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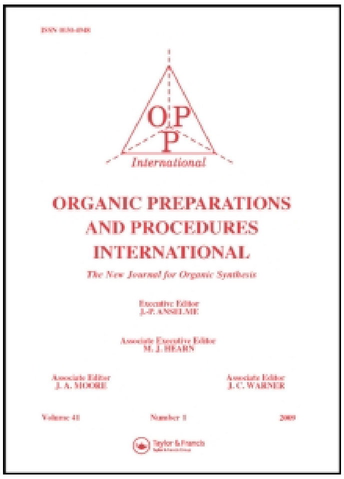

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α-HALONITROSO COMPOUNDS. A REVIEW

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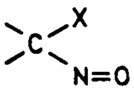
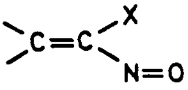
I. INTRODUCTION

Although several articles dealing with the chemistry of nitroso compounds in general have appeared in monographs, handbooks[1-3] and in review journals,[4,5] the behavior of α-halonitroso compounds has been covered only cursorily in these compilations. To our knowledge, the recent report on the synthesis and properties of aliphatic fluoronitroso compounds[6] constitutes the sole exception to the above statement. This is certainly due to the fact that compounds of type A and B have been curiosities for a long time.



A

or



B

(X = F, Cl, Br)

Work on the structure and the chemistry of such compounds in the last three decades has, however, revealed some properties of general interest. The pertinent results of this work are now summarized in this review.

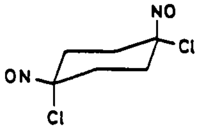
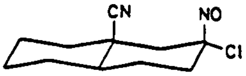
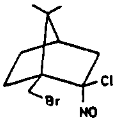
II. α-HALONITROSOALKANES

1. STRUCTURE AND STEREOCHEMISTRY

Bond length and bond angles have been determined for several α-halonitroso compounds and are compiled in Table 1.[405] In at least two cases,[7,8] a characteristic feature of the structure is the coplanarity of the X-C-N=O group. Such an eclipsed conformation has also been assumed to explain the molecular spectra (IR and Raman) of CF_3NO[9,10] and several perhalonitrosomethanes.[11] In the case of Cl_2CBrNO, two stable (eclipsed) conformational isomers (cis and gauche) are observed by IR measurements.[11] The splitting of the IR absorption ν(NO), 1558-1580 cm^{-1}, for chloronitroso steroids has also been attributed to rotational isomerism of the nitroso group.[12] The barrier to internal rotation was calculated to be of the order of 3217 J mol^{-1} for CF_3NO.[9] Assignments of the fundamental frequencies of CF_3NO[377] and CCl_3NO have been made.[13]

In the case of α-chloronitroso terpenes and steroids, some information about the stereoisomerism has been obtained from the ^1H- and ^{13}C-NMR spectra. Diastereomeric compounds show differences in the chemical shift values of methyl groups attached to the ring and, sometimes, of the ring β-methine hydrogen atoms.[12,14,15] The position (equatorial or axial) of the NO group may be deduced, in some cases, by such shift differences due to the magnetic anisotropy of the NO group.[14,15] The ^{13}C-NMR spectra of such diastereomeric chloronitroso derivatives show significant differences for the shift of the carbon atom α to the Cl/NO moiety,[16] the deshielding for the isomers with an axial NO group being less than that of the equatorial NO isomers. ^{14}N and ^{15}N NMR spectra offer information about another structural aspect of nitroso compounds. There is a general proportionality between the N chemical shift and the wavelength of the low lying $n \rightarrow \pi^x$ band.[17-20] When fluorine or perfluoroalkyl groups replace alkyl

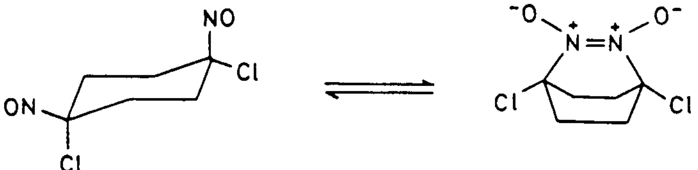
Table 1: Bond Lengths (r) and Bond Angles (∢) for α-Halonitroso Compounds

Compound	r(N=O) (Å)	r(C-N) (Å)	r(C-X) (Å) [X]	(C-N=O)	Ref.
CF_3NO	1.198	1.512	1.324 [F]	112.4°	25
	1.171	1.555	1.321 [F]	121.0°	26
	1.139	1.505	1.784 [Cl]	116.5°	8
	1.121	1.542	1.804 [Cl]	128.0°	24
	a) 1.16; 1.21	1.52; 1.44	1.81; 1.75	117°; 119°	27

a) The asymmetric crystal unit consists of two molecules

substituents on the α-carbon, an increase in nitrogen shielding by ca. 140 ppm follows the stabilization of the N(N) HOMO relative to the π LUMO with the increase in electronegativity of the group bonded to the nitrogen.[20] The dipole moment of CF_3NO (0.31 D) is rather low.[21]

Whereas aliphatic C-nitroso compounds and α-haloderivatives of the structure RCHXNO[22] almost invariably exist as dimers, at least in the solid state, intramolecular dimerization of α-chloronitroso compounds RR'CXNO occurs only in a few cases: *cis*-1,4-dichloro-1,4-dinitrosocyclohexene (1) has been shown to exist as an azodioxide (1a) even in solution.[8,23] The dissociation of this "dimer" seems to be effected by warming the solution



1 ⇌ 1a

as well as by irradiation with UV light.[57] Other, bicyclic cis-azo N,N'-dioxides with α-chloro substituents do not give nitroso monomers in observable concentrations up to 250°C[166] (cf. p. 347). From the absence of color in solution, dimerization has been deduced for 2-chloro-2-nitrosonorbornane;[28] the same conclusion has been reached for the reaction products of chlorine with aliphatic aldoximes[29] on the basis of ^{1}H-NMR spectra.

Trifluoronitrosomethane (CF_3NO) yields an orange-red dimer when irradiated with UV and visible light. This dimer is not analogous to that of other nitroso compounds but has the structure $(CF_3)_2N\text{-}ONO$;[30,31] its formation is reversible and the dimer is subject to further phototransformations[32] and thermolysis.[33]

2. ELECTRONIC SPECTRA, DISSOCIATION AND PHOTOCHEMISTRY

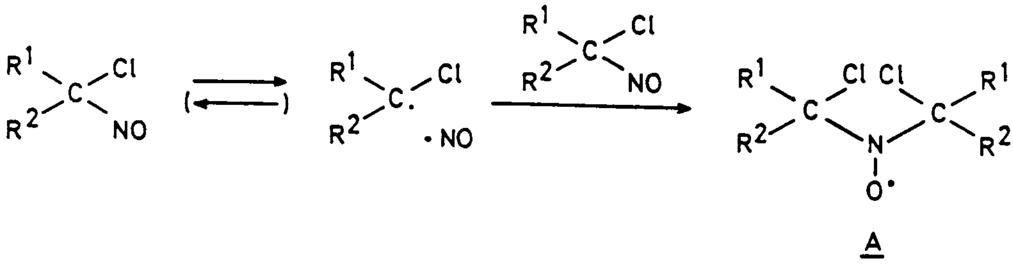
The α-halonitroso compounds possess the three electronic transitions shown usually by all C-nitroso compounds:

$n \rightarrow \pi^*$ (or: $n_N \rightarrow \pi^*$, $n^* \rightarrow \pi^*$)	appr. 15,000 [cm^{-1}] ($\varepsilon \sim 20$) (with vibrational fine structure)	refs. 15,34,35
$n_O \rightarrow \pi^*$ (or: $n \rightarrow \pi^*$)	30,000 - 35,000 (shoulder)	ref. 15
and $\pi \rightarrow \pi^*$	40,000 - 45,000 (ε = 62 500)	refs. 15,35

The $n_N \rightarrow \pi^*$ absorption band is shifted bathochromally by 500 cm^{-1} going from eq-NO derivatives to ax-NO compounds in the menthane series;[15] it is observed for CCl_3NO at 16,750 (ε = 5.6 in CCl_4)[13] and for CF_3NO at 14,500 (ε = 23.8).[36] This compound as well as other perfluoro nitroso alkanes and analogues have been investigated in detail with respect to the geometry of the excited state[36,37] and to fluorescence excitation and life times.[38-46] For a critical evaluation of the electronic structure of α-halogeno nitrosocompounds cf. lit. 81-83, p. 337.

ORD and CD spectra have been reported for some nitrosoterpenes,[14,15] for (-)-2-chloro-2-nitroso-camphane and the (+)-enantiomer of its 10-sulfonic acid derivatives,[46] as well as for some α-halogeno nitroso steroids.[47] 2- And 3-substituted chloronitroso menthanes show a Cotton effect of the $n_N \rightarrow \pi^x$ band which depends on the stereochemistry.[14,15] The relation between the temperature dependence of the CD spectra and the hindrance of rotation of the nitroso group has been discussed. trans- and cis-1,4-Dichloro-1,4-dinitrosocyclohexane are highly efficient O_2 ($^1\Delta_g$) quenchers and sensitizers of triplet states. [48]

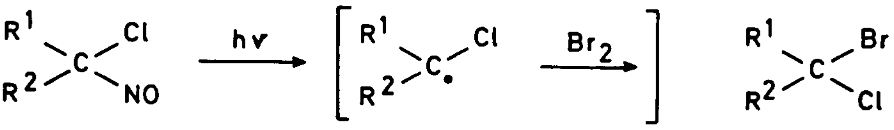
The above data form the basis for many studies in the photolysis of nitroso compounds (for earlier work on fluoronitroso compounds see ref. 6). By excitation of the $n_N \rightarrow \pi^*$ transition, homolysis of the C-NO bond of α-chloronitroso compounds occurs invariably as the first step [34,49-55] followed by the formation of a nitroxide A.



The fate of this intermediate A depends on the structure of the nitroso compound and on the reaction conditions. In most cases, in aprotic solvents, the dichloro derivative $R^1R^2CCl_2$, the ketone R^1R^2CO and the oxime $R^1R^2C{=}NOH$ are the main products in variable yields, whereas in methanolic solution methyl nitrite and the acetal $R^1R^2C(OMe)_2$ have been observed.[34,49,5o,52]

The primary step seems to be reversible at least in the case of stereoisomeric α-chloronitroso terpenes, the recovered starting material consists of an epimeric mixture.[51,56,57] Quantum yields for the photolysis of geminal chloronitroso compounds depend on the structure of the substrate and on the reaction conditions but are wavelength independent.[16,51,58] The kinetics of photolysis of α-chloronitroso compounds has been investigated by several groups.[51,59]

The photochemical homolysis of α-chloronitroso compounds in the presence of excess bromine leads to the formation of *gem*-bromochloroalkanes. This represents a useful method for the synthesis of such compounds.[60]



75 - 92%

In the case of chloronitrosomenthanes, mixture of diastereomers [52:48 - 66:34] are produced.[51]

Photodissociation lifetimes for CCl_3NO, CF_3NO and similar molecules have been determined in connection with the fate of fluorocarbons in the atmosphere.[53,62] For CF_3NO, the photodissociation caused by visible light[63-69,406] or vacuum ultraviolet,[70-74] (data for $ClCF_2NO$ cf. ref. 75) has been investigated in great detail, mostly to get information about the electronic and vibronic states of the fragments. The so-called "spontaneous" formation of radicals from CF_3NO has been shown to be due to inadvertent photolysis.[76] The action of radicals produced by the photolysis of nitroso compounds has been used for sensitizing photodegradations of polymers.[77-79]

Besides dissociation, photoionization has been observed during the vacuum UV photolysis of compounds $CF_nCl_{3-n}NO$.[80] Photoelectron spectra of perhalogenonitrosomethanes[81,82] and of several α-halogenonitroso compounds[83] indicate generally that the electronic structure is characterized by unusually strong lone pair interactions on the NO group giving rise to n_-/n_+ splitting up to 6 eV and increasing considerably with increasing electronegativity of the α group. The upper antibonding orbital (n_-) is followed by strongly bonding and closely adjacent π (NO) and n_+ M.O.'s their ionizations are preceded by halogen lone-pair ionizations. The NO group in aliphatic C-nitroso compounds is thought to have an electron-withdrawing character comparable with that of fluorine.[81]

Mass spectrometric measurements supplement the above photochemical results. From appearence potential measurements of α-substituted C-nitroso compounds, the following C-N bond dissociation energies are obtained: D(CF_3-NO) 32 and D(CCl_3-NO) 32 kcal/mol[84]; D(Me_2CCl-NO) is estimated to be 35 kcal/mol[85]. These low values were thought to explain the possibility of C-NO fission by photolysis in the red region of the spectrum as well as the fact that the dissociative ionization dominates the ion chemistry of CF_3NO.[86] More recent investigations, however, show that the D(C-N) values determined by appearence potential measurements are too low. As more reliable values for CF_3NO have to be considered 39.6 ± 0.2 kcal/mol[400] or 42 ± 2 kcal/mol[401], for CF_2ClNO 39 kcal/mol.[402]

Thermolysis of CCl_3NO[87,88] resulted in a multitude of products. As usual, the first step here and in the shock-wave thermolysis of CH_3NO[89,90] (cf.ref.91) consists in the CX_3-NO dissociation. γ-Irradiation of CCl_3NO, too, leads to CCl_3-radicals, the major electron capture radical being probably NO.[92]

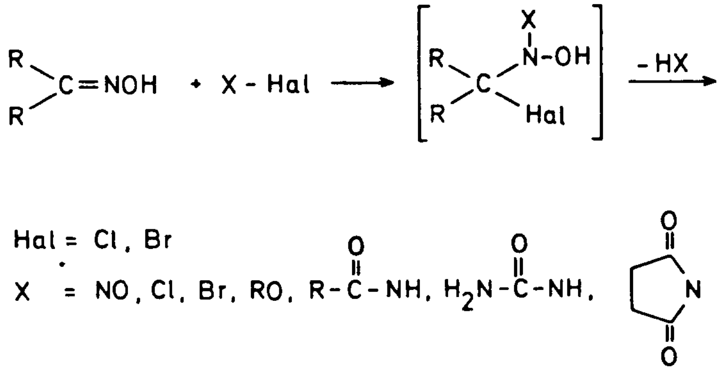
3. PREPARATION

The various methods for the synthesis of α-halonitroso compounds are compiled in this and in the next section. In general, the older examples for these methods, covering the literature up to ca. 1970, have been summarized in Houben-Weyl. The more recent developments on the synthesis of α-halonitroso compounds are described below with particular emphasis on the synthetic applications.

Caution! α-Halonitroso compounds are thermally unstable. Great caution should be exercised especially in distilling them, because if the pressure is allowed to rise, explosions may occur ![119]

a) From Oximes

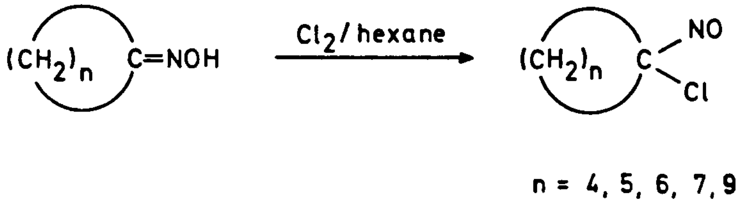
The reaction of aldoximes and ketoximes with halogenating agents constitutes the classical method for the synthesis of α-halonitroso compounds. The halogenating reagents most widely used are chlorine,[15,50,93-123] bromine,[96,100,108,124-132] nitrosyl chloride[130,133-143] and preferably alkyl hypochlorites.[14,144-150] N-bromosuccinimide,[151-155] N-bromoacetamide[153] and N-chlorourea[100] have also been used. The formation of *gem*-halonitroso compounds is thought to proceed *via* an addition-elimination mechanism.



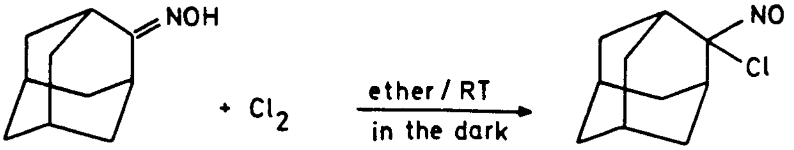
The reaction conditions used commonly depend on the halogenating agents. The reactions of oximes with elemental chlorine or bromine are usually carried out in aqueous acidic or basic solution. In alkaline medium, further oxidation of the intermediate gem-halonitroso compound by hypochlorite or hypobromite to the corresponding α-halonitro compound has been observed occasionally.[156] Organic solvents (ether, di-, tri- and tetrachloromethane, methanol, glacial acetic acid) have been employed advantageously for the reactions of elemental halogens at lower temperatures. gem-Chloronitroso compounds may also be obtained by treatment of ethereal solutions or suspensions of oximes with somewhat more than two equivalents of NOCl with cooling. A mild procedure for the synthesis of α-chloronitroso compounds from aldoximes or ketoximes involves the use of alkyl hypochlorites in trichlorofluoromethane solution. Due to its ease of preparation,[157] t-butyl hypochlorite is most frequently used; the work-up is convenient and the yields are good.[145] If chiral alcohols (e.g., (-)-isoborneol) are used for the preparations of alkyl hypochlorites, optically active α-chloronitroso compounds are formed stereoselectively.[146] Typical examples for the application of these methods are given below.

i) α-Halonitrosoalkanes

α-Chloronitrosocycloalkanes have been synthesized from oximes with chlorine in hexane solution. 1-Chloro-1-nitrosocyclodecane is a blue, crystaline material; the 5-, 6-, 7- and 8-membered ring compounds are dark blue liquids which may be purified by distillation under reduced pressure.



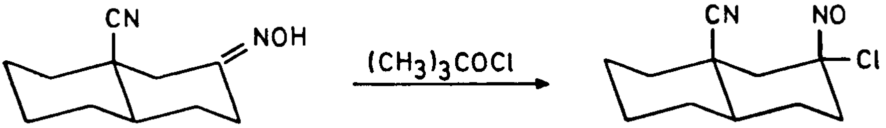
The same method was used to prepare *gem*-chloronitrosoadamantane 2 from the oxime as shown below. Even the severely hindered 2,2,6,6-tetramethylcyclohexanone oxime has been successfully converted (Cl_2, in $CFCl_3$) to the *gem*-chloronitroso compound (40%).[158]



94%

2

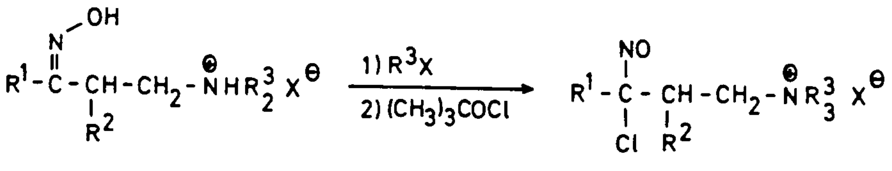
Only one of the diastereomeric chiral α-chloronitroso compounds (3) with the axial nitroso group was formed from the oxime of optically active 9-cyano-*trans*-2-decalone and *tert*-butyl hypochlorite.[148] As in similar cases, this probably is due to the steric approach control of the reaction.



60%

3

Geminal chloronitroso compounds with an ammonium group in the β-position have been prepared from Mannich base oximes by the use of *tert*-butyl hypochlorite. The compounds are blue crystalline solids which are stable in the dark.[147] With N-bromosuccinimide[151,153] or N-bromoacetamide[153] as



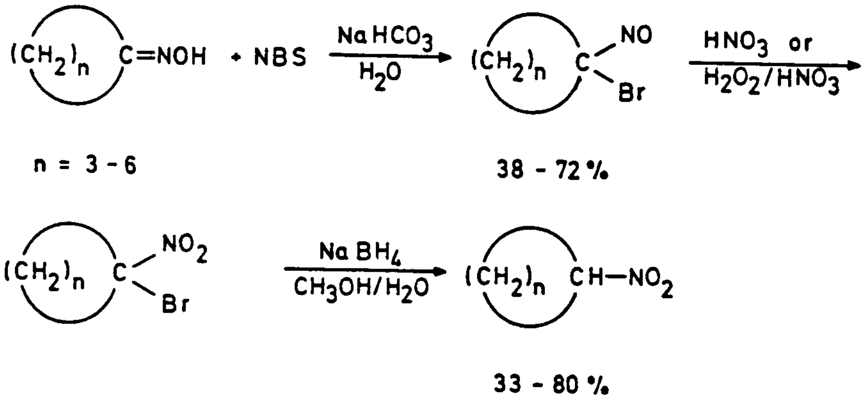
$$R^1\text{-}\overset{\overset{\text{OH}}{\text{N}}}{\overset{\|}{C}}\text{-}\underset{R^2}{\underset{|}{CH}}\text{-}CH_2\text{-}\overset{\oplus}{N}HR^3_2\,X^{\ominus} \xrightarrow[2)\,(CH_3)_3COCl]{1)\,R^3X} R^1\text{-}\underset{Cl}{\underset{|}{\overset{NO}{\overset{|}{C}}}}\text{-}\underset{R^2}{\underset{|}{CH}}\text{-}CH_2\text{-}\overset{\oplus}{N}R^3_3\,X^{\ominus}$$

64 - 87%

$R^1 = R^2 =$ $-(CH_2)_3-$; $-(CH_2)_4-$; $R^1 = CH_3$, $R^2 = H$

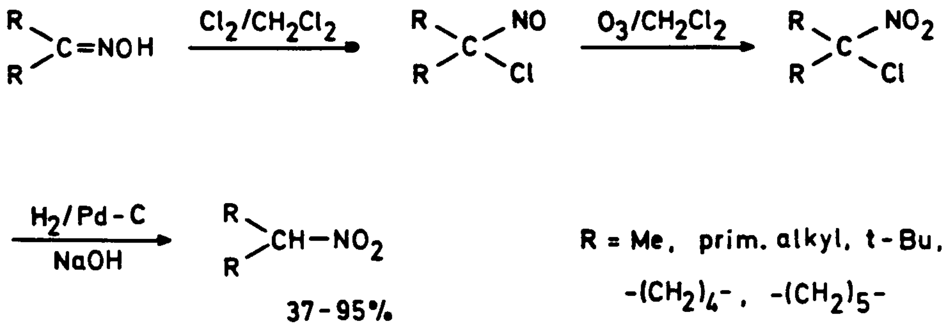
$R^3 =$ alkyl, aralkyl, $X = Cl$, BF_4, FSO_3

brominating agents, dialkylketoximes or cycloalkylketoximes afford α-bromonitroso derivatives which are easily oxidized to α-bromonitro derivatives with nitric acid or a mixture of 30% hydrogen peroxide/conc. nitric acid. Subsequent reduction with sodium borohydride provides a practical synthesis of secondary nitroalkanes (yields 10-48%) and nitrocycloalkanes, respectively.



