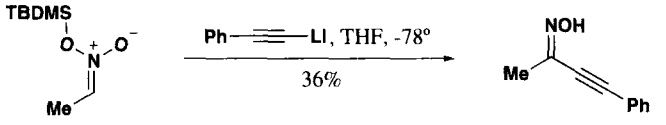
moyl chloride (**38**) with aromatic compounds afforded corresponding diaryl ketoximes (**39**) (*Eq. 16*).



38 **39** 48-92% (16)

R = alkyl, aryl

Treating of silyl nitronate **40** with lithium phenylacetylide affords α-acetylenic ketoxime **41** in modest yield along with variable amounts of 3-methyl-5-phenylisoxazole, which presumably arises from 1,3-dipolar cycloaddition of an intermediate nitrile oxide (*Eq. 17*).[45]



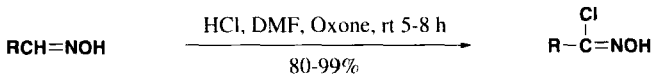
40 **41** (17)

Aldoximes and ketoximes (RR'C=NOH, where R, R'=H, alkyl, aryl) can be also prepared by transoximation of carbonyl compounds RR'CO with acetone oxime (Me_2C=NOH) in the presence of an acid catalyst (expecially aliphatic carboxylic) with distillation of formed acetone from the reaction mixture.[46]

2. Synthesis of Hydroximoyl Chlorides

Hydroximoyl or oximyl chlorides as nitrile oxide precursors are important intermediates in organic synthesis, particularly in [3+2] cycloaddition reactions to form isoxazolines or isoxazoles.[47]

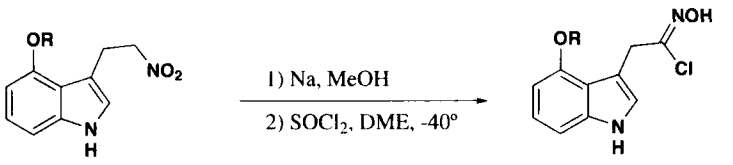
It has been found that anhydrous hydrogen chloride in DMF/Oxone (potassium peroxymonosulfate) system provides a convenient method of the preparation of benzohydroximoyl chlorides **43** from corresponding aldoximes **42**. Products **43** are isolated in excellent yields. The method can be applied to substituted benzaldoximes regardless the electronic nature of substituents (*Eq. 18*).[48]



42 **43** (18)

R = *t*-butyl, aryl, hetaryl

Nitro derivative of indole **44** is sucessfully converted to corresponding oximoyl chloride **45** in quantitative yield by treatment with sodium in methanol followed by interaction with thionyl chloride (*Eq. 19*).[49]

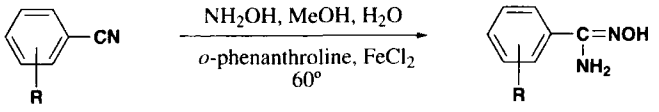


(19)

44 45

3. Synthesis of amidoxime derivatives

Amidoximes are of interest as intermediates in the preparation of pesticides and drugs. Chemistry of amidoximes and related compounds is reviewed by Eloy and Leaners.[50] Some modification of classical method of synthesis of amidoximes from nitriles is described in patent.[51] Thus, benzonitriles **46** in the presence of hydroxylamine solution and chelating agent (*o*-phenanthroline and ferrous chloride) in a mixture of water and methanol at 60° afford corresponding amidoximes **47** in good yields (*Eq. 20*).

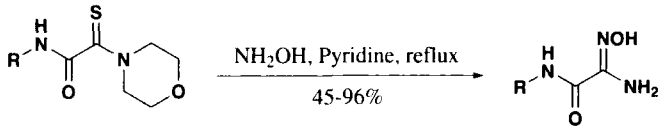


(20)

46 47

R = halo, alkyl, amino, mercapto, alkylthio

A convenient method of carbamoylamidoxime **49** synthesis by the reaction of *N,S*-substituted monothiooxamides **48** with hydroxylamine in pyridine is presented (*Eq. 21*). Surprisingly, the formation of morpholino derivatives of **49** practically was not observed.[52]

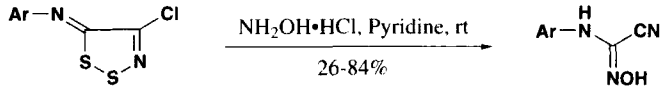


(21)

48 49

R = alkyl, hetaryl

The reaction of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles **50** with hydroxylamine hydrochloride in pyridine at room temperature gave *N*-arylcyanoformamidoximes **51** in yields up to 84% (*Eq.* 22).[53] The obtained oximes **51** are utilized as starting materials for the synthesis of 4-alkyl- (or aryl)-2-cyanoquinazolines and 4-aryl-3-cyano-1,2,4-oxadiazin-5(6*H*)-ones.



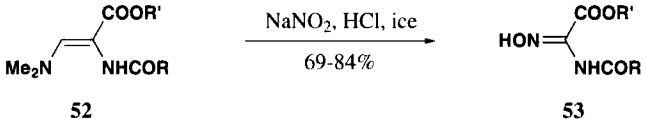
(22)

50 51

Ar = aryl, hetaryl

Treatment of 2-(substituted cinnamoylamino)-3-dimethylaminopropenoates **52** with sodium nitrite in aqueous hydrochloric acid at 0° produced alkyl *N*-cinnamoyloxalic acid

hydroxyimidic amides **53** in good yields (*Eq.* 23).[54] Compounds **53** can be easily tranformed into substituted alkyl 5-styryl-1,2,4-oxadiazole-3-carboxylates by standing in aqueous hydrochloric acid at room temperature.



