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Conjugated nitrosoalkenes †

I M Lyapkalo, S L Ioffe

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Abstract. Published data on the preparation, structure, physical and chemical properties, and reactivity of nitrosoalkenes are described systematically. The influence of the structure and stereoelectronic effects of substituents at the double bond on the stability of nitrosoalkenes is analysed. Primary attention is paid to concerted cycloaddition of nitrosoalkenes to miscellaneous multiple bonds, in particular, to the problems of regio-, stereo-, and enantioselectivity of [4 + 2]-cycloaddition of nitrosoalkenes to alkenes. The bibliography includes 183 references.

I. Introduction

The nitroso group is a powerful electron-withdrawing substituent; this has a crucial effect on the chemical properties of all conjugated systems containing this group. In particular, the nitroso group is known to promote efficiently nucleophilic substitution in benzene derivatives, and in some cases its activating influence is even more pronounced than that of the nitro group.[1,2]

The main methods for synthesis, physical properties, structures, and reactivities of conjugated nitrosoalkenes are considered in only one review covering publications which appeared before 1983.[3] However, more recently, some important aspects of the chemistry of these compounds have been further developed, most of all, owing to the efforts of the research groups headed by Reissig and Gilchrist. In the present review, we generalise and describe systematically the data published up to the end of 1997 including those concerning participation of nitrosoalkenes in concerted processes, primarily, in [4 + 2]-cycloaddition to alkenes.

The formation of nitrosoalkenes as reactive intermediates was hypothesised as early as 1898;[4] however, it was not until 1960 that synthesis of the first stable compound of this type, trifluoronitrosoethylene, was reported.[5] Since then, only a few stable nitrosoalkenes have been prepared; they usually contain bulky aryl, *tert*-alkyl, or halo substituents at the β-carbon atom. Nitrosoalkenes in which the β-carbon atom is included into a heterocyclic system can also be put into this group.

However, there is strong evidence indicating that many nitrosoalkenes can exist in solutions as unstable intermediates. They comprise a large number of β-alkyl- and β-aryl-substituted nitrosoalkenes, several halo-substituted derivatives, and only few compounds containing OR or NR_2 groups at the β-position. Some of these intermediates have been identified by spectroscopy, while others have been detected on the basis of their characteristic blue colour. The lifetimes of these compounds vary a over wide range.

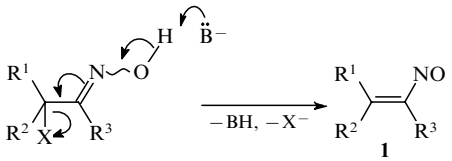
Finally, there exist nitrosoalkenes, which cannot be detected due to their instability. The formation of these compounds is judged based on experiments on their trapping. Thus all the known intermediates of the general formula $CH_2=C(R)NO$ belong to this group. The properties of typical representatives of nitrosoalkenes **1** are listed below in Table 1.

This review consists of three parts. The first part is devoted to the methods for the synthesis of nitrosoalkenes, and the second one deals with their physical properties and structures. The third part describes chemical transformations of nitrosoalkenes, classified according to the type of reaction.

II. Methods for generation of nitrosoalkenes

1. 1,4-Elimination in α-substituted oximes under the action of bases

In recent years, the chemistry of nitrosoalkenes **1** (Table 1) has been developing especially successfully, mostly owing to the elaboration of a simple and reliable method for their generation from available precursors, α-substituted oximes.



1

This method has been used to prepare all the compounds listed in Table 1, except for trifluoronitrosoethylene **1a**. The chloride ion is the most frequently used leaving group; however, other halides are also suitable. Since nitrosoalkenes are sensitive to nucleophilic attacks, it is very important to choose appropriate conditions for their generation. The reaction should be carried out using weakly nucleophilic solvents and bases, except for those cases where they are used to trap nitrosoalkenes. Stable nitrosoalkenes have been synthesised using tertiary amines, Et_3N[6] and 1,5-diazabi-

I M Lyapkalo, S L Ioffe N D Zelinskii Institute of Organic Chemistry, Russuan Academy of Sciences, Leninskii prosp. 47, 117913 Moscow, Russian Federation. Fax (7-095) 135 53 28. Tel. (095) 135 53 29

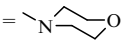
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† The review is dedicated to Professor Seebach in connection with his 60th birtday.