33 - 80 %

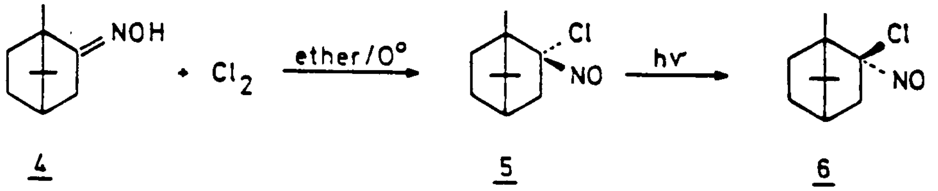
Another convenient preparation of secondary nitroalkanes in moderate to good yields also involves the intermediacy of chloronitroso compounds, prepared by treatment of an oxime with chlorine; the corresponding chloronitro derivative, obtained by oxidation of the chloronitroso compound with ozone, gives the nitroalkane on catalytic hydrogenation in the presence of sodium hydroxide.[114]



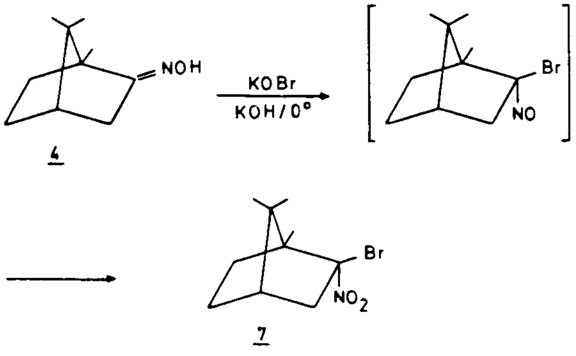
Several classes of α-halonitroso compounds derived from natural products have been prepared from oximes and are described in section ii-iv.

ii) α-Halonitroso Terpenes

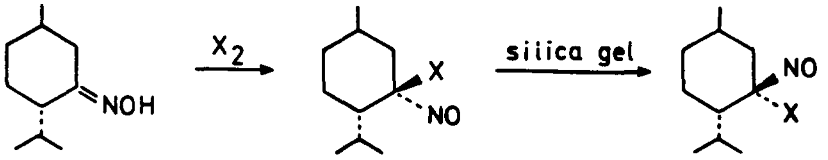
2-Chloro-2-nitrosocamphane 5 with the NO group in the exo position has been isolated as the sole product from camphor oxime 4 and chlorine.[14,46,56]



However, chlorination of camphor oxime under similar conditions was later[160] reported to give a 3:2 mixture of the endo- and exo-compounds [160] [in that reference, possible by a result of a mix-up, the NMR data ascribed earlier to the exo-compound[14] were incorrectly assigned to the endo-isomer]. Irradiation of 5 with red light produces isomer 6, which has been shown to arise by interchange of the NO and Cl group in position 2.[159] The 2-chloro-2-nitroso derivatives of pinane, carane and menthane, prepared analogously from the oximes and chlorine, also showed photoisomerization.[56] Treatment of 4 with potassium hypobromite without isolation of the intermediate bromonitroso compound gave diastereoselectively 2-exo-bromo-2-endo-nitrobornane 7.[132] Surprisingly, the attack of bromine in this case takes place exclusively from the more hindered exo side.



Halogenation of (-)-menthone oxime gave 3-halo-3-nitrosomenthanes (8) which could be isomerized on silica gel to the corresponding diastereomers 9.[15] The menthane skeleton remains unchanged during this isomerization as shown by the synthesis of both the diastereomeric α-chloronitroso derivatives starting with isomenthone oxime.[15]

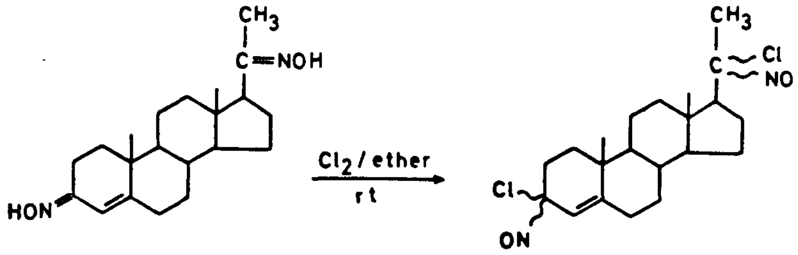


8	9
X = Cl, 69%	X = Cl, 12%
X = Br, 21%	X = Br, 67%

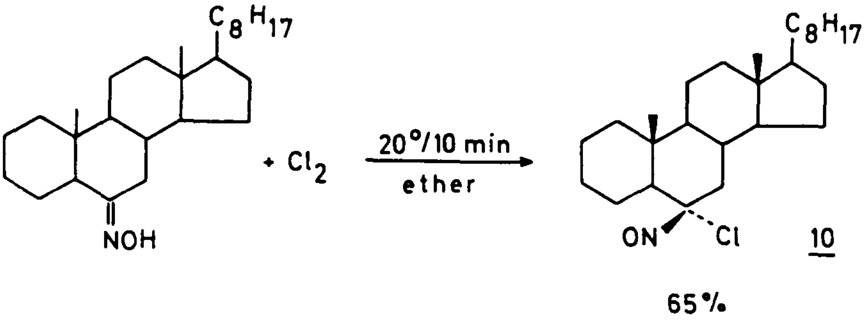
Mixtures of diastereomeric α-chloronitroso terpenes have been obtained from the reactions of tert-butyl hypochlorite with the oxime of 3-methylcyclohexanone, carvomenthone, fenchone[14,56] and thujone.[160] One diastereomer of 2-chloro-2-nitrosofenchane was found to be quite unstable; it underwent epimerization during work-up by column chromatography even at -30°.[14]

iii) Steroidal α-Halonitroso Compounds

Treatment of the 3,20-dioximes of pregn-4-ene-3,20-dione, 5α-pregnane-11α-ol-3,20-dione and 5α-pregnane-3,11,20-trione with chlorine gave the corresponding 3,20-dichloro-3,20-dinitroso derivatives.[154,161,162]

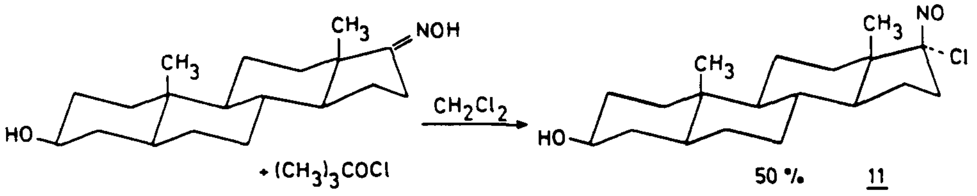


3,7,12-Trioxocholanic acid trioxime gave the 3,7,12-trichloro-3,7,12- trinitroso compound. These blue crystalline compounds did not dimerize and were stable at room temperature for years.[162] Chlorination of the 4α-cholestan-6-one oxime in the dark yielded the 6α-chloro-6β-nitroso derivative <u>10</u>.[154] Analogously, the 3-, 4- and 7-<u>gem</u>-chloronitroso derivatives of 5α-cholestane could be prepared. 17-Hydroxyimino-5α-androstane gave the 17-chloro-17-nitroso derivative.[154] The 3-chloro-3-nitroso-5α-cholestane

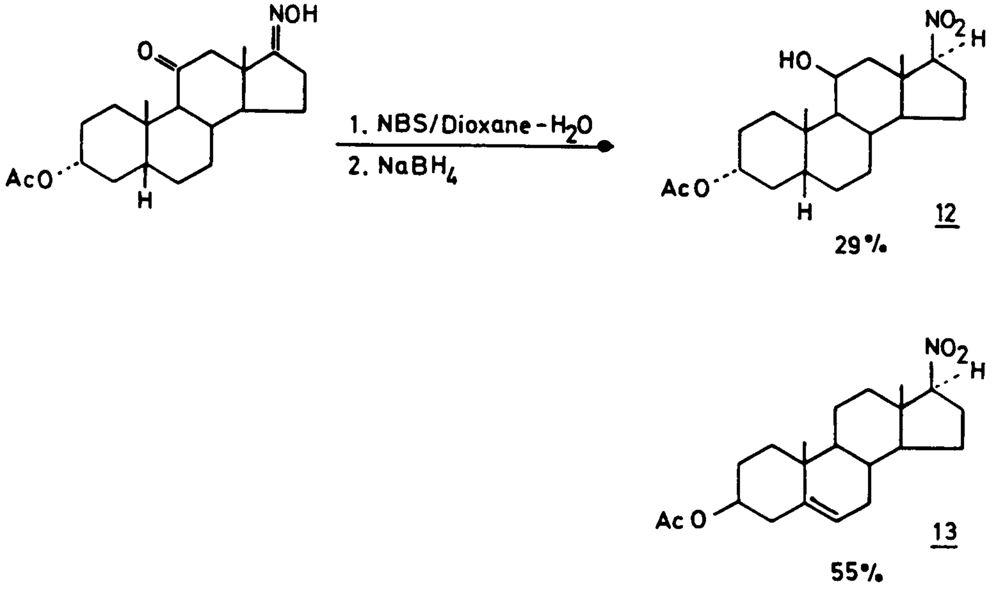


was later shown to be a mixture of the 3α-chloro-3β-nitroso (main product) and 3β-chloro-3α-nitroso derivatives.[15]

By treatment of epiandrosterone oxime with <u>tert</u>-butyl hypochlorite, a mixture of the two diastereomeric α-chloronitroso compounds is formed from which the enantiomerically pure 17α-chloro-17β-nitroso isomer <u>11</u> could be separated by HPLC.[149] The two-step procedure for the synthesis of



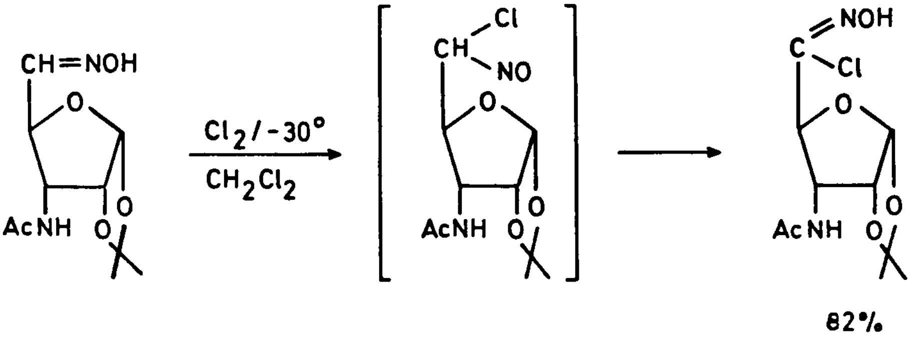
nitro compounds from oximes[151,155] has been applied to steroid oximes, for example, 3α-acetoxy-11β-hydroxy-17β-nitro-5β-androstane <u>12</u> and 3β-acetoxy-17β-nitro-5-androstene <u>13</u> were prepared from the corresponding steroid

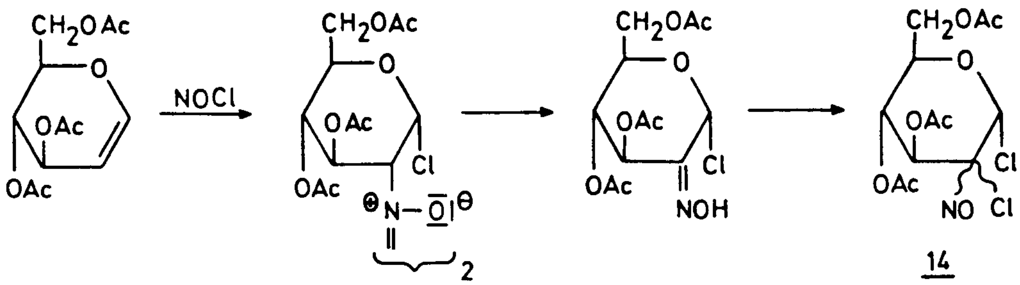


gem-bromonitroso and bromonitro compounds in low yield.[154]

iv) Carbohydrate Derived α-Halonitroso Compounds

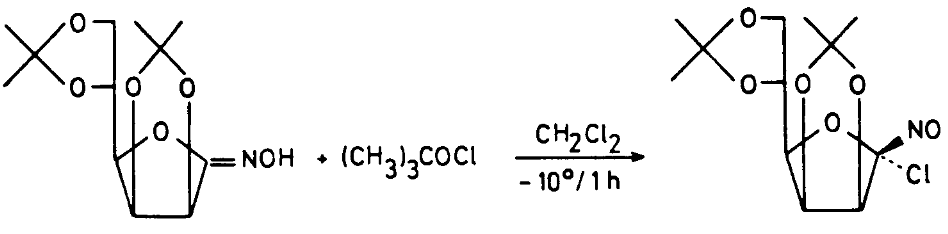
The intermediate formation of geminal chloronitroso compounds and their dimers in the chlorination of aldehydo sugar oximes to hydroximoyl chlorides [116,163] could be demonstrated by NMR. [164] In some instances, these intermediates could be isolated.[116] Treatment of tri-O-acetyl-D-glucal with an excess of nitrosyl chloride yielded the gem-chloronitroso compound 14 via the dimeric nitroso compound and the oxime.[137] Diastereoselective bromination of several aldonolactone oximes (e.g. 15) gave the





14

corresponding bromonitroso compounds which were oxidized to the stable bromonitro derivatives in overall yields ranging from 38 to 86%.[165] The reaction of 15 with *tert*-butyl hypochlorite gave diastereoselectively the α-chloro-α-nitrosoether 16 in nearly quantitative yield.[150]



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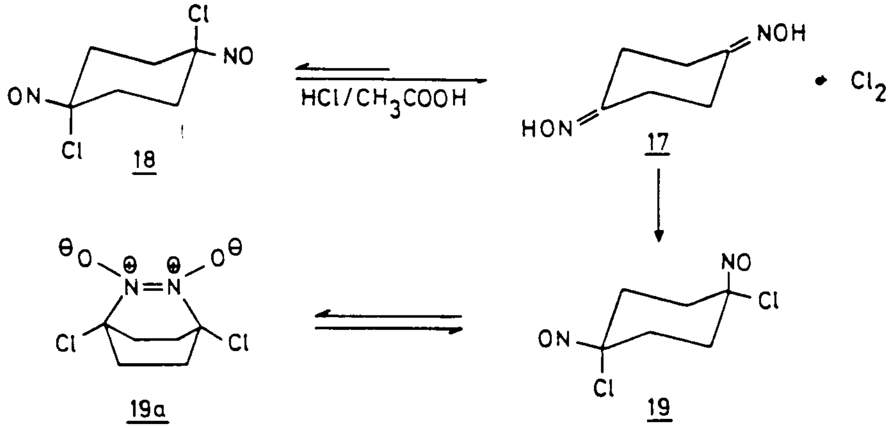
16

v) Bifunctional α-Halonitroso Compounds

The chlorination of the cyclohexane-1,4-dione-dioxime 17 in concentrated HCl gives a mixture of the *trans*- and *cis*-dichloro dinitroso compounds (18 and 19). On standing in HCl/acetic acid at room temperature, 18 is converted *via* the reverse reaction to the thermodynamically more stable *cis*-



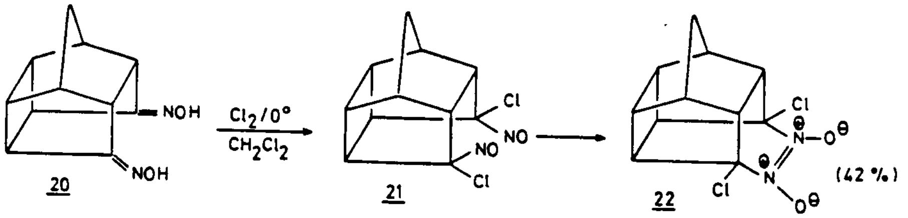
18

17

19a

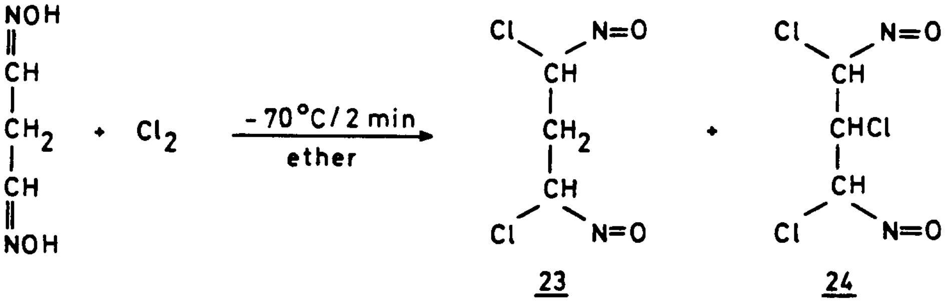
19

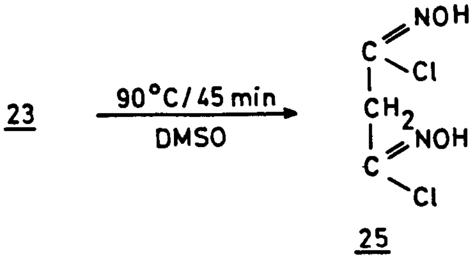
isomer 19 [120] (cf. p.333) which "dimerizes intramolecularly" to the azodioxide 19a. In contrast to the above example, the colorless azo dioxide 22 - prepared from dioxime 20 *via* the blue dichloro dinitroso compound 21 - once formed, is not equilibrated with the "monomer" 21 prior to decomposition.[166]



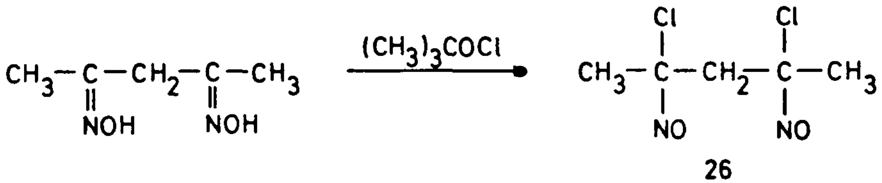
For dichloro-dinitroso and trichloro-trinitroso derivatives of steroids see p. 343.

Chlorination of malonaldehyde dioxime normally leads to polychlorinated derivatives. Under carefully controlled conditions, the 1,3-bis-chloro-1,3-nitroso propane 23 could be obtained in 30% yield together with the trichlorinated compound 24.[115,165] Compound 23 is stable in ether, ethanol or benzene solutions even upon warming. By heating in DMSO the isomeric bis-hydroxamic acid dichloride 25 could be obtained in 67% yield.[115] 2,4-Di-





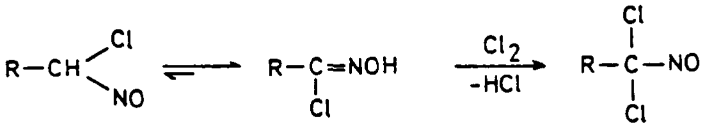
chloro-1,4-dinitrosopentane 26 has been synthesized from pentane-2,4-dione dioxime and tert-butyl hypochlorite. The bifunctional chloronitroso compound may be useful in crosslinking polymers.[144]



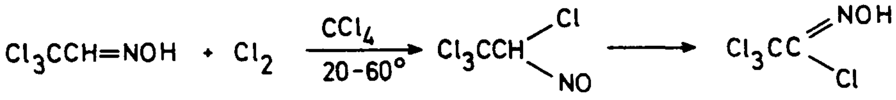
26

vi) Exceptions and Side-reactions

The formation of α-halonitro compounds from oximes and elemental halogen[132,156,177] or N-bromosuccinimide[131,151,153] by further oxidation of the intermediate nitroso derivatives has been reported. With aldoximes, tautomerization to the corresponding hydroximic acid chlorides and further chlorination to give 1,1-dichloronitroso compounds occurs.[178]

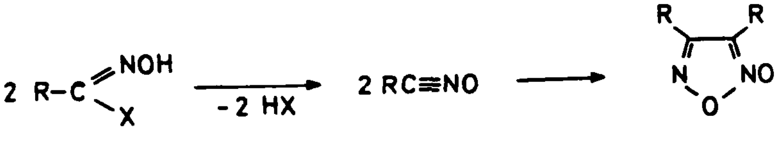


The chlorination of chloral oxime gives tetrachloronitrosoethane 27 as a blue liquid, which deposits colorless crystals of trichloroacethydroximic acid chloride 28 on standing. No pentachloronitrosoethane was obtained.[117] Dehydrohalogenation of hydroximic acid halides formed in side-reactions in basic media may yield nitrile oxides, which may dimerize to furoxanes.[133,179-184]

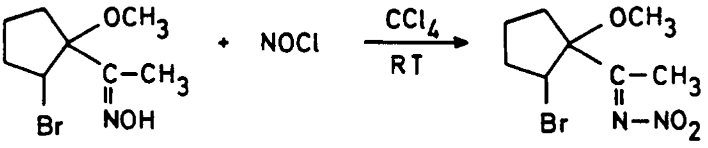


27

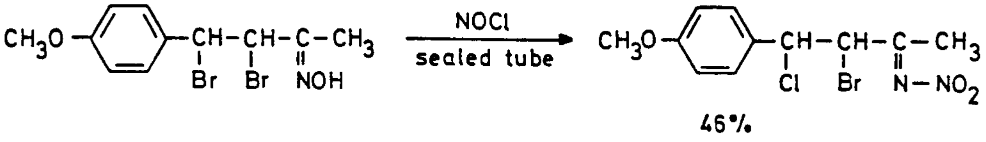
28



The addition of nitrosyl chlorides to oximes normally leads to *gem*-chloronitroso compounds, but exceptions are also known for this method;in special cases the oximino group is oxidized and nitrimines are isolated.[142]



The reaction of nitrosyl chloride with α,β-dibromooximes also gives chloronitrimines. This process consists of two separate reactions: replacement of the activated bromine by chlorine and oxidation of the oximino function to a nitrimine.[143]