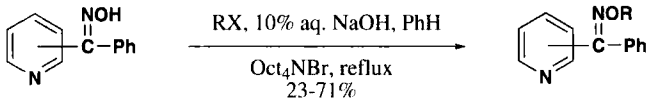
(23)

52 **53**

R = aryl, R' = alkyl

II. SYNTHESIS OF OXIME O-ETHERS AND ESTERS

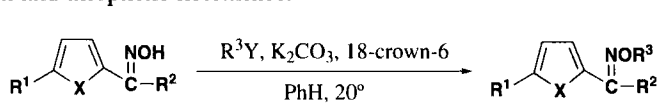
Oxime O-ethers and esters exibit wide spectrum of biological activity. The main group of classical methods of oxime O-ether synthesis are based on the oxime alkylation with alkyl halides or dialkyl sulfates in the presence alkali metal alkoxide[55,56] , NaH/DMF[57] , K_2CO_3/DMF[58] or NaOH/*N*-methylpyrrolidone.[59] The perfomance of the oxime alkylation reactions under PTC conditions considerably simplifies the alkylation procedure. Thus, pyridyl phenyl ketoxime O-ethers **55** are easily prepared under PTC conditions (10% aq. NaOH/Oct_4NBr/benzene) by interaction of corresponding oximes **54** with alkyl halides (RX where R = alkyl, allyl, benzyl; X = Br, I). During the reaction partial Z/E isomerization occurred (*Eq. 24*).[60]



(24)

54 **55**

Thiophene and furan containing oximes **56** can be transformed to corresponding O-ethers **57** in two phase system R^3Y/solid K_2CO_3/18-crown-6/benzene at room temperature. The products **57** are isolated as a mixture of *E* and *Z* isomers in yields up to 74%. The formation of nitrones was not observed (*Eq. 25*).[11] Similar PTC system was used also for the O-acylation of furan and thiophene ketoximes.[61]



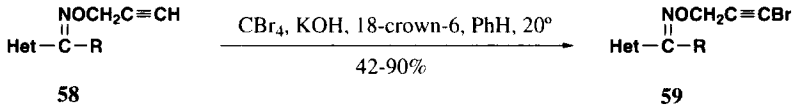
(25)

56 **57**

X = O, S; R^1 = H, Me Br; R^2 = alkyl; R^3 = alkyl, allyl, propargyl; Y = Br, I

However, the high yields of corresponding oxime O-ethers are obtained only when alkyl iodides or bromides are used as alkylating agents. In the presence of alkyl chlorides usually low yields or trace amounts of products were obtained. It has been found that PTC systems alkyl chloride (RCl)/solid K_2CO_3/solid KI/18-crown-6/toluene and RCl/solid KOH/solid KI/18-crown-6/benzene are the best for the synthesis of ketoxime O-ethers. Using these PTC systems synthesis of silicon containing oxime O-ethers is carried out.[62]

Heteroaromatic *O*-(propargyl)oximes **58** in two-phase system CBr_4/solid KOH/18-crown-6 at room temperature selectively afford *O*-(bromopropargyl)oximes **59** in yields up to 90%.[63] Bromination of *E*-ketoxime and aldoxime *O*-ethers proceeds stereoselectively giving only *E*-isomers of products (*Eq. 26*).

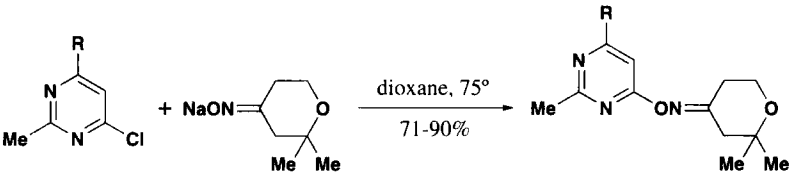


(26)

58 **59**

Het = 2-furyl, 2-thienyl, 5-bromo-2-thienyl, 2-, 3- and pyridyl; R = H, Me, Et

Oxime salts usually are used in the preparation of O-aryl or O-hetaryl oxime ethers. Thus, reaction of chloropyrimidines **60** with sodium salt of 2,2-dimethyltetrahydro-4-pyranone oxime **61** in dioxane leads to corresponding O-pyrimidinyl oximes **62** in good yields (*Eq. 27*).[64]



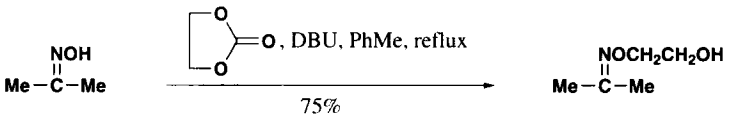
(27)

60 **61** **62**

R = Me, ON=CMe_2

Sodium or potassium salts of starting oxime are used in the preparation of O-alkyl derivatives of 2-cyano-2-(hydroxyimino)acetamide.[65] O-Aryl- or O-hetaryloximes are also prepared by interaction of corresponding oxime with activated aryl fluoride/$NaNH_2$/Et_2O[66], chlorohetarene/NaH/DMF or NaOH/acetone systems.[67]

Interestingly, that aldoximes and ketoximes are hydroxyalkylated using substituted ethylene or propylene carbonate in the presence of N-alkylated amidines or secondary amine substituted pyridines as catalysts. For example, acetone oxime (**63**) in the presence of ethylene carbonate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is transformed to acetone *O*-(2-hydroxyethyl)oxime (**64**) in 75% yield (*Eq. 28*).[68]