Table 1. Typical representative nitrosoalkenes **1**.

Alkene **1**	R^1	R^2	R^3	Properties	Ref.
a	F	F	F	blue gas, stable up to 100 °C	5
b[a]	H	Mes	Me	blue crystals, m.p. 47–58 °C	6
c	Bu^t	Bu^t	H	blue crystals, m.p. 38 °C	7
d	Cl	Cl	Me	can be isolated at room temperature	8
e	Cl	Cl	$CCl=CCl_2$	m. p. 44 °C at 0.02 mm Hg	9
f	H	$-(CH_2)_4-$		blue crystals at −50 °C, decomp. above −30 °C	10
g[a]	H	Cl	Cl	long-lived in solution	8
h	Cl	Cl	H	the same	8
i[a]	H	Ph	Me	detected in solution (colour)	11
j[a]	Me	Mor[b]	Ac	the same	12
k	H	H	H	lifetime in the gas phase 30 s	13
l	H	H	Ph	the existence was confirmed by trapping and by kinetic studies	14, 15
m	H	H	Ac	detected only by cycloaddition	16
n	H	H	CF_3	the same	17

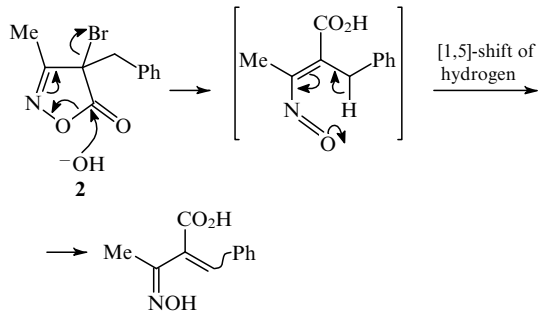
[a] The stereochemistry at the C=C bond was not studied;

[b] Mor = 

cyclo[4.3.0]non-5-ene (DBN).[7] Unstable intermediates are better generated by treatment of α-halo oximes in non-nucleophilic organic solvents with insoluble inorganic bases such as Na_2CO_3 [17,18] or $Ca(OH)_2$.[10] These conditions ensure maintenance of a very low steady-state concentration of the highly reactive intermediates **1** and, as a consequence, suppression of the undesirable side processes involving more than one nitrosoalkene molecule, for example, polymerisation.

Denmark *et al.*[19,20] proposed a very interesting and useful modification of this method, namely, generation of nitrosoalkenes under 'neutral' conditions by treating *O*-trialkylsilyl derivatives of α-halo oximes with fluoride ions in weakly nucleophilic aprotic solvents. The best results were obtained with CsF and KF in MeCN;[20] however, AgF or Bu^n_4NF can also be used.

One of the synthetic modifications of the general method for the generation of the compounds **1** is rupture of the C–O bond in the isoxazoline ring of compound **2** as a result of deacetylation of the oxyimino group on treatment with a base and subsequent elimination of Br^-.[21]



Since α-halo oximes are important precursors of nitrosoalkenes, we considered it pertinent to outline here the three main methods for the synthesis of these compounds.

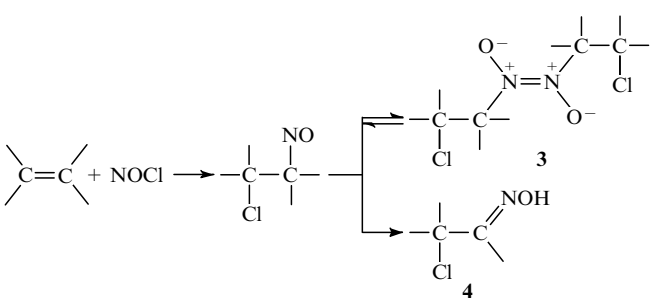
The first method is based on the reaction of the corresponding halo ketones with hydroxylamine. In particular, α-chloro oximes are prepared from α-chloro ketones and hydroxylammonium chloride in protic solvents.[19] To synthesise α-bromo oximes, hydroxylammonium sulfate is used in order to avoid halogen exchange.[22] It is undesirable to use alcohols as solvents, because they can substitute the halogen if the reaction time is long.[16] According to the Denmark modification,[19] *O*-trialkylsilyl derivatives of α-chloro oximes are prepared by condensation of the corresponding chloro ketones with *O*-trialkylsilylhydroxylamine in $CHCl_3$ in the presence of 4 Å molecular sieves.