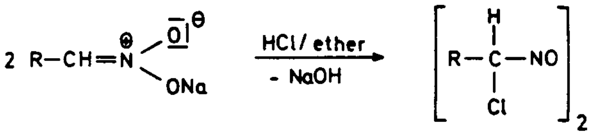
b) From Nitro Compounds

Only a few examples for the preparation of nitroso compounds by reduction of nitro compounds are described because of the difficulty in stopping the reaction at the correct stage.[167] Trichloronitrosomethane has been prepared by cathodic reduction of trichloronitromethane in yields up to 70%.[168]

$$Cl_3C-NO_2 \xrightarrow[EtOH/H_2SO_4]{Electrolysis} CCl_3NO$$

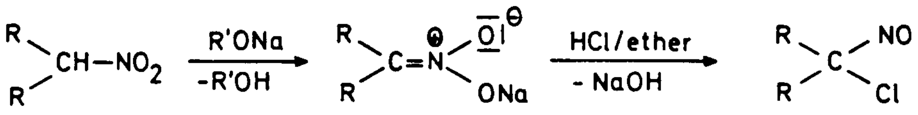
29

Dimeric α-chloronitrosoethane is reported to be formed by treatment of the sodium salt of nitroethane with excess hydrogen chloride.[169]



30

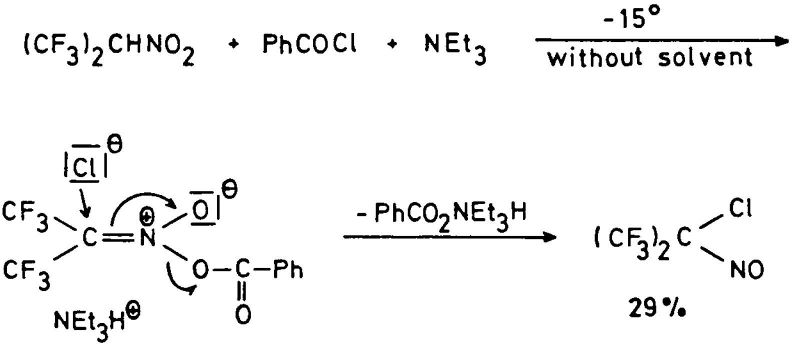
If R is an acceptor group (R = COOH, COOR, CN, Ph) only the corresponding hydroximic acid chlorides can be isolated.[169,170] Monomeric chloronitroso compounds, however, have been obtained in a similar way from α-disubstituted nitro compounds in good yield.[171]



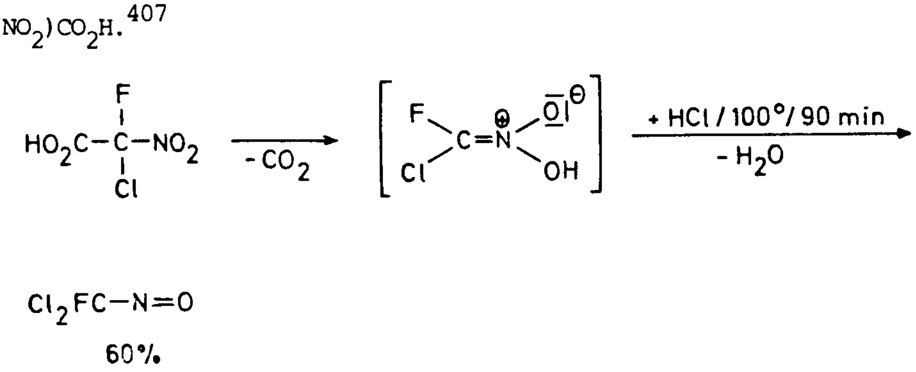
R = CH_3 (90%)

R = $-(CH_2)_5-$ (93%)

The reaction of polyfluoronitroalkanes containing an acidic hydrogen atom with benzoyl chloride in the presence of triethylamine gives α-chloronitrosoalkanes and, as a secondary product, the corresponding ketoxime.[172]

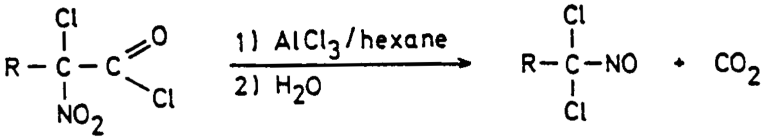


When chlorofluoronitroacetic acid is heated with 21% hydrochloric acid dichlorofluoronitrosomethane 31 is formed. The aci-form of the nitro compound is thought to be an intermediate.[173] The same reaction occurs with $FCH(NO_2)CO_2H$.[407]



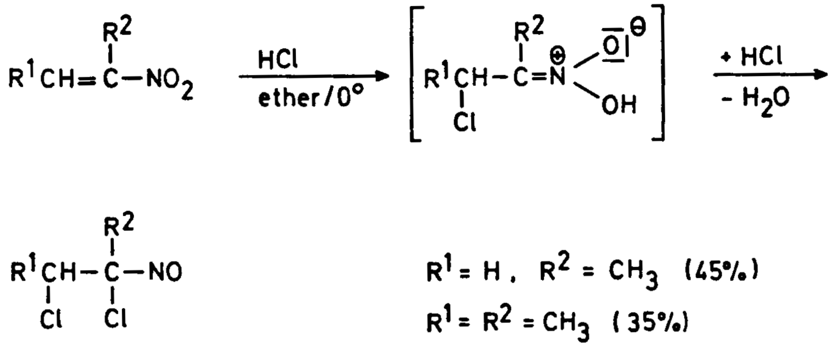
31

α-Nitrocarboxylic acid chlorides, e.g. chloronitroacetyl chloride or dichloronitroacetyl chloride are converted to chloronitroso compounds 32 and 33 in the presence of $AlCl_3$ or AlF_3.[174]



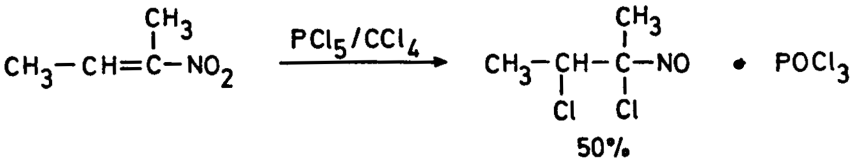
32 R = H (42-48%, as dichloroformoxime)
33 R = Cl 50%

From α-substituted nitroalkenes and hydrogen chloride, 1,2-dichloronitroso compounds have been prepared. It was suggested that the initial step is a 1,4-addition of hydrogen chloride to the nitroolefin.



$R^1 = H,\ R^2 = CH_3$ (45%)
$R^1 = R^2 = CH_3$ (35%)

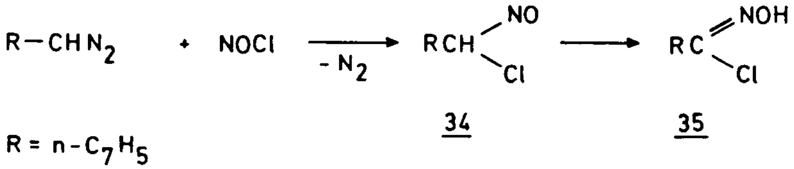
If an α-hydrogen is present ($R^2 = H$), the corresponding α-chlorohydroxamic acid chlorides are formed.[175] The conversion of nitroolefins into 1,2-dichloronitroso compounds may be achieved also by reaction with phosphorus pentachloride.[176]

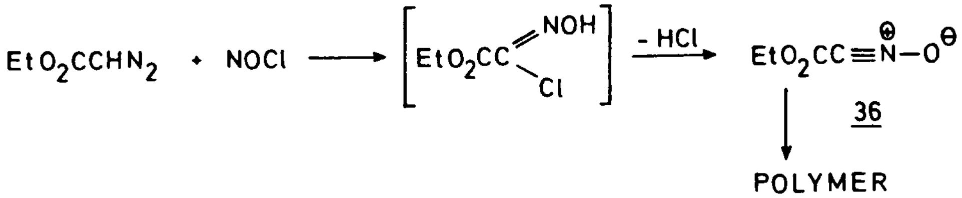


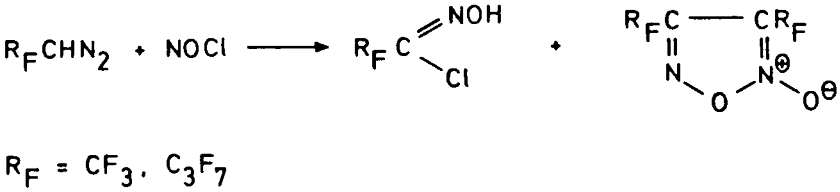
c) From Diazoalkanes

α-Chloronitroso compounds should be the primary reaction products of diazo compounds with NOCl. However, they have been isolated only in a few cases; thus, the deamination of *n*-octylamine with nitrosyl chloride in aprotic solvents gave two main products, 1-chlorooctane and 1-chloro-1-nitrosooctane 34, which rapidly rearranged to octanoyl chloride oxime 35. Compound 34 was also shown to be one of the products from the reaction between diazooctane and nitrosyl chloride.[185] The formation of diazoalkanes from primary amines and nitrosyl chloride in aprotic solvents is well documented.[185,186] Nitrosyl chloride converts ethyl diazoacetate into ethyl chloroacetate and a polymer believed to have arisen from nitrile oxide 36.[187] Nitrosyl chloride reacts with two moles of perfluoroalkyl diazomethanes in an analogous way to form hydroximoyl chlorides and the dimers of the nitriloxides, furoxanes, the former predominating.[188]

$$2\ RCH_2{-}NH_2 + NOCl \longrightarrow RCHN_2 + H_2O + RCH_2NH_3^{\oplus}\ Cl^{\ominus}$$

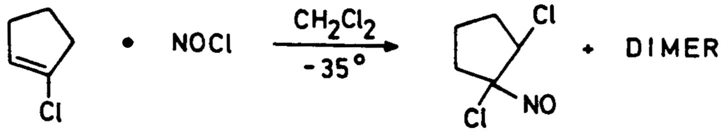




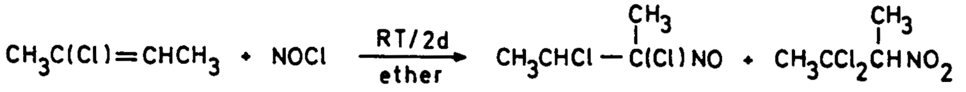


d) Chloronitrosation of Haloalkenes

In general, chloronitrosation with nitrosyl chloride without catalysts and without irradiation takes place only with olefins highly reactive in electrophilic additions. In the reaction of 1-chlorocyclopentene 37 with nitrosyl chloride, 1,2-dichloronitrosocyclopentane is formed as a mixture of the monomeric and dimeric forms.[189] The reaction of 2-chloro-2-butene with NOCl in a sealed tube gives 2,3-dichloro-2-nitrosobutane 38 and 2,2-dichloro-3-nitrobutane 39. The formation of the nitro derivative has been explained by a radical process.[189]



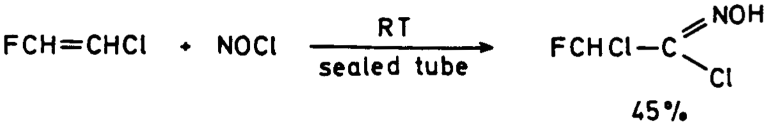
37 58% 19%



$$CH_3C(Cl){=}CHCH_3 + NOCl \xrightarrow[\text{ether}]{RT/2d} CH_3CHCl{-}\overset{CH_3}{\overset{|}{C}}(Cl)NO + CH_3CCl_2\overset{CH_3}{\overset{|}{C}}HNO_2$$

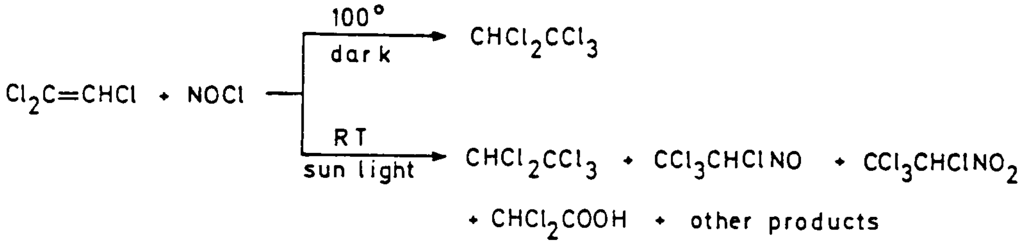
38 35% 39 42%

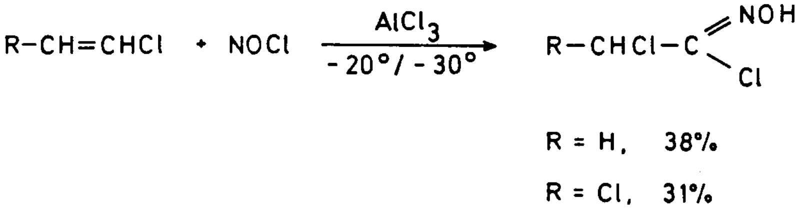
Prolonged standing (3-15 days at 20°) of mixtures of nitrosyl chloride and chloro- or fluoroethenes in sealed tubes did not give nitroso compounds. Instead, nitro compounds along with other products were isolated.[190] Only in the case of 1-chloro-2-fluoroethene did nitrosochlorination occur; the hydroximic acid chloride 40 was isolated.[191] In the dark and above 100°,

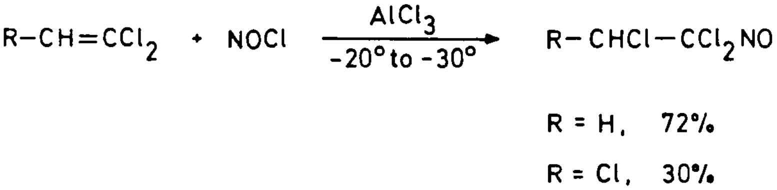


40

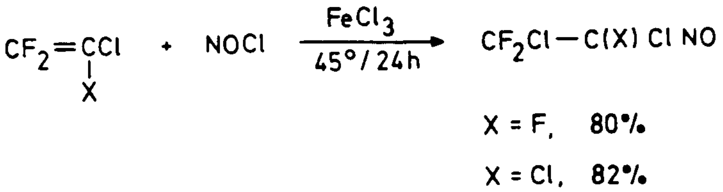
nitrosyl chloride behaves as a chlorinating agent; in sunlight at room temperature it reacts as a chlorinating, nitrosating, nitrating and oxidizing reagent.[192] Tetrachloroethene yields hexachloroethane, pentachloronitrosoethane and tetrachloro-2-(pentachloroethyl)-1,2-oxazetidine. With $AlCl_3$ as a catalyst, chloronitrosation of chloro-, dichloro-, trichloro- and tetrafluoroethenes has been achieved; tetrachloroethene failed to react.[193]







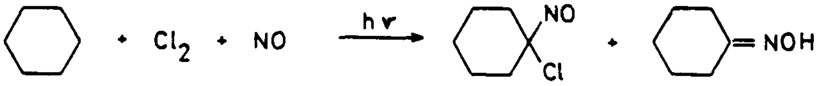
The addition proceeds with anti-Markovnikov orientation and is accompanied by telomer formation. The nitrosochlorination of fluorochloroethenes may be achieved also in the presence of $FeCl_3$ at 45° in a flow reactor.[194]



α-Halonitroso derivatives have also been obtained by photochemical reactions of nitrosyl chloride with haloethenes.[194]

e) Photochemical Syntheses

The photochemical gas-phase reaction of an alkane with nitric oxide and chlorine or with nitrosyl chloride may lead to bis(nitrosoalkanes) and gem-chloronitroso compounds and oximes, depending on the reaction conditions and the concentration of starting materials.[101,102,195,103] Trichloronitrosomethane 41 has been prepared by irradiation of an equimolar mixture of nitrosyl chloride and chloroform.[197] High-energy electron radiation-induced reactions of nitric oxide with tetrachloromethane or bromotrichloromethane gave 41, while dichloronitrosomethane, dichloroformaldoxime and 41 were obtained from chloroform.[198,199]



$$XCCl_3 + NO \xrightarrow{\beta\text{-rays}} \underset{\mathbf{41}}{Cl_3CNO} \qquad X = Cl,\ Br$$

f) Other Methods

One of the syntheses of trihalonitrosomethanes (41 or 42, resp.) involves a two-step reaction starting with methyl trihaloacetate and hydroxylamine. Thermal decomposition of the primary products, trihaloacethydroxamic acids, gives 41 (or 42) and paraformaldehyde as the main products.[200] Compound 41 was prepared first by the reaction of trichloromethylsulfinic acid with nitric acid at relatively high temperatures.[201, 202] An improved low-temperature synthesis from sodium trichloromethanesulfinate and nitrosyl chloride has been reported.[88, 203]

$$X_3CCOOCH_3 \xrightarrow{NH_2OH} X_3C{-}CONHOH \xrightarrow{\Delta} X_3CNO + CH_2O$$

X = Cl, 85%   41, X = Cl, 62%

X = F, 76%   42, X = F, 63%

$$Cl_3C{-}SO_2Na + NOCl \longrightarrow \underline{41} + SO_2 + NaCl$$

g) α-Fluoronitroso Compounds by Special Methods

As reported before, a comprehensive review[6] of the synthesis and properties of fluoronitroso compounds, covering the literature up to 1981, has been published. The intention here is to update this review.

i) via Radical Reactions

Photochemical nitrosation of dichlorofluoromethane and chlorodifluoromethane with nitrosyl chloride afforded the corresponding fluoronitroso compounds 43 or 44 respectively.[196]

$$R{-}H + NOCl \xrightarrow[\text{500W mercury arc}]{h\nu} R{-}N{=}O + HCl$$

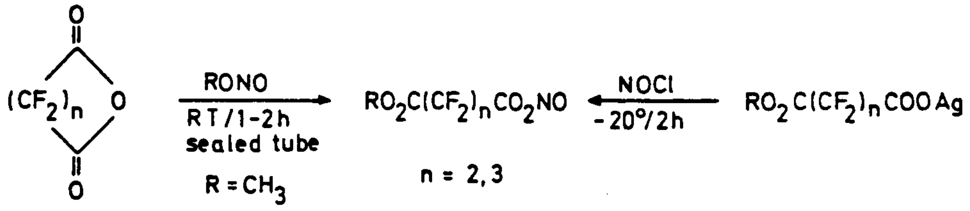
$$R = CCl_2F(\underline{43}),\ CClF_2(\underline{44})$$

Analogues treatment of trifluoromethane and formyl fluoride failed to give the corresponding nitroso compounds. CF_3NO has been prepared by the photochemical reaction of CF_3I with an excess of NO in the presence of Hg.[283,381]

ii) Decarboxylation of Perfluoroacyl Nitrites

Compound 44 was prepared in a one-pot reaction from nitrosyl chloride and sodium chlorodifluoroacetate.[204] Nitrite esters of perfluorosuccinic and perfluoroglutaric acid are easily prepared from the corresponding diacid anhydrides and methyl nitrite in nearly quantitative yields.[205-207] The same products were obtained in yields of 85-95% by the nitrosation of the silver salts of the monoalkyl perfluorodicarboxylates with nitrosyl chloride.[208,382] Thermolysis under reduced pressure (yields 38-45%), pyro-

$$ClF_2CCOONa + NOCl \xrightarrow[\text{diglyme}]{148^\circ/2\,h} \underset{\underline{44}}{ClF_2CNO} + NaCl + CO_2$$

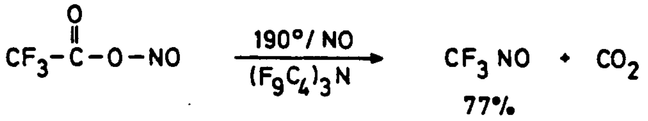


lysis or UV irradiation (yields 20-47%) of these nitrite esters gave the corresponding nitroso compounds.[203,382] The nitroso esters may be converted into the corresponding acids by hydrolysis in neutral media[205] or in boiling acetic acid.[208]

$$RO_2C(CF_2)_n{-}CO_2NO \xrightarrow[-CO_2]{\Delta \text{ or } h\nu} RO_2C(CF_2)_nNO$$

$$RO_2C(CF_2)_n{-}NO \xrightarrow[\text{or } 70\%\ CH_3COOH/\text{reflux}/40\,\text{min}]{H_2O/RT/4\text{-}5\,d} \underset{70\text{-}75\%}{HO_2C(CF_2)_nNO}$$

Trifluoronitrosomethane 42 has been prepared in 77% yield by pyrolysis of nitrosyl trifluoroacetate in a flow of nitrogen monoxide at 190^o using refluxing perfluorobutylamine as a diluent.[209] Other perfluoroalkylnitroso compounds (C_1-C_{12}) may be obtained analogously.[210]

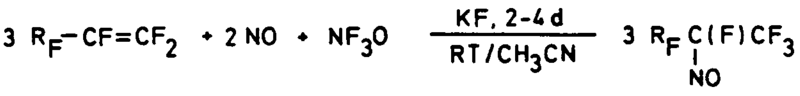


$$CF_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}NO \xrightarrow[(F_9C_4)_3N]{190°/NO} \underset{77\%}{CF_3NO} + CO_2$$

42

iii) Addition of Nitrosyl Compounds (NOX) to Fluoroalkenes

Trifluoramine oxide has been found to react rapidly with nitric oxide to give nitrosyl fluoride. This reaction has been used as an in situ



$$3\ R_F{-}CF{=}CF_2 + 2\,NO + NF_3O \xrightarrow[RT/CH_3CN]{KF,\ 2\text{-}4\,d} 3\ R_F\underset{NO}{\underset{|}{C}}(F)CF_3$$

R_F = n-C_5F_{11} (yield 78%), SF_5 (77%), OC_2F_5 (58%)

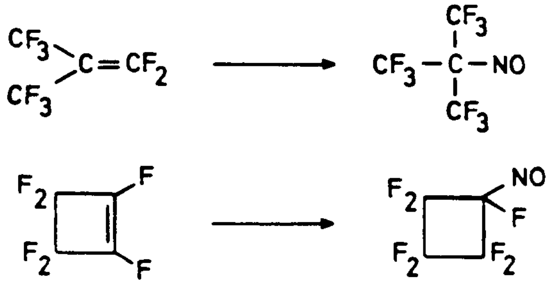
source of nitrosyl fluoride to synthesize α-fluoronitroso compounds from fluoroalkenes.[211]

The preparation of perfluoro-2-nitrosopropane 45 from hexafluoropropene and nitrosyl chloride via the indirect "silver salt route" proved to be highly useful.[212]

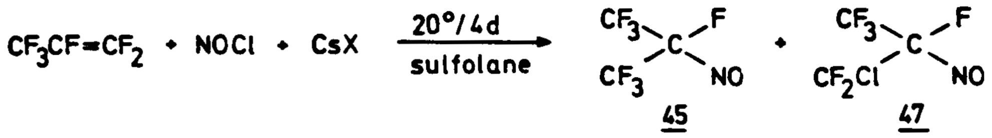
$$CF_3-CF=CF_2 \xrightarrow[\substack{\text{CH}_3\text{CN/RT/1h} \\ \text{sealed tube}}]{\text{KF/CF}_3\text{COOAg}} (CF_3)_2CFAg$$

$$\xrightarrow[20^\circ/2\text{h}]{\text{NOCl}} \underset{\underline{45}}{(CF_3)_2CFNO} \quad (80\,\%\ \text{over all})$$

The method works also well for the following conversions.[213] Perfluoronitrosoalkanes prepared by this route from perfluoroalkenes are interesting intermediates for the conversion of these alkenes into perfluoroketoximes (e.g. 45 46).[214] Direct fluoride-initiated reaction of hexafluoropropene with nitrosyl chloride and cesium fluoride was found to give an approx. 6:1 mixture of heptafluoro- and 1-chlorohexafluoro-2-nitrosopropane (45 and 47). When CsF was substituted by CsCl, 47 could be isolated in 91% yield.[212]



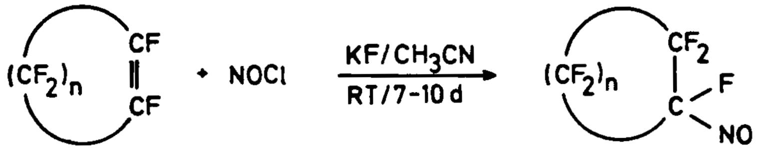
$$CF_3CF=CF_2 \longrightarrow \underset{\underline{45}}{(CF_3)_2CFNO} \xrightarrow{\text{KHSO}_3/20^\circ} \underset{\substack{62\,\% \\ \underline{46}}}{(CF_3)_2C=NOH}$$



X = F : 6 : 1

X = Cl : — 91%

Hexafluorocyclobutene and octafluorocyclopentene reacted with an excess of nitrosyl chloride in the presence of excess KF to give an 80% yield of heptafluoronitrosocyclobutane 48 and nonafluoronitrosocyclopentane 49, respectively.[215] Unlike CF_3NO, both cyclic nitrosofluoroalkanes were found to be stable monomers.