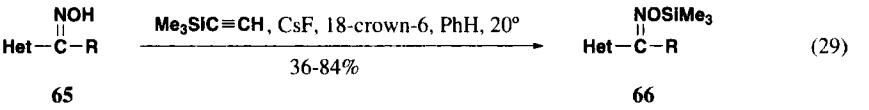
(28)

63 **64**

From other side, alkylation of oximes with dialkylcarbonate catalyzed by sodium methylate in methanol afforded ordinary O-alkyloximes.[69]

O-Silyl aldoximes and ketoximes are important intermediates in organic synthesis.[70] It has been found that the reactions of oximes **65** with trimethylsilylacetylene in the PTC

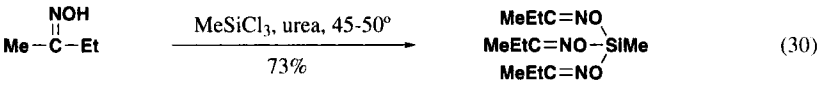
system CsF/18-crown-6/benzene at room temperature led to silylated oximes **66** in 36-84% yields (*Eq. 29*).[71]



65 **66** (29)

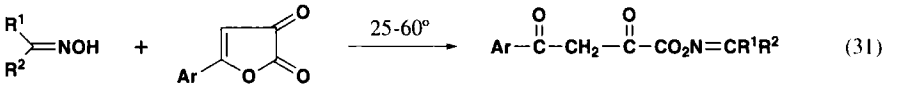
The reaction of oximes with phenylethynyltriethylgermane in the system CsF on Al_2O_3/18-crown-6/benzene at 20° or 50° led to *O*-triethylgermyloximes in yields up to 100%. The formation of by-product - phenylacetylene is observed in all cases.[71]

Aromatic, aliphatic, cyclic and acyclic O-*tert*-butyldimethylsilyloximes are prepared in 77-85% yield by the reaction of corresponding oximes with *tert*-butyldimethylchlorosilane using imidazole/DMF system.[70] Silanes bearing one or more oxime groups [72] are useful as vulcanization inhibitors.[73] These silyl oximes are prepared from oximes and halosilanes in the presence of urea and/or base as acid acceptors. Thus, adding methyl ethyl ketoxime (**67**) to $MeSiCl_3$ (the molar ratio **67**:$MeSiCl_3$ = 3.6:1) in the presence of urea gave oxime silyl ether **68** in 73% yield (*Eq. 30*).[73]



67 **68** (30)

An unusual method of O-(arylpyruvoyl)oximes synthesis **70** from oximes **2** and dihydrofurandiones **69** is described. Oxime ethers **70,** obtained in yield nearly to quantitative, possess a pronounced antiinflammatory activity (*Eq.* 31).[74]

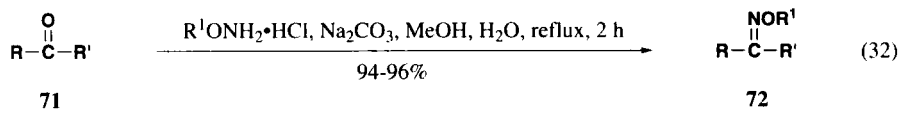


2 **69** **70** (31)

Ar = aryl; R^1 = H, alkyl, aryl; R^2 = aryl

Oxime ethers can be also prepared by reaction of corresponding oximes with epoxides/tertiary amine[75], hexafluoropropylene/NaOH/DMF[76] or ethyl propiolate/PPh_3[77] systems. Enzymatic synthesis of O-acyloximes or O-(*tert*-butoxycarbonyl)oximes from oximes and vinyl esters or di-*tert*-butyl dicarbonate, respectively, using lipases as biocatalysts is carried out.[78]

The second group of methods of oxime O-ether synthesis is based on interaction of carbonyl (or thiocarbonyl) compound on with O-alkylhydroxylamines.[55] For instance, treatment of aldehydes and ketones **71** with O-alkylhydroxylamine hydrochlorides in the presence of Na_2CO_3/MeOH/H_2O system afforded corresponding oxime O-ethers **72** in excellent yields (*Eq. 32*).[79,80]

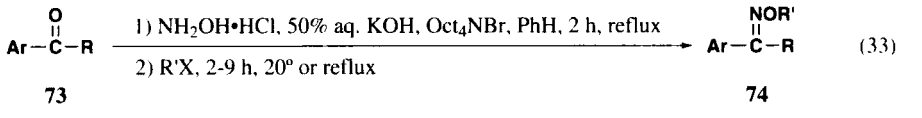


71 72 (32)

R = aryl, hetaryl; R' = H, Me; R^1 = Me, Et, *i*-Pr, Bu, *t*-Bu

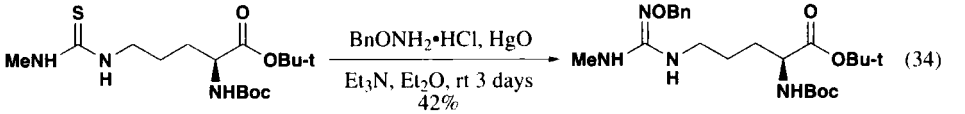
Sodium acetate in methanol [81] or pyridine [82] as bases can be used in the synthesis of O-alkyloximes from carbonyl compounds and O-alkylhydroxylamine salts. However, the stereoselectivity in oxime O-ether synthesis is not usually high.

A simple one-pot PTC synthesis of aryl and heteroaryl aldoxime and ketoxime O-ethers **74** directly from corresponding carbonyl compounds **73** is presented. The proposed mechanism involves the formation of the corresponding oxime K-salts by interaction with NH_2OH and KOH, which then undergo alkylation with alkyl and propargyl halides. The formation of oxime ethers **74** usually is *E*-stereoselective. Low stereoselectivity is obtained only in the synthesis of thiophene containing aldoxime and ketoxime O-ethers (*Eq. 33*).[83]



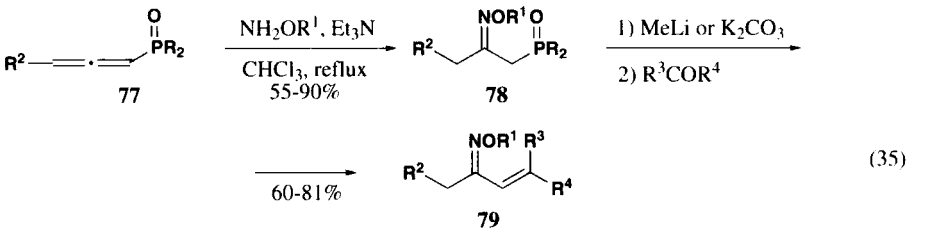
73 74 (33)

Recently a method of construction of benzyloxyguanidine group containing compounds **76** is described using activation of thiocarbonyl group in thioureas **75** with mercury (II) oxide and subsequent displacemement with *O*-benzylhydroxylamine hydrochloride (*Eq. 34*).[84]



75 76 (34)

β-Functionalized oxime derivatives **78** derived from phosphine oxides, phosphonates and phosphonium salts are easily obtained by simple addition of hydroxylamine compounds to substituted allenes **77** or to propargylphosphonium salts (*Eq. 35*). These oxime derivatives **78** are used for the synthesis of O-ethers of α,β-unsaturated oximes **79** and isoxazole derivatives.[85]

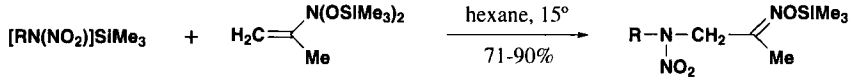


77 78 79 (35)

R = Ph, OEt; R^1 = H, alkyl; R^2 = H, alkyl, aryll R^3 = H, aryl; R^4 = aryl, hetaryl

O-Phosphorylated oximes are prepared by Allen reaction of a-chloronitrosoalkane derivatives with diphenylphosphinous acid trimethylsilyl ether [86] or by interaction of oxime salts with halogen derivatives of phosphates or thiophosphates under PTC conditions [87].

Trimethylsilyl derivatives of methyl- and ethylnitramine **80** react with 2-*N,N-bis*(trimethylsiloxy)aminopropene **81** to give silyl derivatives of α-(N-nitro)alkylamino substituted oximes **82** in good yields (*Eq. 36*).[88]

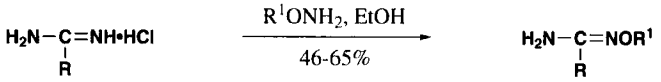


(36)

80 **81** **82**

R = Me, Et

O-Alkylamidoximes **84** can be successfully prepared from the corresponding imides **83** by interaction with O-alkylhydroxylamines in ethanol. Products **84** are isolated in 46-65% yields (*Eq. 37*).[89]

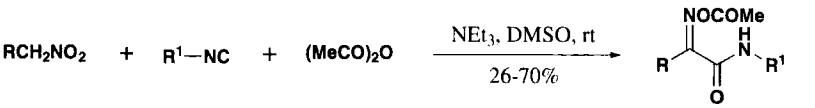


(37)

83 **84**

R = H, Me, Et

Nitro compounds **4**, isocyanides **85** and acetic anhydride (**86**) react together in the presence of triethylamine giving α-oximinoamides **87** as single products. The best results in the synthesis of **87** are obtained when DMSO is used as a solvent (*Eq. 38*).[90,91]



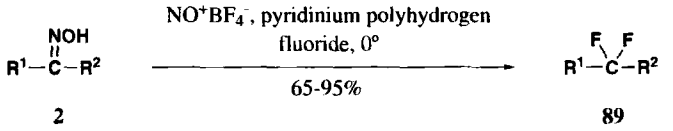
(38)

4 **85** **86** **87**

III. REACTIONS OF OXIMES, OXIME O-ETHERS AND ESTERS

Halogenation of oxime derivatives to corresponding *gem*-dihalocompounds is an important reaction. Usually, treatment of oximes with strong acids (for example, sulfuric acid) or chlorinated agents (phosphorus pentachloride or thionyl chloride) at elevated temperatures gives the products of Beckmann rearrangement.[92] At lower temperatures, treatment of oximes with chlorine in HCl or under neutral conditions leads to *gem*-chloronitrosoalkanes. It has been found that chlorination of oximes in the presence of Lewis acid, such as $AlCl_3$ produces *gem*-dichloroalkanes.[93] Action of chlorine on oximes in HF gave *gem*-dihalogenalkanes.[94] The reactions proceeds through the intermediates *gem*-chloronitrosoalkanes with subsequent transformations.