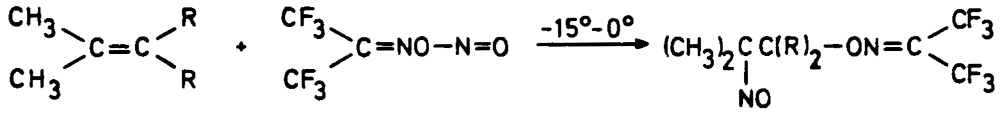
n = 2, 3

80%

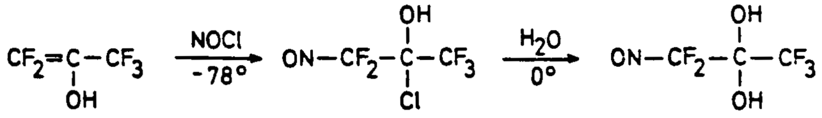
48 : n = 2

49 : n = 3

Hexafluoroacetone oxime nitrite adds to 2-methylpropene and tetramethylethene at -15° to 0° to give nitrosoalkenes containing the hexafluorodimethylmethyleneaminoxy group.[217] NOCl reacts with the enol of pentafluoroacetone without solvent at -78° to give the corresponding nitroso compound 51 which is stable at -60° but decomposes on warming to room temperature. The corresponding ethyl enolether does not react with NOCl either at -78° nor at 25°.[216] Hydrolysis of 50 yielded the gem-diol 51.



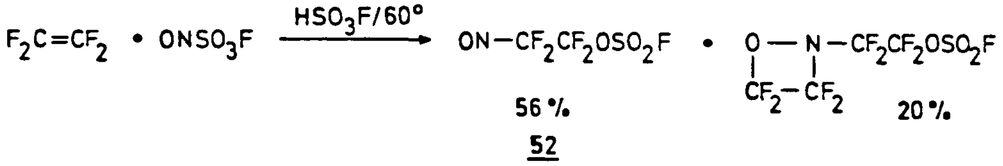
R = H, CH_3



50

51 65%

Nitrosyl fluorosulfate does not react in inert solvents with tetrafluoroethene in the absence of strong acid. However, when an excess



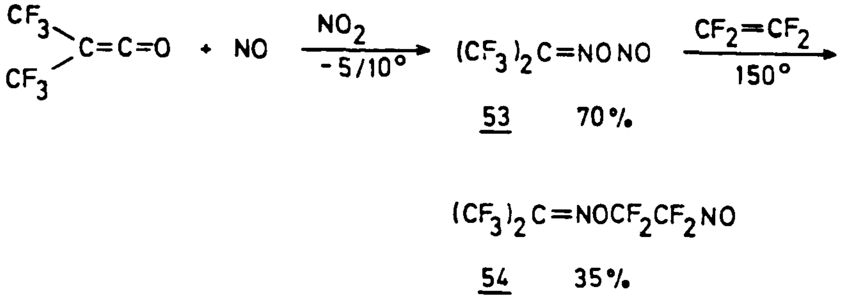
of tetrafluoroethene is bubbled through a mixture of nitrosylfluorosulfate and fluorosulfonic acid dissolved in tris(perfluorobutyl)amine, the blue, liquid nitroso compound 52 is collected from the gaseous current in a cooled trap. From the remaining solution, the 2+2 cycloaddition product of tetrafluoroethene and 52 could be isolated.[218] The addition of nitrosylfluorosulfate to trifluoroethene takes place analogously.[219]

$$CHF{=}CF_2 \;+\; ONO_3SF \xrightarrow{20^\circ} ON{-}CHF{-}CF_2O_3SF$$

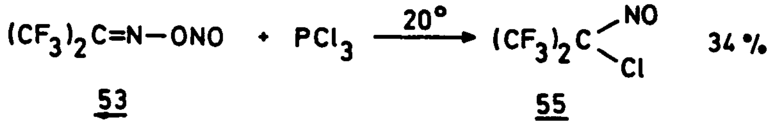
49 %

iv) Other Methods

Treatment of hexafluorodimethylketene with nitrogen monoxide in liquid NO_2 gave perfluoroacetone oxime nitrite 53, which reacted with tetrafluoroethene at 150° to yield the addition product 54.[220] With PCl_3, 53 gave the



gem-chloronitroso compound 55 among other products.[220] Trifluoronitrosomethane is formed in the reaction of $(CH_3)_3Sn(ONO_2)$ with $(CF_3)_2Cd$(diglyme) as the only volatile product.[221]



$$(CF_3)_2C{=}N{-}ONO + PCl_3 \xrightarrow{20°} (CF_3)_2C(NO)(Cl) \quad 34\,\%$$

4. REACTIONS

The often cited analogy between nitroso and carbonyl compounds - nucleophilic additions as the most common reaction type in both cases - holds only as a first approximation; in many cases, subsequent transformations or another course of the first step (e.g. electron transfer instead of polar addition) change the results of a reaction entirely. For α-halogenated nitroso compounds, this is especially true if a single chlorine (or bromine) is the α-substituent whereas perfluoro derivatives behave somewhat more "normally", although these derivatives show many other types of reactions unknown in the case of carbonyl compounds.

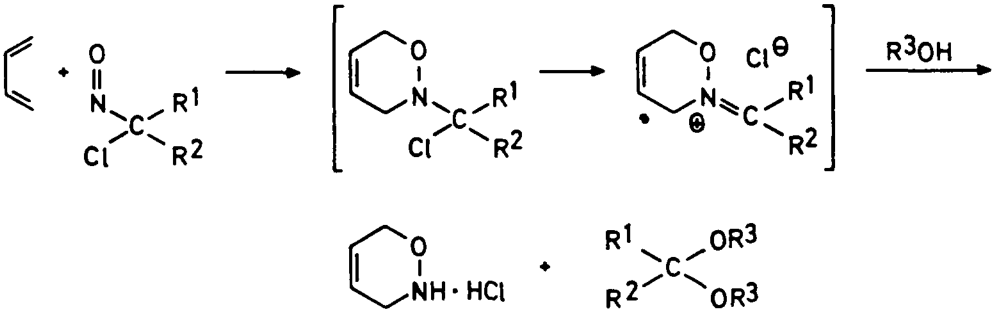
Generally, nitroso compounds and their α-halogeno derivatives are much more prone to pericyclic reactions than aldehydes or ketones; they are among the most reactive dienophiles and some derivatives undergo ene reactions readily. Therefore, this review will discuss these reactions first. 2+2 Cycloadditions of perfluoronitroso compounds form a special topic; as stated earlier, only new developments which have been disclosed since the publication of the Russian review article[6] will be covered.

Nucleophilic additions, reactions with radicals,/(primary) nitroxide formation and oxidation-reduction reactions are discussed in other sections of this chapter which summarizes also some transformations which can be classified only arbitrarily.

a) Cycloadditions and Pericyclic Reactions

i) Diels-Alder Reactions of α-Chloronitroso Compounds

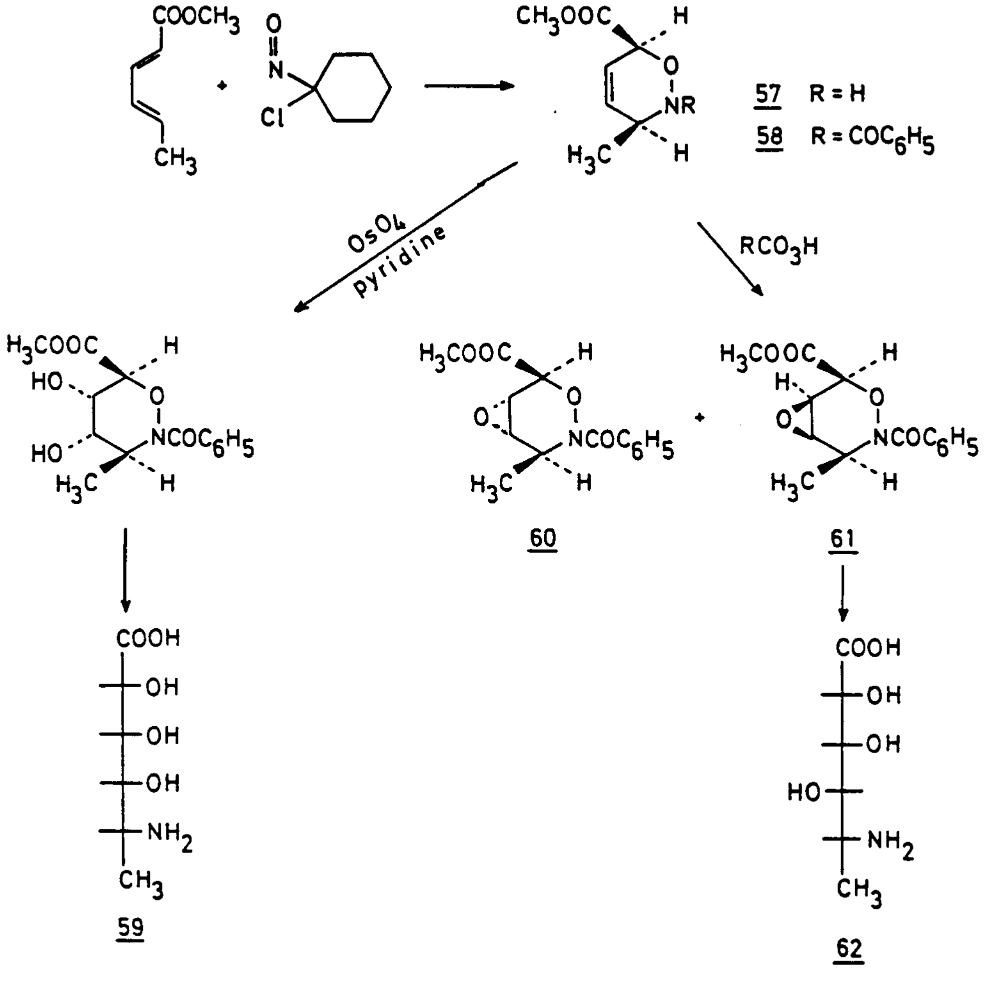
Since α-chloronitroso compounds have been found to act as dienophiles in Diels-Alder reactions by Wichterle,[222] many papers dealing with this reaction have appeared. The subject has been investigated extensively by the groups of Wichterle,[222-228] Arbusov,[229-232] Klamann[233-235] and Kresze[149,150,236-251] and the results have been reviewed several times.[252-255] The first formed cycloadducts ionize to give immonium salts.



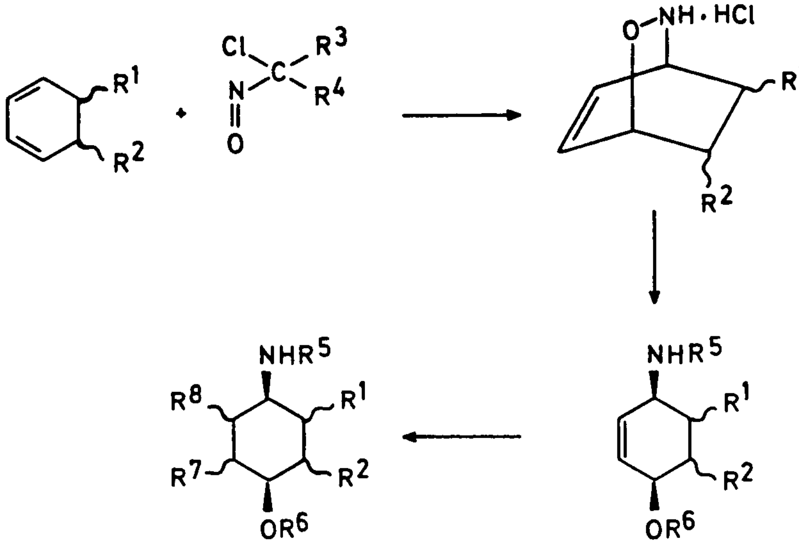
56

In the presence of an alcohol in the medium, these salts are solvolysed to the hydrochlorides of 3,6-dihydrooxazines unsubstituted on the N atom. The reactivity of the NO-compound depends on the electron acceptor properties of the α-substituents. Electron-withdrawing substituents increase the reactivity. Thus, CCl_3NO and especially CF_3NO are known to be among the most reactive α-halonitroso dienophiles.[6,234,236] The regiochemistry of the hetero-Diels-Alder reaction, including that of 1-chloro-1-nitroso compounds, has been surveyed several times.[119,236,237,254,256] In general, the orientation in the cycloaddition depends on steric as well as polar factors. The alkyl group bonded to nitrogen will allow this atom to approach more readily the last bulky end of the diene. On the other hand, the nitrogen atom binds preferentially to the carbon atom of the 1,3-diene with the maximal electron density.

The 3,6-dihydro-1,2-oxazines are widely used in the synthesis of natural products or heterocycles. Most of the reactions will begin with the cleavage of the NO bond, thus providing amino alcohols, which are useful starting materials for the synthesis of aminosugars, inosamines or other polyhydroxyamino derivatives.

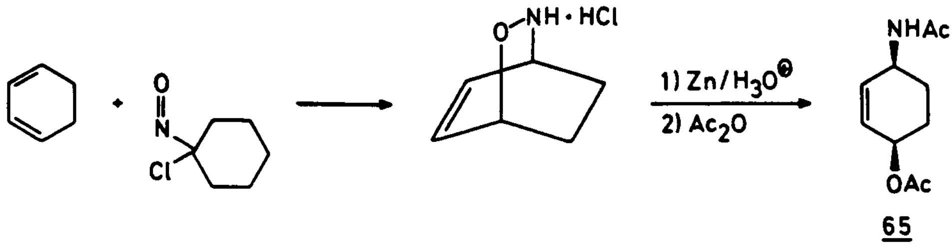


The first route to some aminosugar derivatives was devised by Belleau and Yum-kin Au-yang.[257] The reaction sequence involves a Diels-Alder condensation between methyl sorbate and 1-chloro-1-nitrosocyclohexane to give the adduct 57. Selective hydroxylation affords, stereospecifically, different amino sugar derivatives. Thus, hydroxylation of the N-benzoyladduct 58 with osmium tetroxide followed by hydrolysis and catalytic hydrogenolysis gives the amino acid 59 of the allose series, while epoxidation to a 1:1 mixture of the epoxides 60 and 61, oxirane ring opening with formic acid, methanolysis and, finally, hydrogenolysis leads to the amino acid 62 of the gulose series. Kresze and coworkers have utilized the adducts of 1-chloro-1-nitrosocyclohexane with various 1,3-cyclohexadienes as key intermediates in the synthesis of inosamine and inosamine derivatives.[238-243,245-250] Reductive cleavage of the NO-bridge of these cycloadducts leads to the *cis*-4-aminocyclohexenols 63. Simple but highly specific reactions on the double bond afford the polyhydroxyamines 64 which may serve, *inter alia*, as substrates in the mutasynthesis with *streptomyces griseus*. For example, cis-hydroxylation and acetylation of compound 65 gives the 2t,3t,4c-trisacetoxy-1r-amino



64

63



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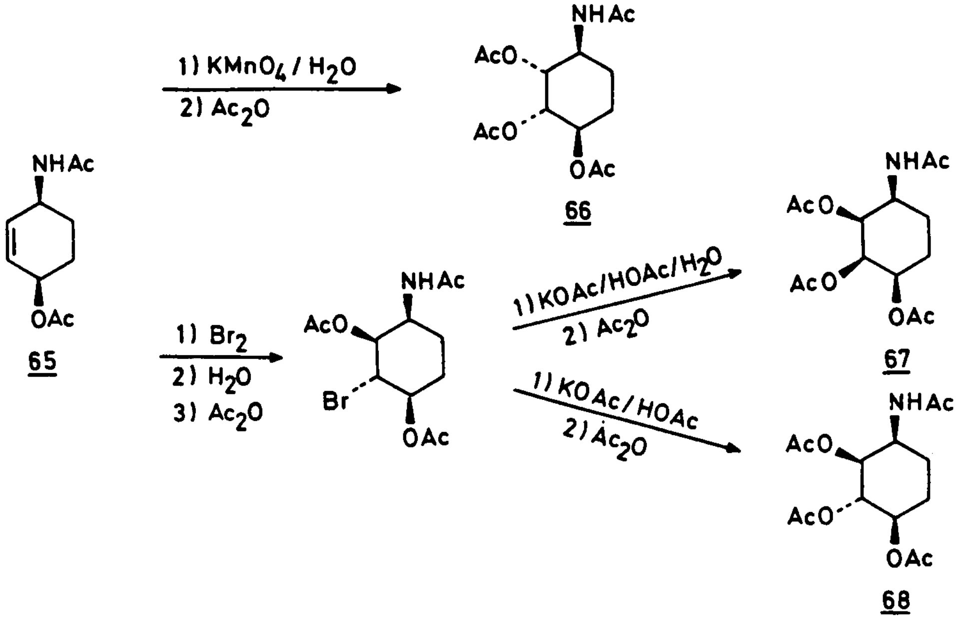
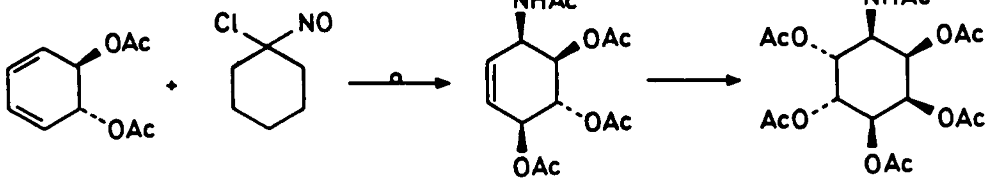


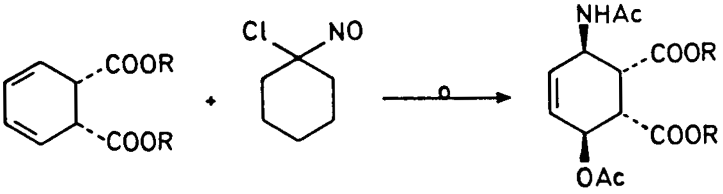
65 66 67 68

derivative 66 while reaction with Br_2 with neighboring group participation and solvolysis under different conditions leads to the all-*cis*-67 or the 2c,3t,4c-compound 68, respectively.[238,246] In an analogous way, konduramine F1 69 and chiroinosamine-1-hexaacetate 70 have been synthesized from adduct 63 (R^1,R^2 = OAc).[239,240,243,247]



69 70

Deacylated 69 is incorporated in some S. griseus mutants, the resulting aminoglycoside products show antibiotic activity.[248,258] The Diels-Alder reaction of cis-1,3-cyclohexadiene-5,6-carboxylic acid esters as dienes results in formation of 1-acetamido-4-acetoxy-2-cyclohexene-trans,trans-5,6-dicarboxylates 71, which may be transformed into many isomeric tris-hydroxyaminoderivatives.[241] Another of the stereoselective syntheses of



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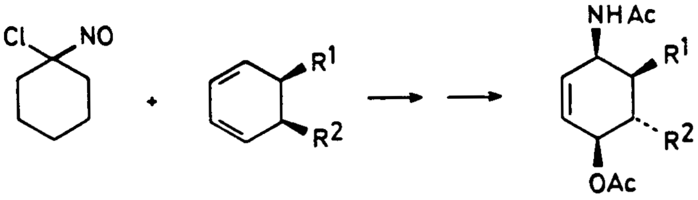
inosdiamine derivatives proceeds via epoxidation on the double bond in the intermediate cyclohexene derivatives 63.[238,241,243] An alternative synthesis



72 R^1 = OH, R^2 = N_3

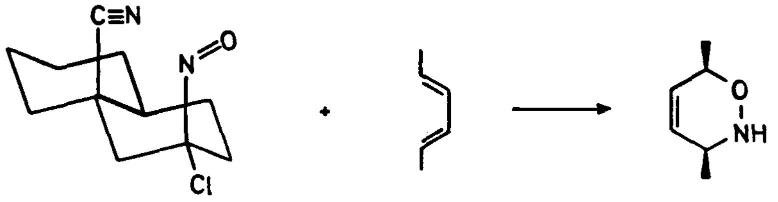
73 R^1 = OAc, R^2 = NHAc

74 R^1 = OAc, R^2 = NHAc

75 R^1 = NHAc, R^2 = OAc

of inosamines has been reported by Kresze, Weiss and Dittel.[243] Diels Alder reaction of trans-6-azido-5-hydroxy-1,3-cyclohexadiene 72 or trans-6-acetamido-5-acetoxy-1,3-cyclohexadiene 73 and reduction affords the isomeric cis-1,4-aminoalcohols 74 or 75, respectively.