A convenient synthesis of *gem*-difluorides **89** from ketoximes **2** with nitrosonium tetrafluoroborate and pyridinium polyhydrogen fluoride is described. The products **89** are isolated in yields up to 95% (*Eq. 39*).[95]

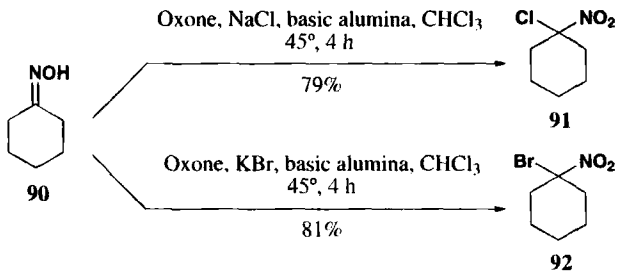


(39)

2 **89**

R^1, R^2 = alkyl, aryl

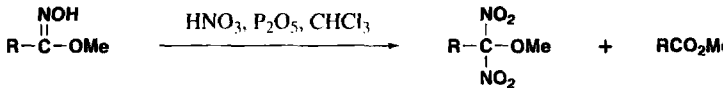
Gem-halo-nitro derivatives are versatile intermediates in organic synthesis for the preparation of compounds containing nitro groups. A mild and efficient process for one-step convertion of oximes to gem-halonitro compounds using Oxone and alkali metal halides is described. For example, cyclohexanone oxime (**90**) is converted to corresponding *gem*-chloronitro- (**91**) or *gem*-bromonitrocyclohexane (**92**) by interaction with Oxone/NaCl or Oxone/KBr systems (*Eq. 40*).[96,97]



(40)

The catalytic effect of chloroperoxidase from *Caldaromyces fumago* in the preparation of *gem*-halonitro compounds from oximes is demonstrated.[98] Oximes are successfully converted to nitroalkanes using Oxone in acetonitrile.[99]

Oximes **93** can be nitrated by N_2O_5, prepared in situ from HNO_3 and P_2O_5, in $CHCl_3$ forming a mixture of aryldinitromethoxymethanes **94** and esters **95** (*Eq. 41*).[100]

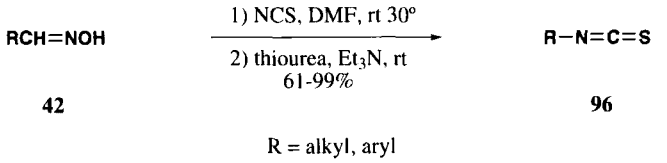


(41)

9 **94** (38-47%) **95** (26-30%)

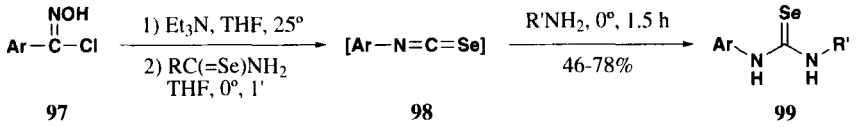
R = Ph, *p*-$NO_2C_6H_4$, *m*-$NO_2C_6H_4$

Isothiocyanates **96** are prepared in excellent yields in a one-pot reaction of aldoximes **42** by successive treatment with *N*-chlorosuccinimide (NCS), thiourea and Et_3N. The formation of isothiocyanates proceeds *via* unstable 1,2,4-oxathiazoline derivatives (*Eq. 42*).[101,102]



(42)

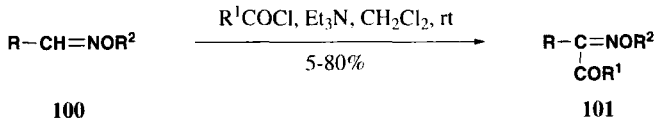
The efficient synthesis of selenoureas **99** using isoselenocyanates **98** by one pot procedure is performed. Thus, treating of oximoyl chlorides **97** with Et_3N and selenamides afforded intemediate **98**, which by interaction with primary amine ($R'NH_2$) gives the desired product **99** (*Eq. 43*).[103]



(43)

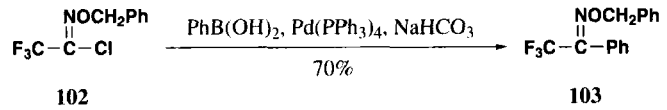
Ar = aryl; R = alkyl, aryl; R' = alkyl, phenol, benzyl

The C-acylation of O-substituted aromatic aldoximes is studied. These aldoximes **100** are treated with acyl chlorides (phthalimidoacetyl chloride or 3,5-dinitrobenzoyl chloride) in the presence of Et_3N yielding the expected C-acylated products **101** (*Eq. 44*).[104]



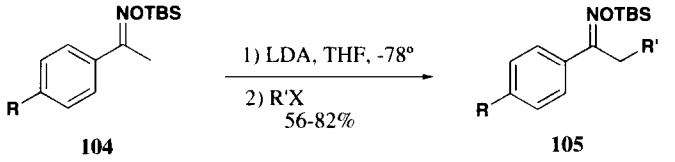
(44)

Acyl halide oxime ethers undergo selective Pd (0) or Pd (II) catalyzed coupling with boronic acid derivatives to afford ketoxime ethers. For example, 1-chloro-2,2,2-trifluoroethanone O-benzyloxime (**102**) was reacted with $PhB(OH)_2$ in the presence of $Pd(PPh_3)_4$ and $NaHCO_3$ and produced selectively phenyl trifluoromethyl ketone O-benzyloxime (**103**) (*Eq. 45*).[105]



(45)

The α-alkylation and silylation of *para* substituted acetophenone O-(*tert*-butyldimethylsilyl)oximes **104** , as well as similar 1- and 2-indanone derivatives, in the presence of lithium diisopropylamide (LDA) are studied. Optimum conversions from 82% to 100% are afforded for the alkylation of silylated ketoximes (O-TBS). Products of reaction **105** are isolated in yields up to 82% (*Eq. 46*).[106]