Asymmetric induction occurs in Diels-Alder-reactions with optically active α-chloronitroso compounds as starting materials. The first example reported by Nitsch and Kresze[148] involves the reaction of 2-chloro-2-nitroso-9-cyanodecaline 76 with excess trans,trans-2,4-hexadiene to yield 3,6-dihydro-3,6-dimethyl-1,2-oxazine 77 in 83% chemical yield and 39% ee.



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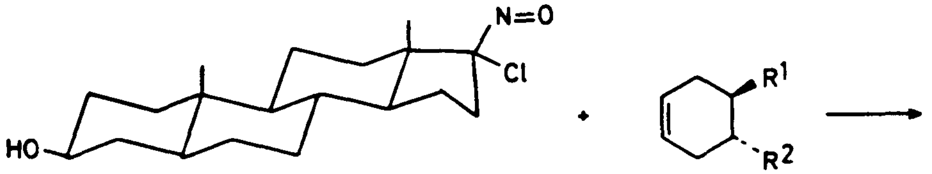
77

Sabuni, Kresze and Braun isolated optically pure 1R,3S-2-aza-3-oxa-[2.2.2]-bicyclo-$\Delta^{5,6}$-octenehydrochloride 79a from 17-chloro-17-nitroso-3-hydroxy-5α-androstane 78 and 1,3-cyclohexadiene.[149,251] Similarly, addition of



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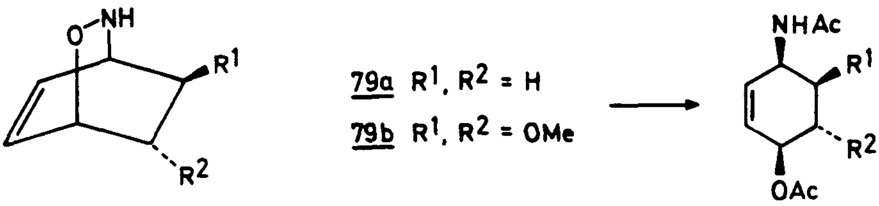
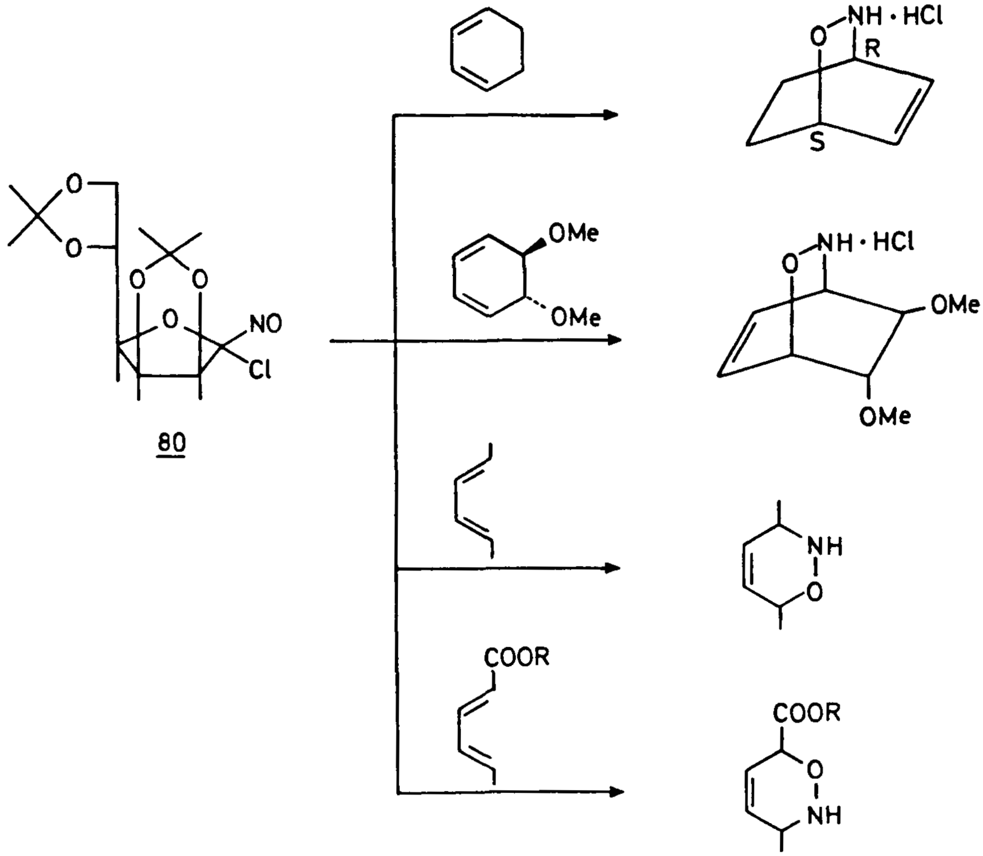


79a $R^1, R^2 = H$

79b $R^1, R^2 = OMe$

trans-5.6-dimethoxy-1.3-cyclohexadiene gives (+)-2-aza-3-oxa-[2.2.2]bicyclo-*trans*-7,8-dimethoxy-$\Delta^{5,6}$-octenhydrochloride 79b in 95% ee.[408]

Another chiral α-chloronitroso dienophile, 1-C-nitroso-2,3:5,6-di-O-isopropylidenemannofuranosylchloride 80 has proved to be highly reactive in Diels-Alder synthesis. It adds to various dienes to yield optically pure mono- and bicyclic oxazines[150,244], some of which have to be considered as potential starting materials for the synthesis of chiral aminosugar and inosamine derivatives.



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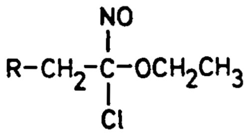
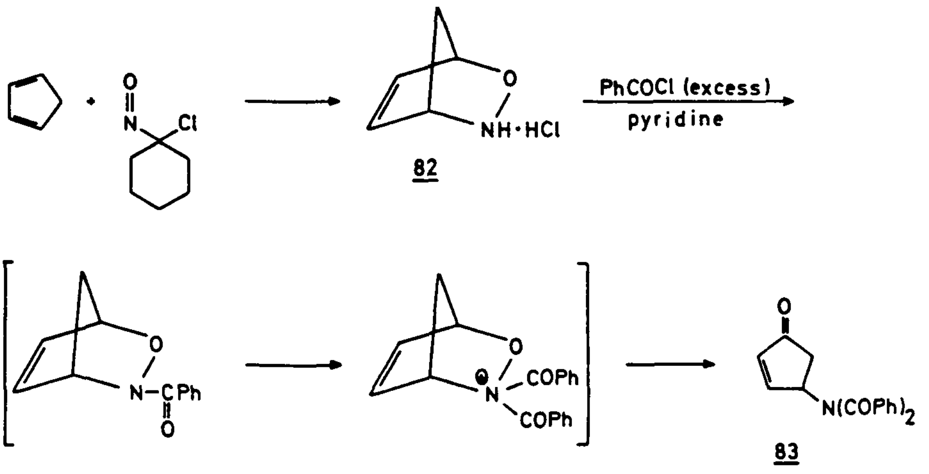
The dependence of reactivity in Diels-Alder reactions on polar effects is shown also by some simple α-chloronitrosoethers 81 which react rapidly under very mild conditions with various dienes, even with the usually sluggishly reactive ethyl sorbate.[244] 1,3-Cyclopentadiene adds to 1-chloro-1-nitrosocyclohexane to give 2-aza-3-oxa-bicyclo[2.2.1]heptane hydrochloride 82 in 89% yield.[259] This provides a novel route to diverse oxazabicyclopentenes. PGG-endoperoxide → PGE type cleavage (known in prostaglandin



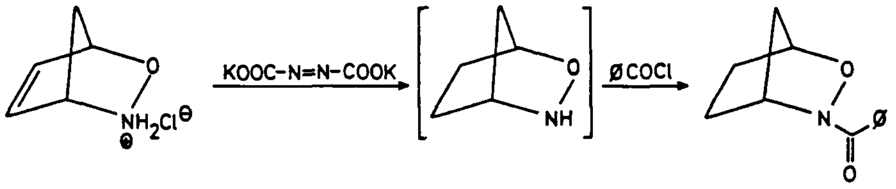
$$R{-}CH_2{-}\underset{\displaystyle Cl}{\overset{\displaystyle NO}{C}}{-}OCH_2CH_3$$

81 R = Cl, H, CH_3

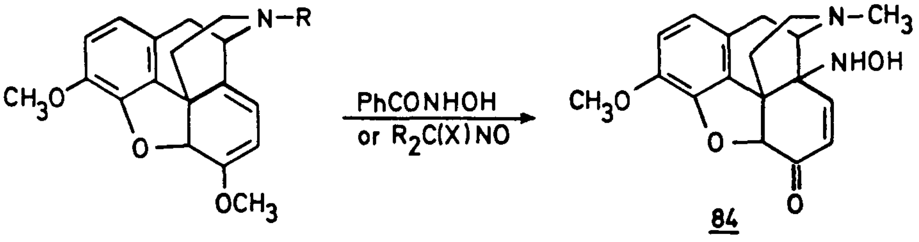
chemistry) to 83 is observed in the reaction of the free oxazine with excess



benzoyl chloride. Diimide reduction gives the parent oxazabicycloheptane system, which is directly related to PG-endo-peroxide.[259] Thebaine reacts

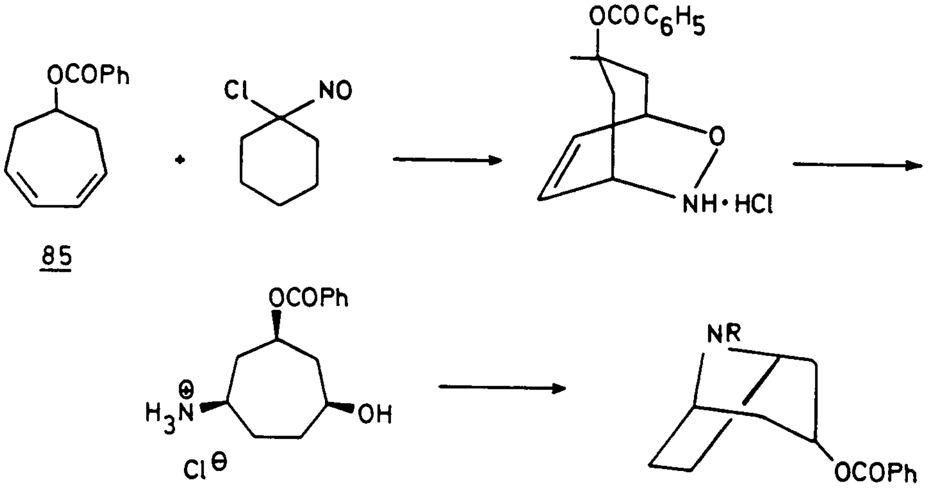


with 1-chloro-1-nitrosocyclohexane under oxidizing conditions to give 14-(hydroxyamino)codeinone, (84) which has analgesic properties.[260] Further



reduction of 84, methylation and bromoacetylation lead to the biological active 14β-(2-bromoacetamido)morphinone.[261]

A new synthesis of tropane alkaloids was recently reported by Kibayashi and coworkers.[262] The approach employs a Diels-Alder cycloaddition of cyclohepta-1,3-dienylbenzoate 85 with 1-chloro-1-nitrosocyclohexane, followed



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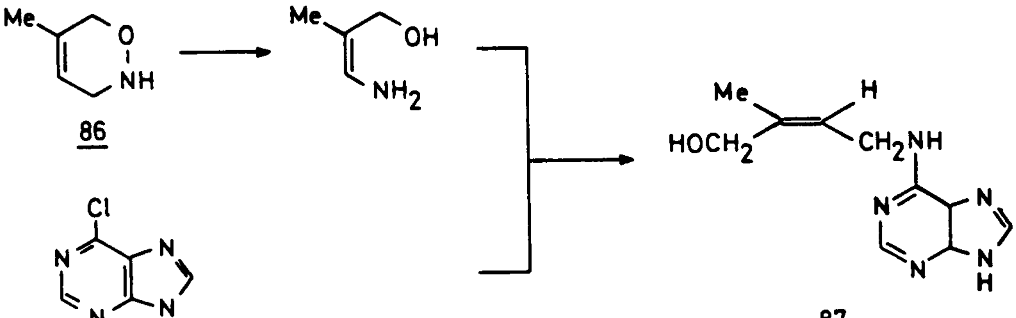
by reduction and intramolecular C-N bond formation, which leads to the tropane skeleton. Final deprotection reactions provide pseudotropine and tropacocaine. A total synthesis of the cell division stimulant cis-zeatin 87 has been described by Leonard.[263] This synthesis starts with the adduct 86 from isoprene and 1-chloro-1-nitrosocyclohexane. Kesler has prepared 2-oxa-3-aza-bicyclo[2.2.2]-$\Delta^{5,6}$-octene hydrochloride by Diels-Alder reaction of 2-chloro-2-nitrosopropane and 1,3-cyclohexadiene.[264]



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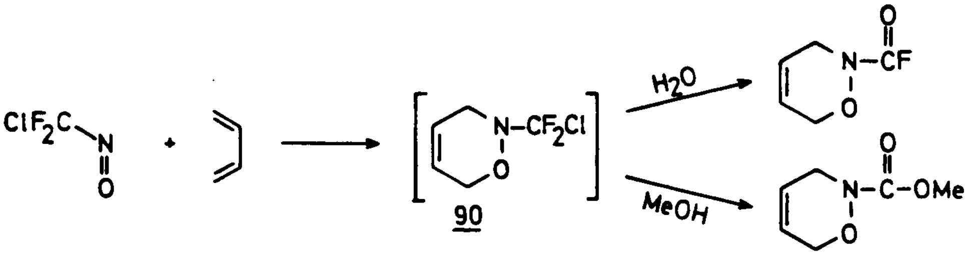
ii) Diels-Alder Reactions of α-Fluoronitroso Compounds

Trifluoronitrosomethane is known to be one of the most reactive dienophiles in Diels-Alder reactions. An extensive compilation of the material may be found in the previously published review.[6] A large part of the work on this subject has been done by the groups of Haszeldine, Banks and coworkers.[265-272] Trifluoronitrosomethane reacts easily with butadiene,[265] cyclopentadiene[270] and its C_6- and C_7-homologues, hexafluorobutadiene,[266] perfluorocyclopentadiene[269] and tetrafluoroallene dimer.[268] The addition of butadiene affords 3,6-dihydro-2-trifluoromethyl-1,2-oxazine 88 in nearly quantitative yield.

88

As Forkin et al. have shown, tetrafluoro-1-nitro-2-nitrosoethane (89) and butadiene react in similar way to give an N-substituted oxazine, while chlorodifluoronitrosomethane yields an unstable adduct 90, which can be solvolysed with water or methanol.[273,274,383] The same nitroso compounds undergo cyclo-addition with hexafluorobutadiene to form the corresponding N-substituted oxazines in yields up to 40% together with 1:1-copolymer, probably struc-

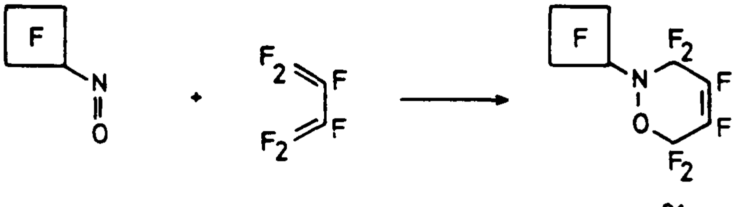
89



90

ture $[\text{-NROCF}_2\text{CF=CF=CF}_2\text{-}]_m$.[275]

The formation of copolymers is probably a peculiar feature of the reactions of fluorinated nitroso compounds with fluorine containing dienes, as many examples show[6]. Recently Marsden and Shreeve[215] isolated the N-substituted oxazines 91 and 92 in 35% yield from hexafluoro-1,3-butadiene and heptafluoronitrosocyclobutane or nonafluoronitrosocyclopentane, respectively.



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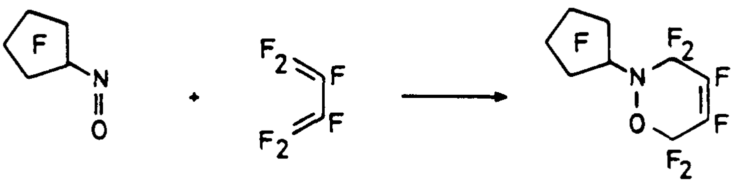

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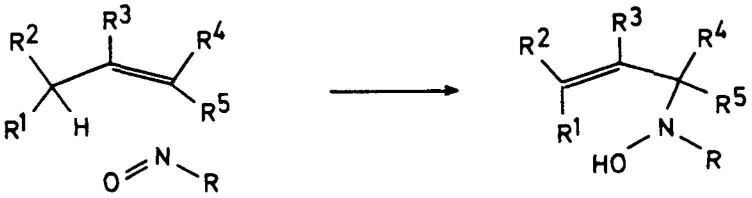
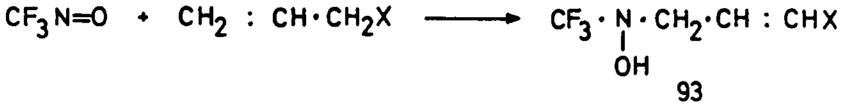
iii) Ene Reactions with α-Halonitroso Compounds

Reactions between aromatic nitroso compounds and alkenes with allylic CH bonds have been studied as early as 1910 by Alessandri.[276] Later, it was shown by Knight and coworkers[277] that the products - labile N-aryl-N-alkenylhydroxylamines - resulted from an addition/hydrogen abstraction process ("ene reaction"). In most cases, further transformations of these products occured. The most frequently investigated α-halonitroso compound in this respect is CF_3NO. Ene reactions of this compound with many alkenes have been described.[265,270,278,383] 2-Propenyl derivatives $CH_2{:}CH.CH_2X$ (X = Cl, Br,



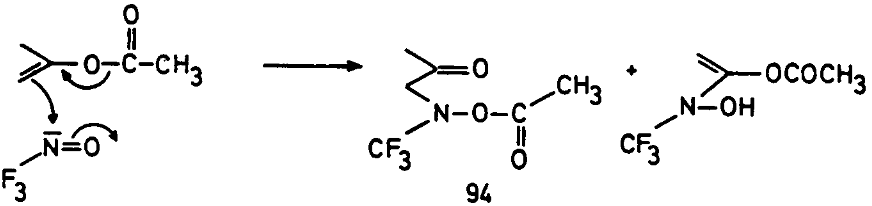
or CN) also give ene reactions with CF_3NO but they are much less reactive than the unsubstituted alkenes and yield mixtures of stereoisomeric adducts 93.[270]



$$CF_3N{=}O + CH_2 : CH{\cdot}CH_2X \longrightarrow CF_3{\cdot}\underset{OH}{N}{\cdot}CH_2{\cdot}CH : CHX$$

93

Reaction of CF_3NO with isopropenylacetate occurs fairly readily and results in a mixture of the expected ene product and the O-acetylhydroxylamine 94, formed possibly by a [2π + 2π + 2σ] process.[270] 1,4-Cyclohexadiene gives the adduct 95, apparently resulting from a Diels-Alder addition of the nitroso compound to the initially formed ene-adduct.[270] Acetylacetone gave a product $CF_3N(OH)CH(COCH_3)_2$ formally derived by an ene-reaction of the enol tautomer.[270]



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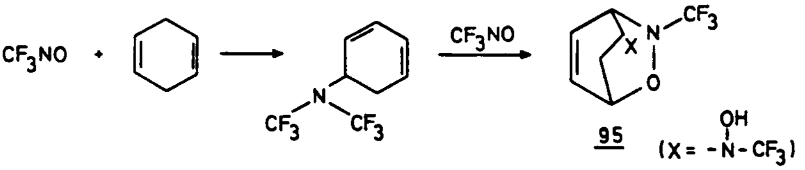
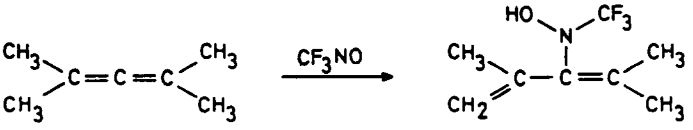
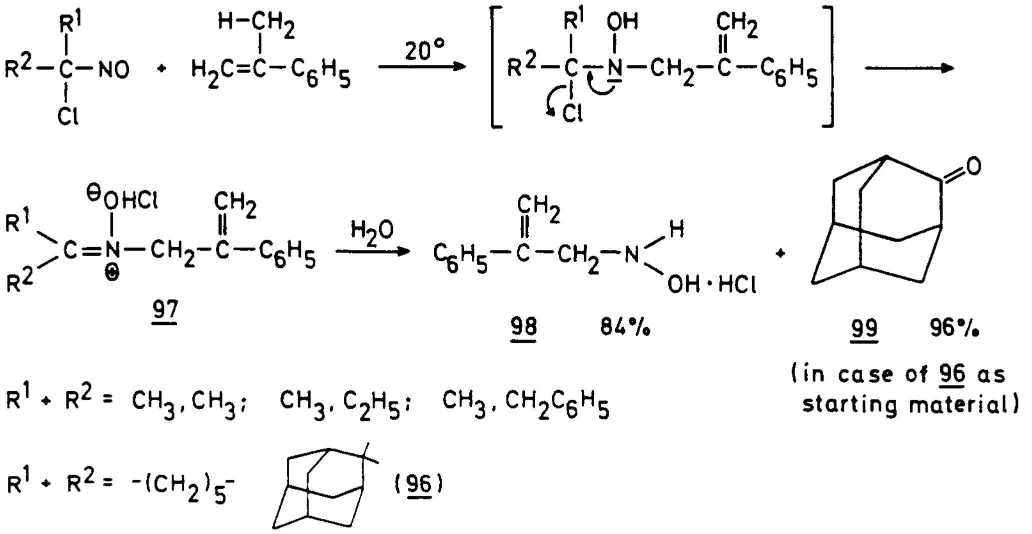


95

The double bond system of allenes often appears to be reactive in addition-hydrogen-abstraction reactions with various type of enophiles. But, among these, reactions with nitroso compounds are rarely encountered (ArNO[314]). A smooth ene reaction is observed between trifluoronitrosomethane and 2,4-dimethyl-2,3-pentadiene. Beside CF_3NO, only two examples of

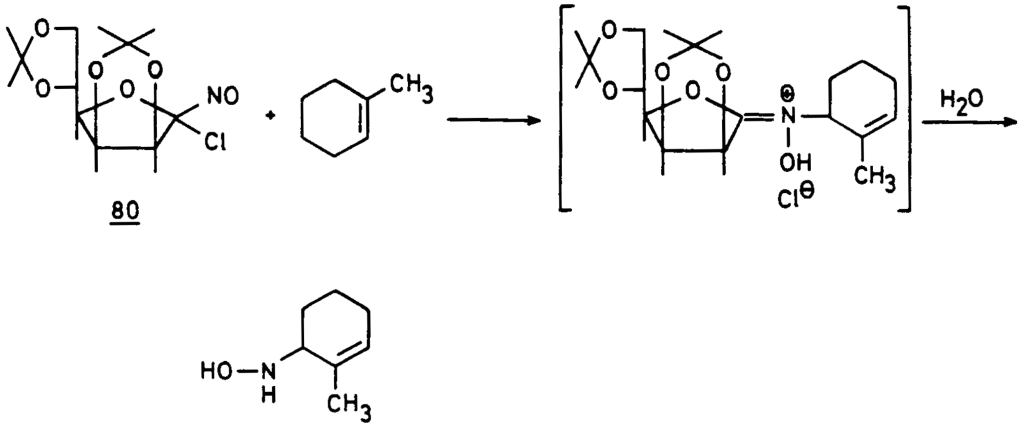


ene reactions of α-halonitroso compounds have been reported so far. Schenk and DeBoer[285] described the addition of several α-chloronitroso compounds to alkenes possessing allylic CH bonds. The products, nitrone hydrochlorides 97, most likely originate from an initially formed N-α-chloroalkyl-N-alkenylhydroxylamine; hydrolysis of 97 at room temperature afforded the hydroxylamine hydrochlorides (98) and the ketone, e.g. adamantanone (99).



Several chloronitroso compounds have been used, the most suitable reagent to undergo ene reactions was the adamantyl derivative 96. Its products were more stable and could be isolated more easily in pure form than those of other α-chloronitroso compounds. Nitrone hydrochlorides are also the reaction products of the ene reaction of tetramethylallene with α-chloronitroso compounds.[279]

The chloronitroso compound 80 derived from mannose undergoes ene reactions with various alkenes even more readily then 96; the resulting nitrone hydrochlorides are rapidly hydrolyzed to the hydroxylamines. These products, if chiral, are optically active; for the 1-methylcyclohexene derivatives 100, an optical yield e.e. > 80% was determined.[398]



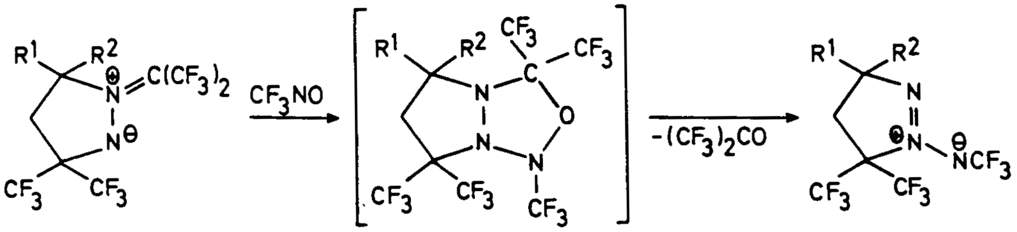
80

100

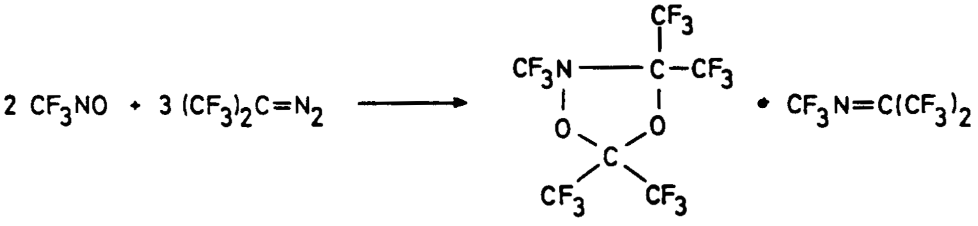
For reactions of CF_3NO with alkenes not possessing allylic CH bonds cf. p. 376.

iv) 2+3 Cycloadditions

There are only a few complex examples for the participation of halonitroso compounds in such processes; CF_3NO reacts with azomethineimines by dipolar cycloaddition and subsequent fragmentation.[280]

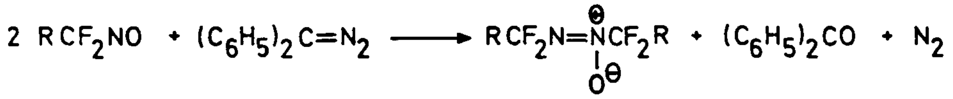


A sequence of [2+3]cycloadditions and eliminations seems to occur also during the interaction of CF_3NO with bis[trifluoromethyl]diazomethane.[281]



101

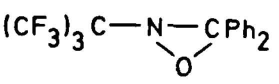
Addition of $(CF_3)_2CO$ increases the yield of the dioxazoline <u>101</u> to 53%. A somewhat similar sequence has been observed for the reaction of perfluoronitroso compounds with diphenyldiazomethane.[385] The reaction of diphenyl-



$$2\ RCF_2NO + (C_6H_5)_2C{=}N_2 \longrightarrow RCF_2N{=}\overset{\oplus}{N}(O^{\ominus})CF_2R + (C_6H_5)_2CO + N_2$$

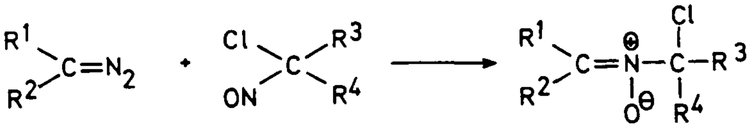
diazomethane with the perfluoro-2-nitrosopropane takes another course,[282] while with $(CF_3)_3CNO$ the oxaziridine <u>102</u> is obtained.[396] With CH_2N_2, CF_3NO

$$(CF_3)_2CF{-}NO + (C_6H_5)_2C{=}N_2 \xrightarrow[-78^\circ]{Et_2O} (CF_3)_2C{=}N{-}OCF(C_6H_5)_2$$



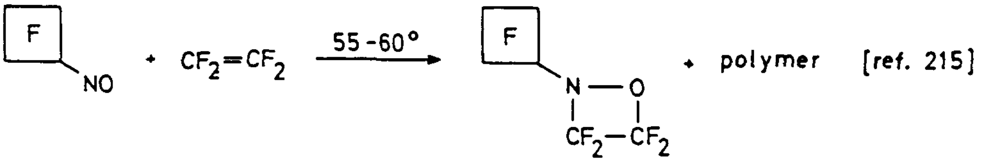
<u>102</u>

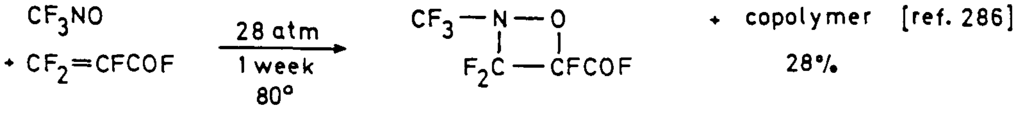
yields a copolymer $[-N(CF_3)-OCH_2-]_n$.[397] α-Chloronitroso derivatives with diazo compounds afforded unstable α-chloronitrones.[386]



v) Reactions with Fluoroalkenes

Whereas interaction of CF_3NO with isobutene or other alkenes leads to nitrosyl or <u>ene</u> addition products (cf. p. 372), its reaction with fluoroalkenes, especially $CF_2{=}CF_2$, gives 1:1 copolymers as the main products





("nitroso rubbers"[6]). In some cases, 1,2-oxazetidines[6,283,284] are observed. In the gase phase, $(CF_3)_3CNO$ yields mixtures of products with $CH_2{=}CF_2$[288] and $CF_2{=}CF_2$ probably *via* radical reactions;[378] in the last case; 35% of the oxazetidine derivative was found, N,N-bis(trifluoromethyl)amino alkines $(CF_3)_2NC{\equiv}CX$ (X = H, Br, CF_3, $N(CF_3)_2$, CH_3) give high yields of the 1:1 adducts (90°C, 3-14 days), mostly of the structure $(CF_3)_2N{-}CO{-}CX{=}NCF_3$, which are supposedly formed *via* 2+2 cycloadducts.[287]

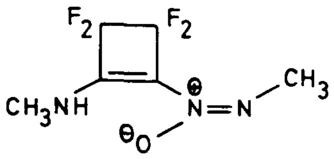
b) Reactions with Nucleophiles

(i) With Nitrogen Compounds

The reaction between primary amines and perfluoronitroso compounds (for a review of earlier work, see ref. 6) may proceed as a nucleophilic addition to the NO group. The group Alk may be also cycloalkyl, bi- and tricyclic derivatives such as adamantyl; diamino compounds also react, as well as fluorine substituted aniline derivatives.[290, 302] Other perfluoro nitrosoalkanes react analogously. The reactivity of the amino compound decreases with the decrease in basicity.[399] This is also true for the reactions of perfluoronitrosocyclobutane and perfluoronitroso cyclopentane with aniline derivatives (relatively low yield).[291] However, the last mentioned nitroso compounds react with methylamine by HF elimination after the primary addition to give 104 or its homologue.[291,292]

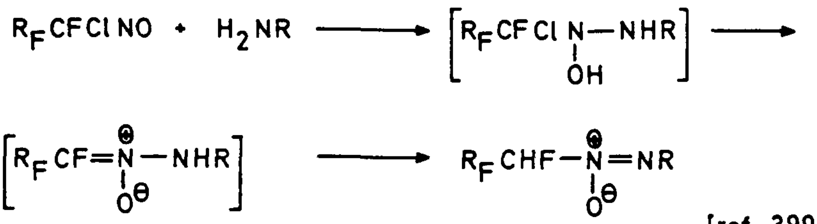
$$CF_3NO + AlkNH_2 \xrightarrow[MeOH]{70^\circ} \underset{\underline{103}}{CF_3N{=}NAlk} \qquad [refs. 289, 310]$$

$$CF_3NO + ArNH_2 \longrightarrow CF_3N{=}NAr$$



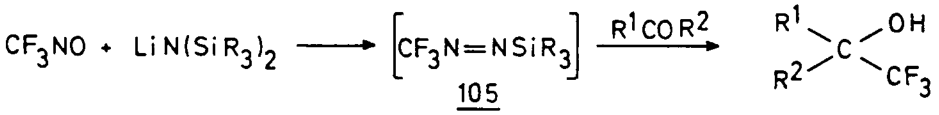
104

Elimination of HCl also occurs to a certain extent in the interaction of primary amines with α-chloronitroso perfluoroalkanes.



[ref. 399]

[Trialkylsilyl]trifluoromethyl diazenes 105 with bulky alkyl groups have been prepared by condensation of lithiumbis(trialkylsilyl)amides with CF_3NO [-80°C, 6-33%);[293,365] they may be used under mild conditions [-100°C, THF) as CF_3 group transfer reagents; CF_3 anion transfer has been assumed.[293]



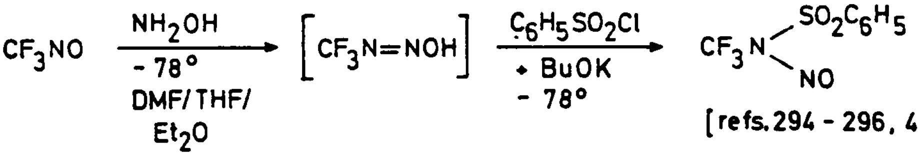
$R^1 = C_6H_5$, $R^2 = CF_3$ 30%; $R^1 + R^2 = -(CH_2)_5-$ 34%

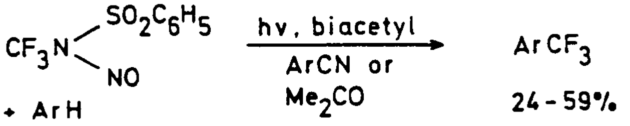
Photolysis of the alkyltrifluoromethyldiazene, on the other hand, results in cage combination of $CF_3\bullet$ and $R\bullet$ radicals.[289]

$$CF_3N{=}N{-}Alk \xrightarrow[-N_2]{h\nu} CF_3{-}Alk \quad (7 - 69\%)$$

The corresponding N-aryldiazenes do not extrude dinitrogen.[290, 291]

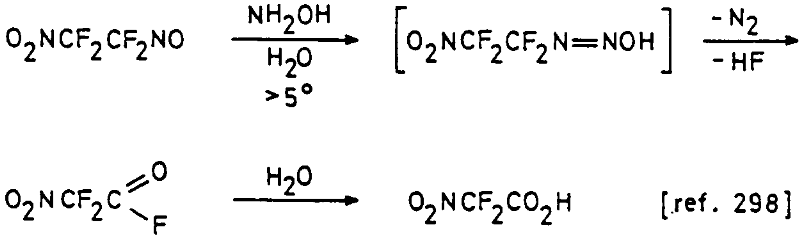
Another trifluoromethylation method consists in the reaction of CF_3NO with hydroxylamine followed by treatment with a base in the presence of sulfonyl halides, carboxylic acid halides or similar reagents.



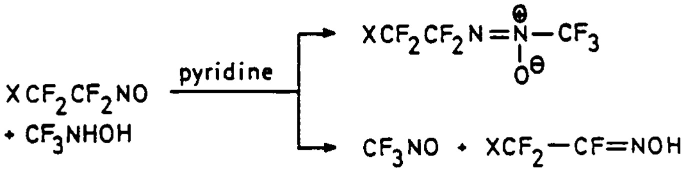


(ArH = C_6H_6, C_6H_5OH, p-$^tBuC_6H_4OH$, p-$(MeO)_2C_6H_4$, pyrrole)

If mixtures of regioisomers are possible, they are formed with some selectivity. Reaction with disulfides RSSR gives CF_3SR.[295, 297a] The same type of intermediate occurs in the following reaction.[298]



For the reactions of CF_3NO with hydroxylamine, hydrazine and their derivatives ref. 387 should be consulted. The reaction between CF_3NO and alkylhydroxylamines RNHOH yields azoxy compounds $CF_3N(O){=}NR$ (-70°C, EtOH).[299, 399] However, there are side-reactions as shown in the following equation.

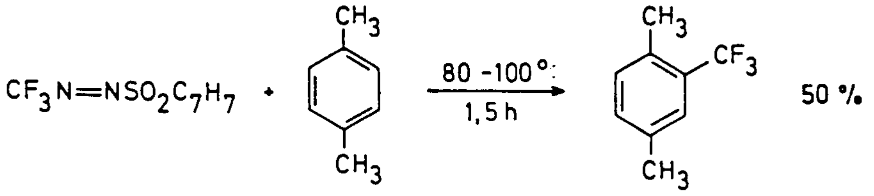


Although CF_3NO does not react with electron-deficient amino compounds such as formamide or urea,[300] many bases cause its condensation with sulfonamides in high yields; these products, too, may serve as trifluoromethylating agents.[303]

$$CF_3NO + ArSO_2NH_2 \xrightarrow[\substack{1)\ \text{liquid } N_2 \text{ temp.} \\ \text{THF} \\ 2)\ \text{room temp.} \\ 2\text{-}3\ \text{h}}]{Na_2CO_3} CF_3N{=}NSO_2Ar$$

81-93 %

[refs. 304, 305]

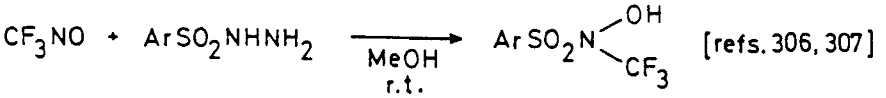


$$+\ C_6H_5SSC_6H_5 \xrightarrow[\substack{80\text{-}95° \\ 1\ \text{h}}]{AcOH} CF_3SC_6H_5$$

Whereas acyl and carbamoyl hydrazines show normal condensations with CF_3NO to give triazenes,[306] sulfonyl hydrazines yield N-trifluoromethyl-N-hydroxyarenesulfonamides probably due to the instability of the initially-formed adduct. The products may be useful as herbicides.[308]

$$CF_3NO + RCONHNH_2 \longrightarrow RCONHN{=}NCF_3$$

(R = Ph, Me, PhNH; 97, 50, 98%)

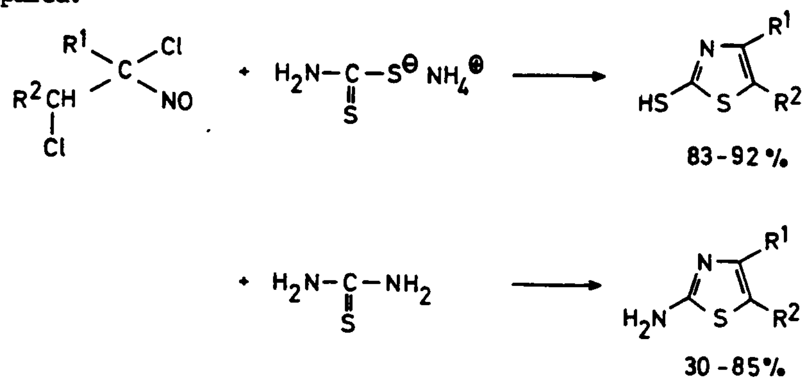


$$CF_3NO + ArSO_2NHNH_2 \xrightarrow[\text{r.t.}]{MeOH} ArSO_2N(OH)CF_3$$

[refs. 306, 307]

74-99%

Clear-cut nucleophilic additions to the nitroso group of α-halogenated derivatives have been investigated almost exclusively in the case of perfluorinated compounds. In the case of other halo derivatives, only the reaction of α,β-dichloronitroso compounds (sometimes prepared in situ) with bifunctional thionamido derivatives has been reported and applied in heterocyclic syntheses. N-Alkyl derivatives of the thionamides have been employed similarly; by using N-amino dithiocarbamates, 1,3,4-thiadiazines have been prepared.[311]

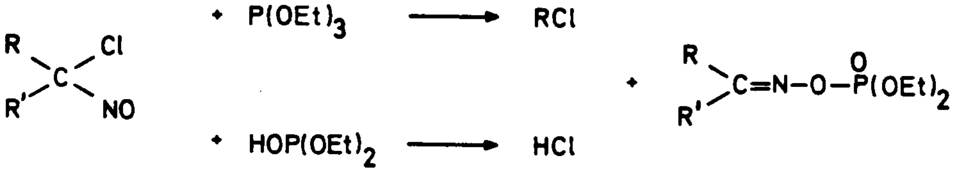


[ref. 309]

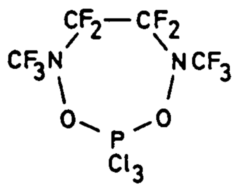
[ref. 310]

(ii) With P(III) Compounds

Perfluoro-gem-chloronitroso compounds react, in some cases extremely readily, with triethyl phosphite (in Et$_2$O, between -80 and -50°C). The same pro-

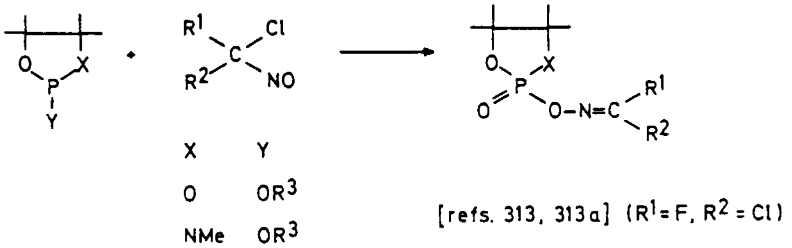


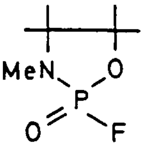
ducts result by treatment of such α-chloronitroso compounds with diethylhydrogenphosphite. 2-Chloro-2-nitrosopropane reacts analogously in the presence of NEt$_3$.[388] The primary product in these reactions is thought to stem from a nucleophilic attack of the P atom on the nitrogen.[312] Diethylhydrogenphosphite combines with CF$_3$NO to give CF$_3$N(OH)P(O)(OEt)$_2$[317] and with C$_2$F$_4$ + PCl$_3$[318] to form 106. Various types of phospholanes give an ana-



106

logous reaction. For Y = F ($R^1 = R^2$ = Me), the primary product is converted into 107 by reaction with Me_2CClNO (Et_2O, 5-10°C, 48%).[314] This transformation corresponds to a mild form of oxidation of the phosphoro fluoridite. Ring-opening of the primary adduct may also occur. For the reaction of $FCCl_2NO$ with phospholane derivatives, see refs. 389 and 390. Triphenylphosphane reacts with 1-chloro-1-nitrosocycloalkanes in the manner of a Beckmann rearrange-





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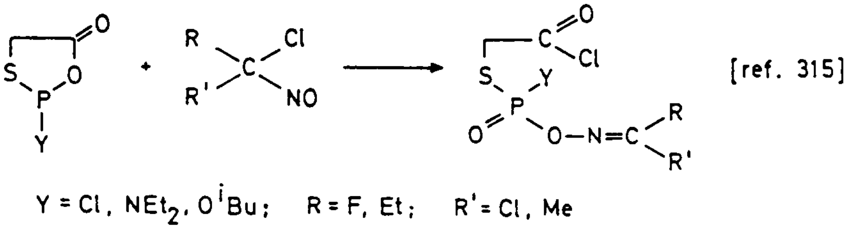
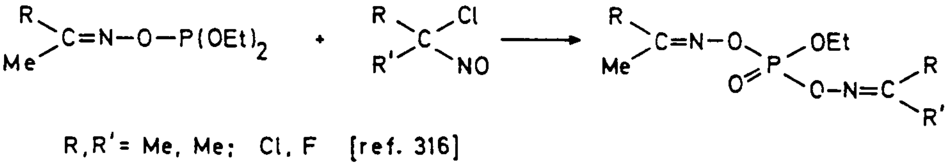
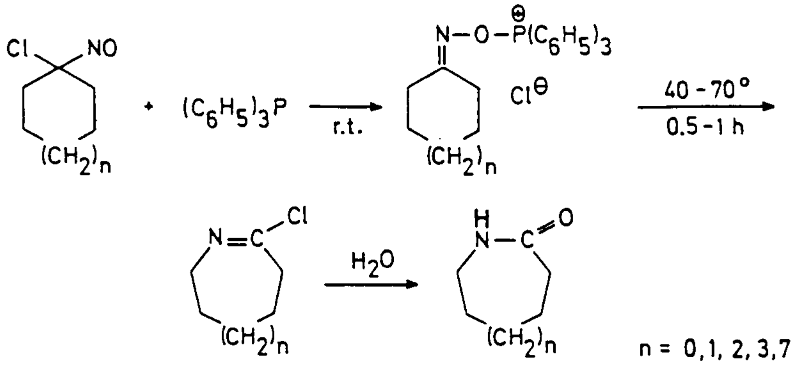