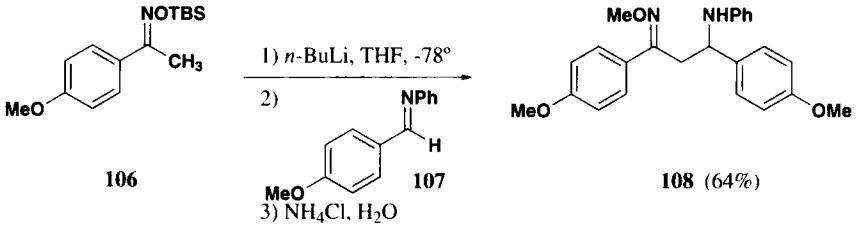


104 105 (46)

R = H, Me, OMe; R'X = MeI, EtBr, BnBr, Me_3SiCl

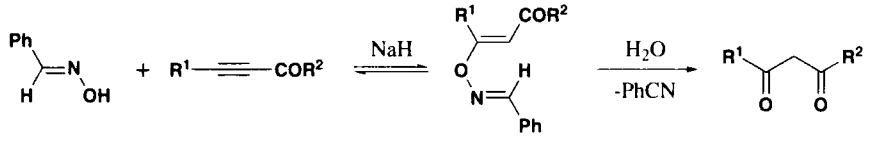
Positionally directed lithiation of O-alkyloximes for the synthesis of linear polyethers is also described.[107] Recently it has been found that nucleophilic substitution reactions of phenacyl bromide oxime is strongly influenced by the solvent and basicity of the nucleophile.[108]

Reactions of lithiated oxime ethers with CN electrophiles are reported in details by Kaiser and Wiegrebe.[109] Thus, reaction of *para*-methoxyacetophenone O-methyloxime (**106**) with *n*-BuLi and imine **107** affords substituted β-amino ketoxime O-methyl ether **108** as the single product (*Eq. 47*). The obtained compounds are precursors of 1,3-diphenylpropane-1,3-diamines.



106 107 **108** (64%) (47)

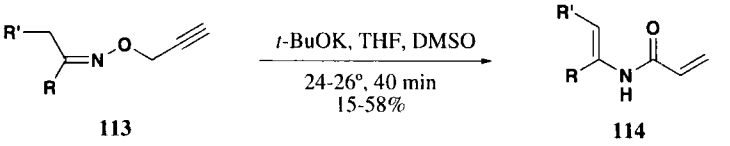
The reactions of *Z*-isomer of benzaldehyde oxime (**109**) with acetylenic carbonyl compounds **110** in the presence of NaH afforded as main products corresponding β–dicarbonyl compounds **112** in 44-88% yields. The mechanism of reaction includes a fast addition of benzaldoximate to give the vinyl anion **111**, followed by a rapid intramolecular fragmentation to the β-diketone enolate and benzonitrile (*Eq. 48*).[110]



109 110 111 112 (48)

R^1 = alkyl, aryl; R^2 = alkyl, aryl, alkoxy

O-Propargyl ketoximes **113**, available from the reaction of ketoximes with propargyl halides in KOH/DMSO system, readily undergo unexpected base-catalyzed (*t*-BuOK in DMSO or THF) rearrangement to *N*-(1-alkenyl)acrylamides **114** (*Eq. 49*).[111]

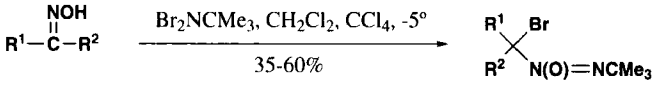


(49)

113 114

R = alkyl, aryl; R^2 = H, alkyl

Reaction of aliphatic and alicylic oximes **2** with *N,N*-dibromo-*tert*-butylamine results in corresponding *C*-bromodiazen-*N*-oxides **115** (*Eq. 50*). In the case of similar reaction of benzophenone oxime *O,O'*-(diphenylmethylene)-*bis*-benzophenone oxime has been obtained.[112]

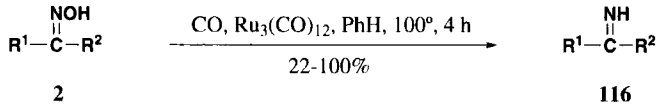


(50)

2 **115**

R^1, R^2 = alkyl, cycloalkyl

Interestingly, that $Ru_3(CO)_{12}$ exhibit high catalytic activity for the deoxygenation of various ketoximes **2** to the corresponding ketimines **116** under carbon monooxide pressure (20 kg/cm^2) (*Eq. 51*). In the deoxygenation of propiophenone oxime, ethyl phenyl ketimine is obtained in 100% yield.[113]

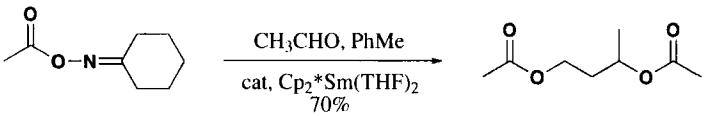


(51)

2 **116**

R^1 = alkyl, aryl; R^2 = H, alkyl, aryl

Recently a novel synthesis of 1,3-diol diesters was described by reaction of aldehydes with oxime esters in the presence of Sm-complex (Cp_2*Sm(THF)$_2$). For instance, reaction of cyclohexanone oxime acetate (**117**) with acetaldehyde in toluene gave 1,3-diacetoxybutane (**118**) and cyclohexanone oxime (*Eq. 52*).[114]