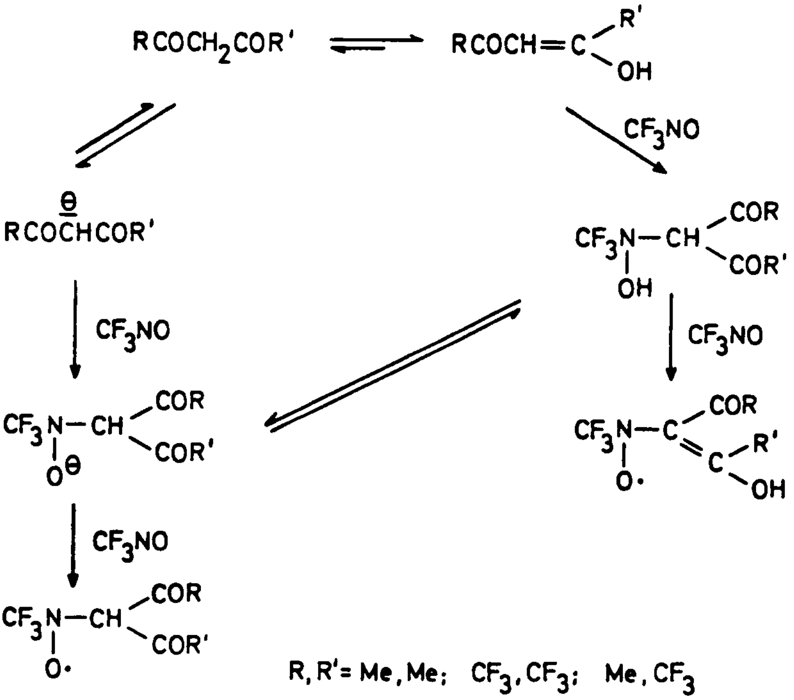




ment. The reaction is exothermic in various solvents and proceeds generally in good yields (57-96%).[188]

iii) With Carbanions and Organometallic Compounds

Nucleophilic attack, followed by one-electron oxidation, has been shown to be the course of reaction of CF_3NO with CH-acidic compounds in CCl_4.[319]

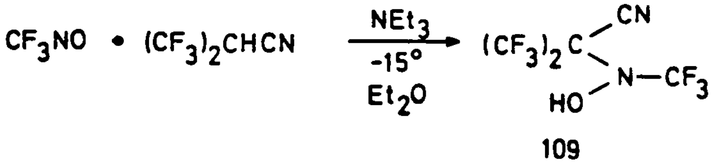


$R,R' = Me,Me;\ CF_3,CF_3;\ Me,CF_3$

The first step may also be regarded as an oxa-ene reaction. In the presence of triethylamine, carbanion addition leads to the imine 108 in the case of acetylacetone[320] and to the hydroxylamine 109 with α-hydroperfluoro isobutyronitrile.[321]

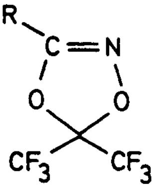
$$CF_3NO + MeCOCH_2COMe \xrightarrow[-10^\circ,\ Et_2O]{NEt_3} (MeCO)_2C{=}NCF_3$$

108



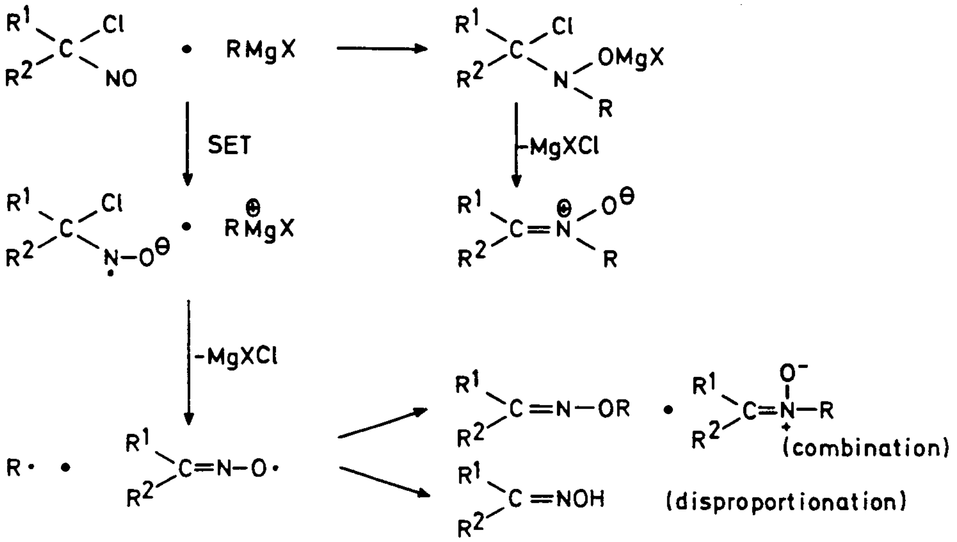
109

The analogous hydroxylamine 110 (R = $CR^1(CF_3N(OH)CF_3)$) is also isolated (70 and 41%) in the reaction (Et_3N, -15^o to -20^oC) of CF_3NO with the dioxaline 110, R = $(CF_3)_2CH$; $CF_3CH(CO_2Me)$. By reaction of α-chloronitroso compounds, especially that of the adamantane derivative, with Grignard reagents RMgX, three products are isolated in strongly varying yields: the corresponding nitrone (6 - 8%), adamantanone oxime (4-60%) and its ether (trace - 28%). Different mechanisms have been suggested for their formation. Their relative influence on the course of the reaction depends on the nature of R: 1,2-Addition (for R = Ph, mainly nitrone) or single electron transfer



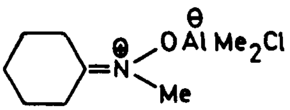
R = $(CF_3)_2CH$; $CF_3CH(CO_2Me)$

110

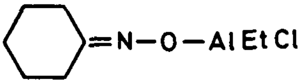


(SET, for R = ^{n}Bu, ^{t}Bu, Me_3CCH_2 and $PhCH_2$, only minor amounts of nitrone[322,323,96]) can occur. Lithium organyls react in the same manner.[392]

The course of the reaction between α-chloronitroso compounds and trialkylaluminium compounds depends also on the structure of the reagents and on the reaction conditions. Ether complexes of AlR_3 afford the same types of products as Grignard compounds via radicals which can abstract hydrogen from various solvents. In the presence of olefinic solvents, radical addition to the double bond also takes place.[350, 403] When the trialkylaluminium compounds are not complexed by ethers, they react with α-chloronitroso compounds predominantly via heterolytic processes; rearrangements [160] (see p. 388) or formation of well-defined complexes like A or salts like B are observed.

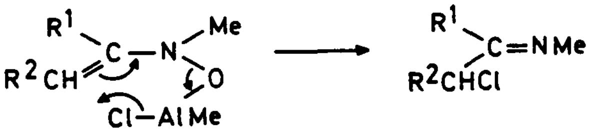


B



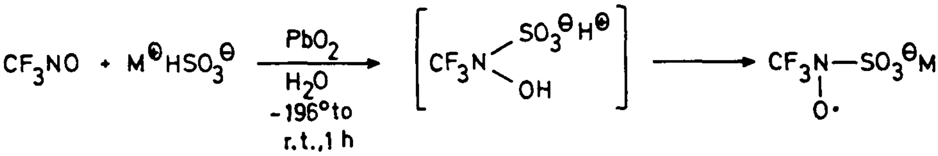
A

These can react further by hydrolysis or rearrangement to α-chloroimines or, in the case of sterically hindered chloronitroso compounds, undergo carbon-carbon bond rupture.[404]



iv) Other (Possibly) Nucleophilic Reactions

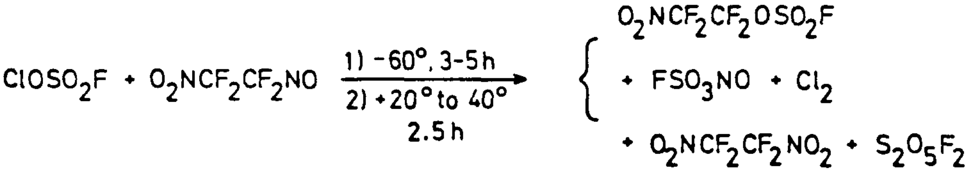
A polar addition occurs in the reaction of CF_3NO with sulfinic acids[410] or with sodium or potassium hydrogen sulfite, the product in the last case is oxidized without isolation to the N-oxyl.[303]



The first process (without PbO_2) is rapid and exothermal at ambient temperature but the intermediate anion disappears fairly quickly (2h) by hydrolysis (product CF_3NHOH). In the analogous reaction of some perfluoro homologs, hydrolysis was followed by HF elimination.[213] Addition of HSO_3^- and

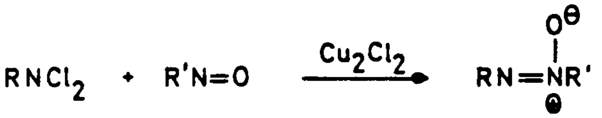
$$R^1_FR^2_FCFNHOH \longrightarrow R^1_FR^2_FC{=}NOH$$

hydrolytic HF elimination to give the oximes is also observed for perfluoronitrosocyclobutane and $(CF_3)_2CFNO$[214] as well as for $CF_3(CF_2Cl)CFNO$ (yield of oxime 41%).[212] Intermediate addition to the N-atom is assumed to explain the complex mixture obtained by the interaction of $ClOSO_2F$ or $S_2O_6F_2$ and fluoronitrosoalkanes.[324]



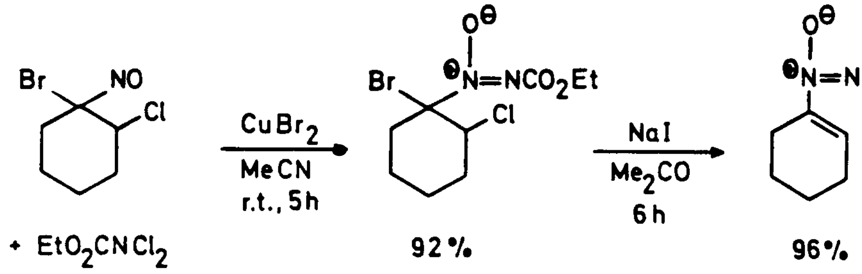
$$ClOSO_2F + O_2NCF_2CF_2NO \xrightarrow[2)\ +20°\text{ to }40°\ 2.5\,h]{1)\ -60°,\ 3\text{-}5\,h} \left\{ \begin{array}{l} O_2NCF_2CF_2OSO_2F \\ +\ FSO_3NO + Cl_2 \\ +\ O_2NCF_2CF_2NO_2 + S_2O_5F_2 \end{array} \right.$$

Nucleophilic attack, of $[RNCl]^{\ominus}$, or involvement of nitrenes is thought to take place in the reaction of nitroso compounds (inter alia, of 1-chloro-1-nitroso cyclohexane and 1,4-dichloro-1,4-dinitroso cyclohexane) with N,N-dichloro-amines. However, other mechanistic possibilities (SET) exist



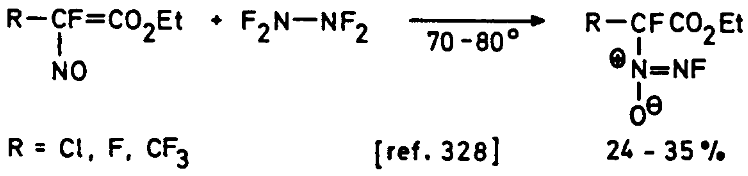
$$RNCl_2 + R'N{=}O \xrightarrow{Cu_2Cl_2} RN{=}\overset{\overset{O^{\ominus}}{|}}{\underset{\oplus}{N}}R'$$

(cf. p. 384) depending on the nature of the promotor.[325,326] This reaction has been used to synthetize the α,β-unsaturated azoxy compounds 111.[327]



111

The formation of an azoxy derivative in the reaction shown below seems



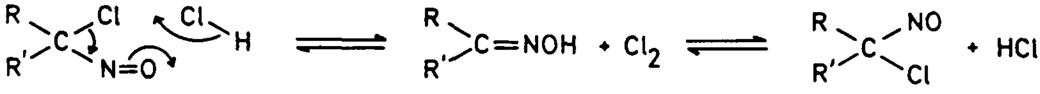
$$\underset{\substack{|\\NO}}{R{-}CF}{=}CO_2Et + F_2N{-}NF_2 \xrightarrow[70-80°]{} R{-}\underset{\substack{|\\ {}^{\oplus}N{=}NF\\|\\O^{\ominus}}}{CF}CO_2Et$$

R = Cl, F, CF$_3$ [ref. 328] 24 - 35 %

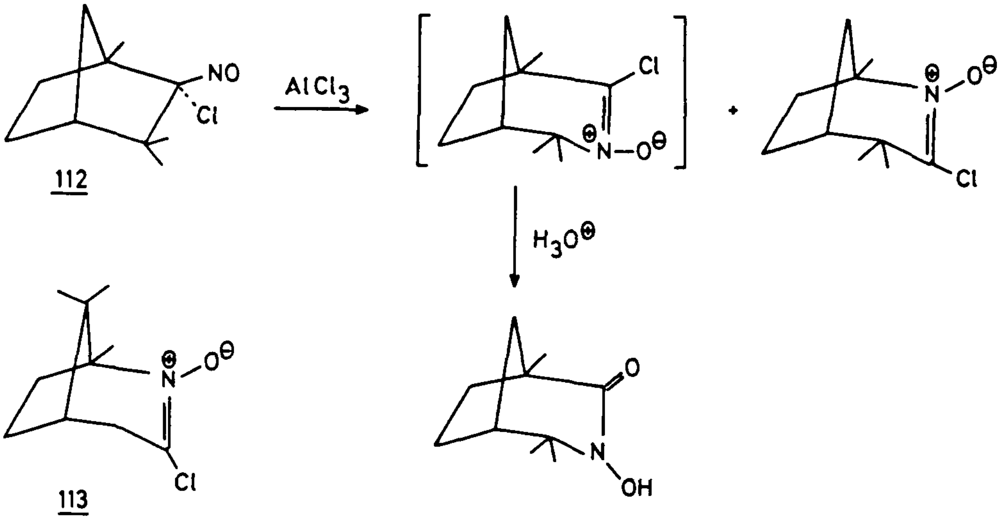
somewhat related.[328] The same reaction occurs with the perfluoronitroso derivatives of cyclobutane or cyclopentane in the presence of finely divided Pyrex glass (55°C, 16h, 50% or 25%, resp.). Without the glass, low yields of R_FNF_2 compounds resulted.[215] For the interaction of N_2F_4 with perfluoronitroso derivatives (formation of fluoroazoxy compounds), see refs. 329-331, 394.

c) Rearrangements

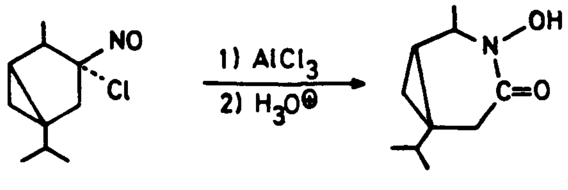
Interconversions of diastereomers in α-halonitroso compounds due to intermediate homolysis were described in Chapter 2. Another way to effect racemization of chiral α-chloronitroso compounds is by reaction with HCl in glacial acid.[120]



This mechanism was established by isotopic exchange[121] and kinetic experiments.[122] A Beckmann-like rearrangement occurs in the reaction of 1-chloro-2-nitrosofenchane 112 with $AlCl_3$ (CH_2Cl_2, $0^{\circ}C$).[160]



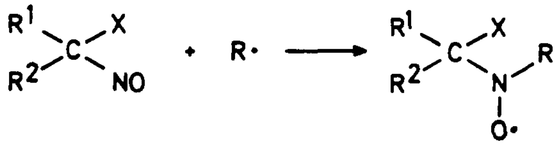
Both endo- and exo-forms of 2-chloro-2-nitroso camphane react with $AlCl_3$ or (with higher yield) with Me_2AlCl to give the chloronitrone 113, which may be hydrolyzed to the corresponding hydroxamic acid. No rearrangement products were isolated from the reaction of 1-chloro-1-nitrosocyclohexane with $AlCl_3$. 2-Chloro-2-nitroso carane 114, however, gives the hydroxamic acid 115 by treatment with $AlCl_3$ and hydrolysis.[160]



114 **115**

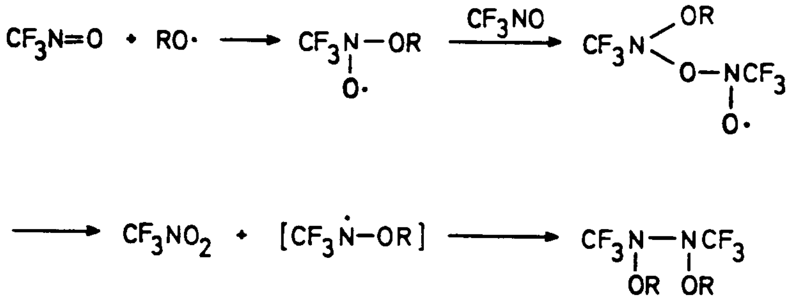
d) Reactions with Radicals

Spin trapping by nitroso compounds, common to almost all derivatives, occurs also with α-halonitroso compounds. Nitroxides are formed by scavenging of alkyl, alkoxy or acyl radicals by α-chloronitroso compounds.[323,332]



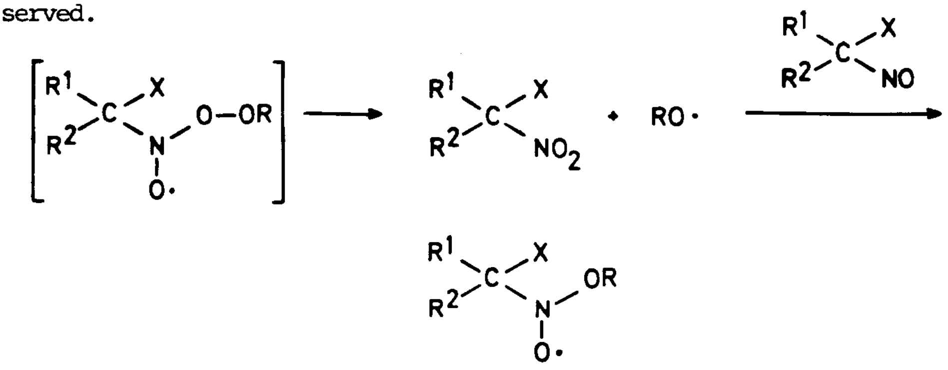
However, these compounds are unsuitable for practical application as spin traps because of the lability of chlorine in the β-position of the nitroxides and because of the complexity of the ESR spectra due to chlorine hyperfine splitting. A review on the interaction of fluoronitroso compounds with radicals and carbenes is available.[6]

CF_3NO reacts with alkoxy radicals generated by nitrite photolysis to yield N,N'-dialkoxy-N.N'-bis(trifluoromethyl)hydrazines 116[333] perhaps in the following manner. Nitroxides generated by addition of peroxy radicals



116

to either 2-chloro-2-nitrosopropane[334] or CF_3NO[335] could not be detected; it is probable that their rapid decay leads to the alkoxynitroxides A observed.



A

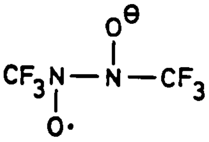
tert.-Butyloxy radicals generated in several ways gave a much more persistent spin adduct with CF_3NO than other alkoxy alkyl nitroxides.[335] The complex reaction sequence for the interaction of the radical NO with α-halonitroso compounds has been discussed in detail mostly in connection with investigations of the photolysis mechanism [cf. Chapter 2, see also refs. 158, 336, 337]. For the kinetics of the reaction CF_3NO + NO, see ref. 338.

The result of reactions of α-halonitroso compounds with radicals usually is equivalent to a reduction. Therefore, this section and the following one are closely correlated.

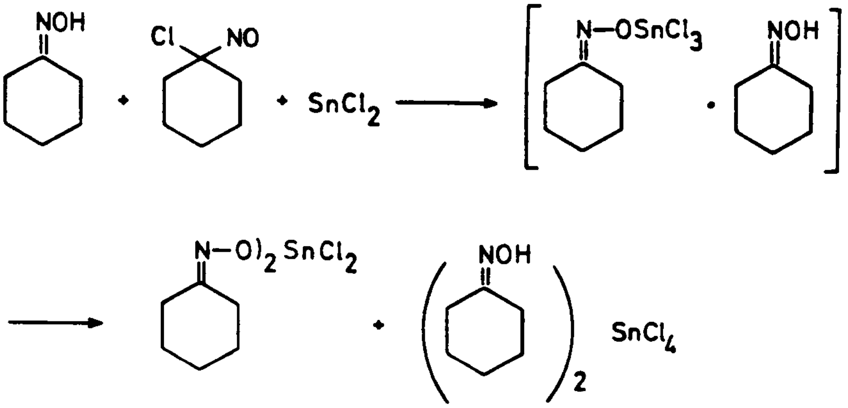
e) Reduction-Oxidation Processes

Electron-transfer in reactions of nitroso compounds has been investigated thoroughly by Ginsburg and his group. Oxidations and reductions of perfluoronitroso compounds are summarized in ref. 6. There, only some pertinent new results will be discussed.

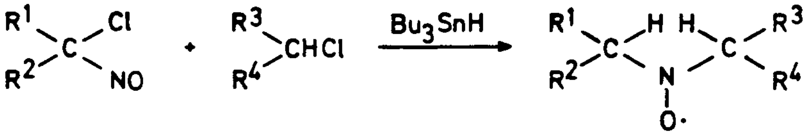
The polarographic half-wave potentials of some halogenonitroso derivatives have been determined [$(CH_3)_2CClNO$ - 0.95 V in ethanol].[345] Me_2CXNO (X = Cl, Br) and $MeCCl_2NO$ are reduced polarographically to the oximes $Me_2C{=}NOH$ or $MeCCl{=}NOH$, respectively.[346] The character of the reduction depends substantially on the nature of the solvent. Electrolytic reduction of CF_3NO ($E_{1/2}$ -0.25 V in DMF, acetonitrile, or DMSO) produces a substance whose ESR spectrum was assigned[347] to the structure shown below.

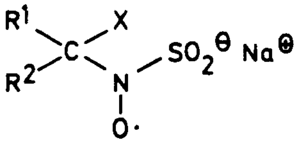


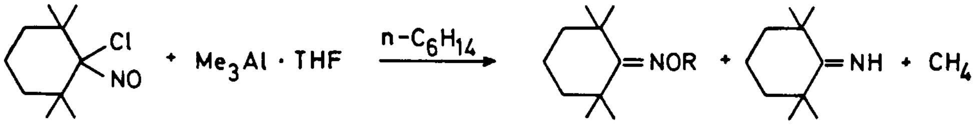
Chemical reduction of 1-chloro-1-nitrosocyclohexane by diborane (25°C, THF) yields N-cyclohexylhydroxylamine.[348] This compound as well as other chloronitroso derivatives RR'CClNO may be reduced by $LiAlH_4$ or $NaBH_4$ to the corresponding oximes RR'C=NOH (yields 41-72% or 50-78%, resp.).[161] These products are also formed exothermally by hydrogenation with PtO_2 as the catalyst in ethyl acetate; Pd/Al_2O_3, $Pd/BaSO_4$ or Raney-Ni are ineffective.[101] Oximes are also produced by the reaction with stannous chloride.[349]



α-Chloronitroso compounds react relatively slowly with Bu_3SnH, but rapidly with alkyl radicals produced by the interaction of this reagent with alkylhalides, to give non-symmetrical di-sec-alkylnitroxides.[158] For the reduction of perfluoronitroso compounds with hydrogen sulfite see p. 386; alkaline sodium dithionite reacts with solutions of α-halonitroso compounds to give stable radicals which are destroyed by excess of reagent or strong acids.[339] Trimethylaluminium functions as an electron-donor towards 1-chloro-1-nitroso-2,2,6,6-tetramethylcyclohexane <u>117</u>;[350] an iminyl radical has been shown to be an intermediate.







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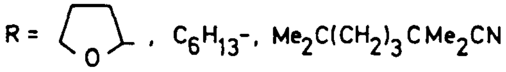
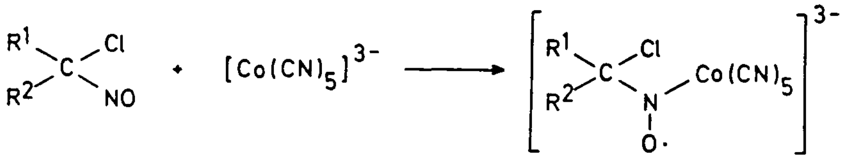


Interaction of aliphatic nitroso compounds with the pentacyano cobaltate(II) anion in aqueous solution affords cobalt-substituted nitroxides <u>118</u> of moderate stability.[340,341] The addition product of CF_3NO persisted



<u>118</u>

for several weeks under nitrogen, the adduct of bis(dimethylglyoximato) cobalt (II) behaves similarly.[342]

Radicals as intermediates have been postulated and/or observed in reactions of CF_3NO with trimethylsilane[343] and with 1,3-dienes.[344] Radical anions $RNO\cdot^-$ or $RN(O\cdot)-N(O^-)R$ are thought to be the products of the interaction of CF_3NO and O_2NCF_2NO with nucleophilic solvents (ether, ethanol, amines).[351] With alkenes $CH_2=CHR$ (R = Me, OEt, Ph) and 2-propenyl compounds $CH_2=CHCH_2X$ (X = Cl, Br, $SiCl_3$, -N=C=S), CF_3NO yields radicals by one-electron transfer reactions.[395]

Aliphatic nitroso compounds, in general, are subject to oxidation to the corresponding nitro compounds by a wide range of reagents.[2,6] Oxidation of perfluoronitroso carboxylic acid esters by N_2O_4 or CF_3CO_3H yields (65%) the corresponding nitro derivatives.[352] The sequence of oxidation of an α-halogenonitroso compound followed by reductive displacement of the halogen has often been used as a valuable synthesis of nitro compounds, cf. p. 341.

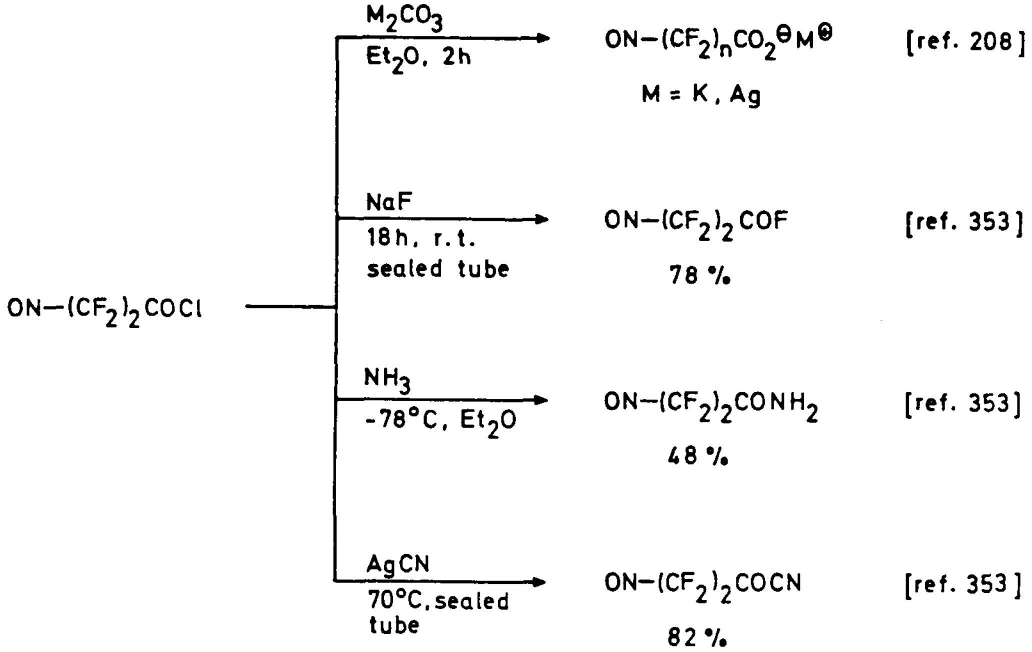
f) Reactions Not Involving the Nitroso Group

Often the success of a synthesis depends on the "chemoselectivity" of one of the steps involved; this means the preferential or exclusive reaction of one functionality in the molecule and the lack of reactivity of the other possible reaction centers under the reaction conditions. In the case of α-halogenated nitroso compounds, only the perfluoro derivatives seem to have been investigated in this respect. The results of such experiments are summarized below. Thionyl chloride gives mixtures which may be separated

$$\underset{(R = Me,\ Et)}{ON{-}(CF_2)_n{-}CO_2R} \xrightarrow[\text{reflux}\ 40\,\text{min}]{70\%\ \text{AcOH}} ON{-}(CF_2)_nCO_2H \qquad \text{[refs. 205, 208]}$$

$$ON{-}(CF_2)_nCO_2H \xrightarrow[80^\circ C,\ 7h]{PhCOCl} \underset{34-48\%}{ON{-}(CF_2)_2COCl} \qquad \text{[ref. 208]}$$

only with difficulty; phosphorus chlorides react with the nitroso group.



$$ON{-}(CF_2)_2CONH_2 \xrightarrow[\text{distillation at } 150°C/100\ mm\ Hg]{P_4O_{10}} \underset{46\ \%}{ON{-}(CF_2)_2CN} \qquad \text{[ref. 353]}$$

$$ON{-}(CF_2)_2CO_2H \xrightarrow[\text{distillation at } 200\ mm\ Hg]{P_4O_{10}} (ONCF_2CF_2CO)_2O \qquad \text{[ref. 353]}$$

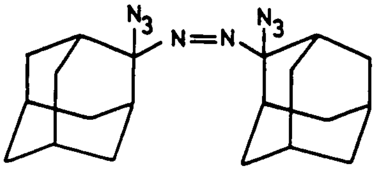
ω-Nitrosoperfluoropropionic and ω-nitrosoperfluoro butyric acids form adducts with many organic compounds (e.g. ethyl acetate, ether, acetone, dioxane, benzoyl chloride) which are reported to decompose only when heated with concentrated sulfuric acid under vacuum.[247]

g) Miscellaneous Complex Reactions

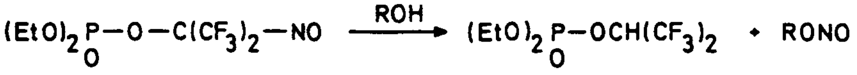
Some of the reactions of α-halonitroso compounds defy systematization. These reactions will be reported here without comment.

When Cl_3CNO in dimethylformamide was treated with NaF (40-80°C), a 12% yield of CF_3NMe_2 was isolated. The yield of this product was much lower when AgF was used instead of NaF. In this case $CF_3NN(O)CF_3$ was the chief fluorocarbon product. In the absence of DMF, $(CF_3)_2NONO$ was found as the main product.[354]

α-Chloronitroso compounds give a very complex reaction mixture with azide ion in methanol. In the case of the adamantyl derivative, the azido azo compound could be isolated.[355]



The perfluoro nitroso compound 119 is solvolyzed by water and ethanol.[356]



$$(EtO)_2\underset{O}{P}-O-C(CF_3)_2-NO \xrightarrow{ROH} (EtO)_2\underset{O}{P}-OCH(CF_3)_2 + RONO$$

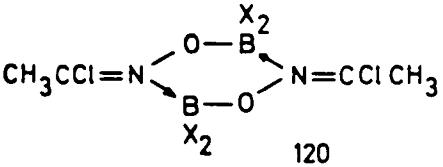
119

Another path for solvolysis is followed by 2-chloro-2-nitrosobutane in methanol which affords 2-butanone oxime and 2,3-butanedione monoxime

A very old publication claims the replacement of bromine by NO_2 in the reaction of Me_2CBrNO by $AgNO_2$.[358] On the other hand, a replacement of the nitroso group is reported to take place in the following reaction.[359]

$$(CF_3)_2CClNO \xrightarrow{Cl_2} (CF_3)_2CCl_2$$

From the reaction of 1,1 dichloronitrosoethane and BCl_3 or BBr_3, dimeric alkylideniminoxyboranes 120 are obtained.[360]



120

Metal carbonyls react with α-halonitroso compounds to give different products, depending on the reagent used. In the interaction of 1-bromo-2-nitroso-propane with $C_5H_5Mo(CO)_3^{\ominus}$, the $Me_2C(NO)$ moiety acts as a three-electron donor to give $C_5H_5Mo(CO)_2C(NO)Me_2$ as the product.[361] On the other hand, with $Na_2M_2(CO)_{10}$ [M = Cr, W], yellow volatile dimethylketimine complexes $[Me_2C=NH] \bullet M(CO)_5$ are formed[361,362] and with $Na_2Fe(CO)_4$, a mixture of $[Me_2C=N]_2Fe_2(CO)_2$ and $[Me_2C=N]_2OFe_2(CO)_6$ has been isolated.[361] $Fe(CO)_5$ reacts vigorously with CF_3NO (starting temperature -20°C) to give a multitude of degradation products.[363]

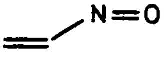
III. α-HALONITROSOALKENES

Detailed reviews for all types of nitroso alkenes have been provided by Gilchrist[5] and Viehes group.[364] These compounds possess a very large synthetic potential. They behave as activated alkenes and as hetero-1,3-dienes; on the other hand, the nitroso group reacts with many reagents.[1,3] A simultaneous incorporation of nitrogen and oxygen takes place by Diels-Alder reactions, ene reactions and [2+2] cycloadditions.

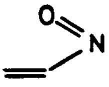
The first 1-halo-1-nitrosoalkene isolated was trifluoronitrosoethene.[366] Other such compounds have usually bulky alkyl or halo substituents at the β-carbon atom.[364,367-373] The lifetimes of α-chlorinated nitroso alkenes vary from many weeks at room temperature to short periods at low temperatures.

1. STRUCTURE AND PHYSICAL PROPERTIES

No X-ray or microwave structure determinations have been carried out on α-chloronitroso alkenes. MO-calculations, using the Hückel-[374] and the CDCO-[375] method have been carried out for nitrosoethene; the transoid structure 122a is calculated to be of slighly lower energy than the cisoid form 122b.[375] The blue color of the α-chloronitrosoalkenes is due to the n→π* absorption band (675-795 nm). Another band in the 250-350 nm region



122a

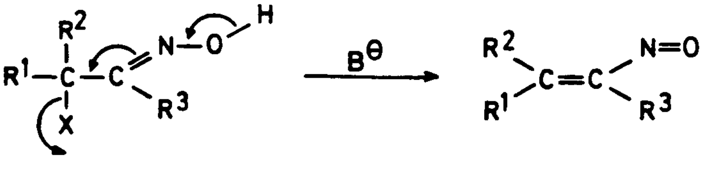


122b

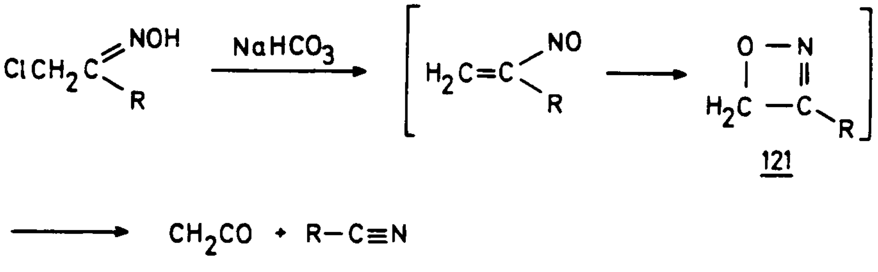
is also observed; this band may be due to an excitation involving considerable charge transfer to the nitroso group.[375] Infrared spectra normally show two bands in the region 1420-1660 cm^{-1}, the lower one [ν(NO)] shows the influence of conjugation (1500-1620^{-1}). The higher frequency band (1500-1660 cm^{-1}) can be attributed to the ν(C=C).[364]

2. SYNTHESIS

A general method for the preparation of nitrosoalkenes consists in the treatment of α-halooximes with $NaHCO_3$ or K_2CO_3 in dichloromethane

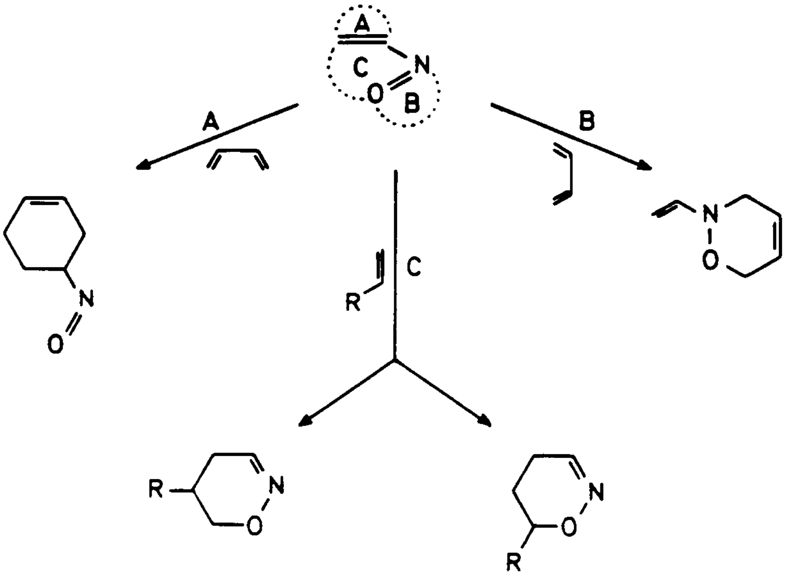


For the long lived species, triethylamine[367] and 1,5-diazabicyclo[4.3.0] non-5-ene[368] have been used as bases. From α-monohalooximes, no nitrosoalkenes could be isolated. Their instability may be explained on the basis of formation of an intramolecular [2+2]-cycloadduct 121 which decomposes readily to yield formaldehyde and the corresponding nitrile.



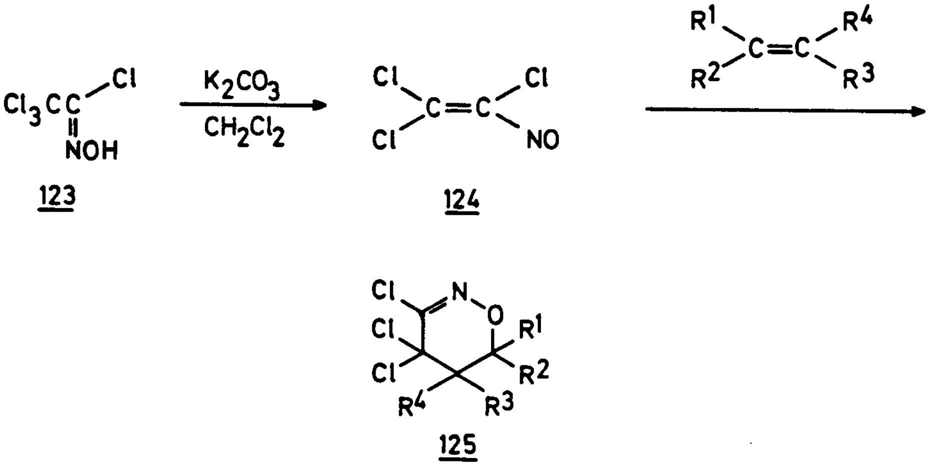
3. REACTIONS

Nitrosoalkenes participate in cycloaddition reactions either as 2π-electron systems (mode A or B) or as a 4π-electron (heterodiene) system (mode C).

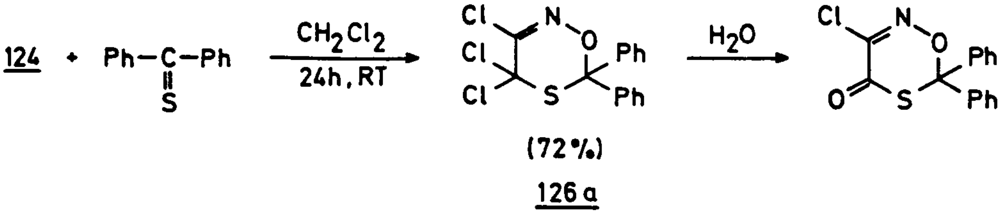


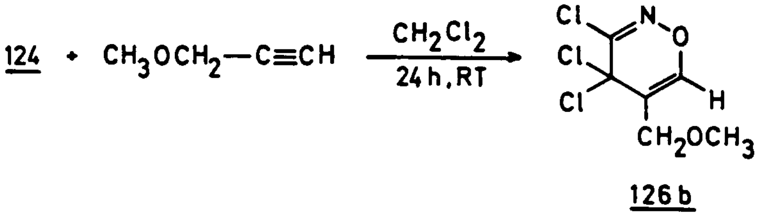
With dienes, products are usually formed via mode B. The realization of mode A remains uncertain; possible products of mode A may easily undergo a [3,3]-sigmatropic rearrangement to give one of the possible products formed directly by mode C.

Reactions of the title compounds with monoalkenes have been described only recently. Trichloronitrosoethene (124), generated from trichloroacethydroxamic acid chloride (123),[364] was shown to react with a number of electron-rich mono-alkenes via [4π + 2π] reaction to yield 1,2-oxazines (125) in good yield.[376]

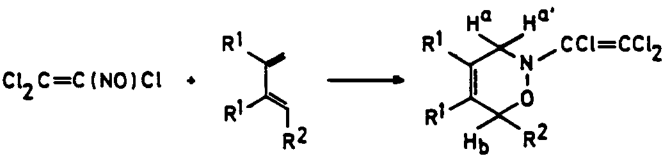


In all cases only one regioisomeric product was isolated. Compound 124 also reacts with thiocarbonyl compounds and with alkines to form [4+2]cycloadducts,[376] 126a or 126, respectively; the oxazine 126a is very sensitive to moisture.



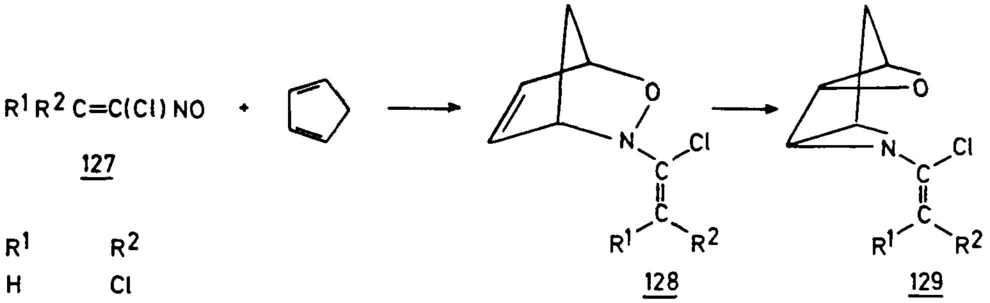


With substituted butadienes, cycloaddition occurs according to mode B.[364]



R^1	R^2
H	H
CH_3	H
H	OCH_3

α-Chloronitrosoalkenes 127 react with cyclopentadiene,[380] cyclohexadiene[379] and oxepin[371] to form [4π + 2π] adducts; these products are unstable and isomerize at room temperature to form epoxyaziridines.[364] Compound 124 gives



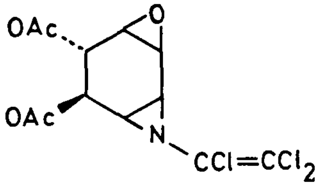
127

R^1	R^2
H	Cl
Cl	Cl
C_6H_5	H

128

129

only one stereoisomeric product, 130, with trans-5,6-diacetoxy-1,3-cyclohexadiene.



130

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