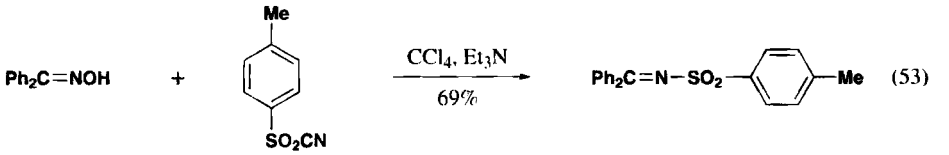


(52)

117 **118**

A new alcohol acylation method using an oxime ester and Cp_2*Sm(THF)$_2$ as catalyst has been devoloped.[115]

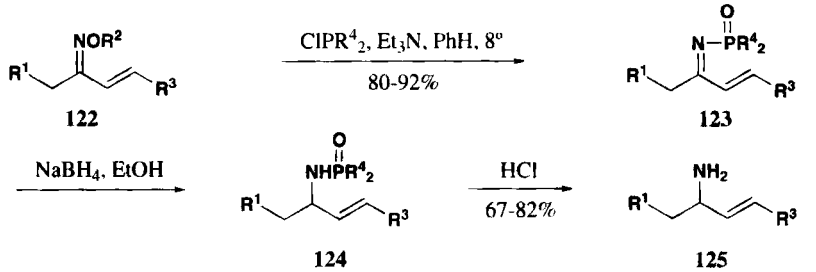
A convenient and general method for the synthesis of *N*-sulfonylimines is presented by Boger and Corbett.[116] Treatment of benzophenone oxime (**119**) with tolylsulfonyl cyanide (**120**) gave sulfonylimine **121** (*Eq. 53*).



(53)

119 **120** **121**

A simple and stereoselective synthesis of primary (*E*)-allylamines and 1-azadienes is reported. *N*-Phosphorylated azadienes **123** are obtained by addition of phosphorus chlorides to unsaturated oximes **122**. Reduction of azadienes **123** with $NaBH_4$ followed by deprotection of intermediates **124** leads to formation of primary allylamines **125** in good yields (*Eq. 54*).[117]



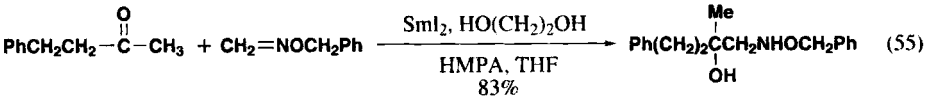
(54)

122 **123** **124** **125**

R^1 = H, Me; R^2 = H, $SiMe_3$; R^3 = alkyl, aryl, hetaryl; R^4 = Ph, OMe

Reactions of oximes (RR'C=NOH) with hydrophosphorous acid (H_3PO_2) gave previously unknown α-substituted α-aminophosphinic acids ($RR'C(NH_2)P(O)(OH)H$), which are oxidized to the corresponding α-aminophosphonic acids ($RR'C(NH_2)P(O)(OH)_2$).[118,119]

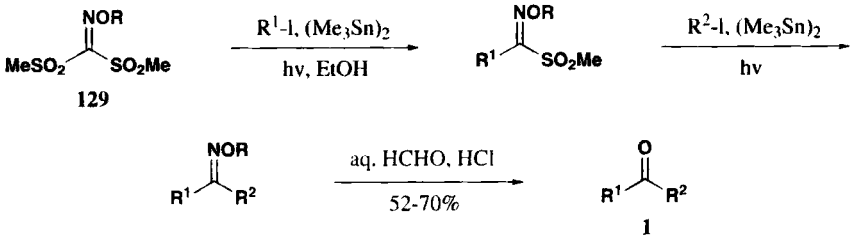
Among radical reactions reductive coupling of carbonyl compounds (for example, **126**) with *O*-benzyl formaldoxime **127** promoted by SmI_2 which leads to the corresponding aminomethylalcohol **128** (*Eq. 55*) is presented.[120]



(55)

126 **127** **128**

Interestingly, that *bis*-sulfonyl oxime ethers **129** undergo sequential radical acylation with two different alkyl iodides and after hydrolysis of intemediate ketoxime afford ketones **1** (*Eq. 56*).[121,122]

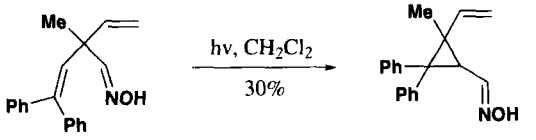


(56)

129 **1**

R = THP, CH_2Ph; R^1, R^2 = alkyl, benzyl

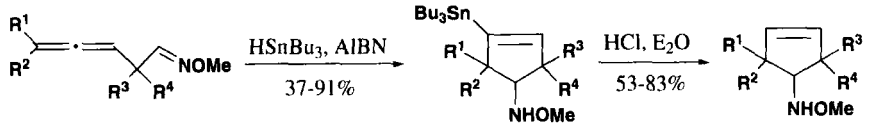
The aza-di-π-methane rearrangement of β,γ-unsaturated oximes is studied. Although previous studies have shown that acyclic β,γ-unsaturated oximes and oxime ethers do not undergo the aza-di-π-methane (ADPM) rearrangement, the 2-methyl-4,4-diphenyl-2-vinylbut-3-enal oxime (**130**) gave the corresponding cyclopropyl derivative **131** by the ADPM path, in the reaction that is controlled by the stability of the intermediate 1,3-biradical (*Eq.* 57).[123,124]



(57)

130 **131**

β-Allenic O-methyl oximes **132** undergo a free radical hydrostannylation reaction to afford cyclopentenes **133**, which are destannylated by treatment with hydrochloric acid in Et_2O to yield corresponding cyclopentenes **134** (*Eq. 58*).[125,126]

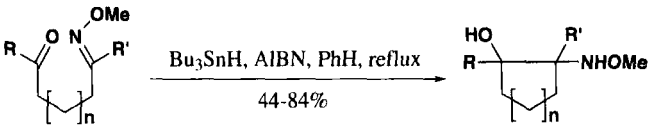


(58)

132 **133** **134**

R^1, R^2, R^3, R^4, = H, alkyl

Treatment of oxime ethers **135** with Bu_3SnH in refluxing benzene with AIBN as an initiator gave 2-methoxycyclopentanols and -cyclohexanols **136** predominantly *trans* isomers (*Eq. 59*).[127]



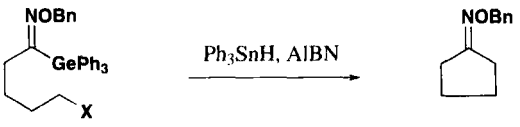
(59)

135 **136**

R^1, R' = H, alkyl; n = 1,2

Similar SmI_2 promoted intramolecular reductive coupling of carbonyl tethered oxime ethers is found to be a powerful method for stereoselective synthesis of aminocyclopentitols.[128-130]

Efficient synthesis of ω-halo- and phenylselenoacylgermane oxime ethers have been developed. Acylgermane oxime O-ethers **137** undergo 5-*exo* cyclization to corresponding cyclopentanone oxime O-benzyl ether **138** in good yieds (*Eq. 60*).[131]



(60)

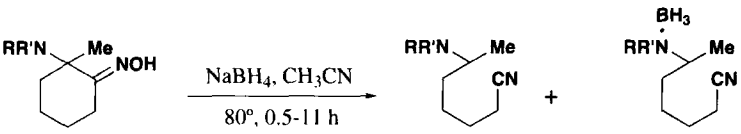
137 **138**

X = Br, SePh

IV. BECKMANN REARRANGEMENT OF OXIMES

Beckmann rearrangement as one of more characteristic reactions of oximes has been used extensively in organic synthesis due to the simplicity of synthesis of different compounds with nitrogen insertion into carbon chain. The Beckmann rearrangement of ketoximes to corresponding amides usually is catalyzed by acids or Lewis acids. Recently high catalytic activity of thionyl bromide[132], tosyl chloride[133], *p*-toluene sulfonic acid[134], HCl/HCONMe$_2$/POCl$_3$[135], P_2O_5[136], polyphosphoric acid[137], $AlCl_3$[138], AlI_3[139] and *i*-Bu$_2$AlH [140] in the above reaction is reported. Rearrangement of oximes to amides can be also successfully carried out in the presence of 2-chloro-1,3-dimethylimidazolium chloride[141], N-bromosuccinimide[142], tetrabutylammonium perrhenate/trifluoromethanesulfonic acid[143], beta zeolites[144] , montmorilonite KSF[145] and K-10 montmorilonite/microwave irradiation[146].

Unusual reductive Beckmann rearrangement is presented by Petukhov and Tkachev[147]. Thus, treatment of α-amino oximes **139** with $NaBH_4$ in boiling acetonitrile results in Beckmann synchronous fragmentation and formation of ω-amino nitriles **140** and corresponding borane-amine complexes **141** in yields up to 87% (*Eq. 61*).

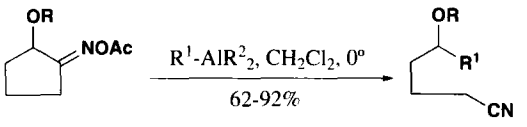


(61)

139 **140** **141**

Treatment of cyclic α-hydroxyamino and α-(*O*-acetyl)hydroxyamino oximes with $NaBH_4$ in CH_3CN medium results in rearrangement by ring-expansion and formation of cyclic amidoximes.[148]

The reaction of α-alkoxycycloalkanone oxime acetates **142** with organoaluminium reagents caused Beckmann fragmentation and subsequent carbon-carbon bond formation to give ω-cyano-α-alkyl ethers **143** in high yields (*Eq. 62*).[149]



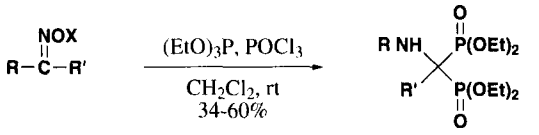
(62)

142 **143**

R, R^1, R^2 = alkyl

Cyclic ketoximes undergo cleavage by interaction with diethylaminosulfur trifluoride to afford fluorinated carbonitriles.[150]

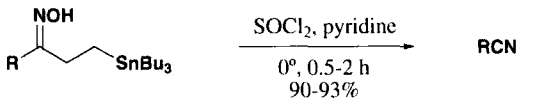
Beckmann rearrangement of oxime derivatives **144** in the presence of P-nucleophiles (e.g. P(OEt)$_3$) afforded the corresponding aminomethylene *gem*-diphosphines **145** in moderate yields (*Eq. 63*).[151]



144 145 (63)

X = H, Ms; R, R' = alkyl, aryl

β-Tributylstannyl oximes **146** upon treatment with thionyl chloride/pyridine fragmented to give nitriles **147** in good yields; no normal Beckmann rearrangement products (amides or lactams) were observed (*Eq. 64*).[152]



146 147 (64)

R = alkyl, aryl

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(Received January 28, 2000; in final form April 7, 2000)