The second method includes interaction of nitro alkenes with $SnCl_2$ [23] or $TiCl_4$.[8] It is used to prepare some α-chloro oximes or α-chlorohydroxyiminoyl chlorides, respectively.

The third method is also applicable only to the synthesis of chloro oximes. It is based on the addition of nitrosyl chloride to alkenes,[24–29] and was first proposed more than a hundred years ago [26] for the synthesis of crystalline derivatives of terpenes. In the 60s, this reaction was extended to a broad range of nucleohilic and electrophilic alkenes mostly in the studies by Ogloblin *et al.*[27–29] It is a convenient pathway to chloro oximes of the type $ClCH_2C(R)=NOH$ [R = C(O)H, Ac, C(O)Ph, and CN]. The reactions of alkenes with NOCl yield initially β-chloro nitrosocompounds, which can subsequently dimerise to give compound **3** and/or rearrange into α-chloro oximes **4**. The latter route is possible if the carbon atom bound to the nitroso group carries a hydrogen atom (Scheme 1).[24,25]

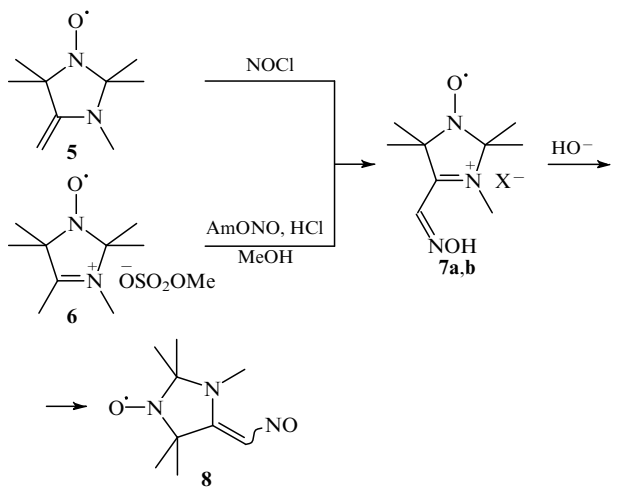
The reactions with ordinary alkenes can be classified as electrophilic substitution, and the adduct is formed in conformity with the Markovnikov rule.[24,25] The fact that nitrosyl chloride adds unexpectedly rapidly to some α,β-unsaturated carbonyl compounds [27–29] might be due to preliminary coordination of the nitrosonium cation (NO^+) to the oxygen atom of the carbonyl group.

Scheme 1



If there are substituents at the C=C bond of the substrate molecule, able to stabilise efficiently the carbocationic site resulting from the attack by the NO^+ cation, the reaction product has an ionic structure. The reactions shown in Scheme 2 are interesting examples of the generation of ionic intermediates of this type.[30]

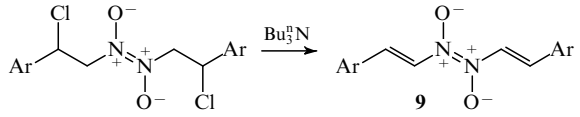
Scheme 2



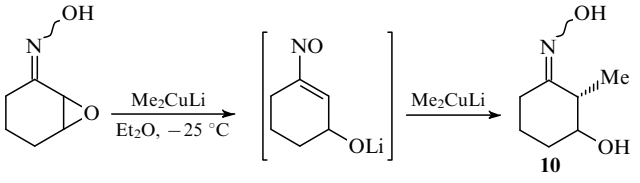
X = Cl (**a**), OSO_2OMe (**b**).

The nitrosation of the double bond in compound **5** by nitrosyl chloride or the acid-catalysed reaction of alkyl nitrate with the immonium cation **6** give compounds **7a**,**b**. To prepare nitrosoalkene **8**, the nitrosation product is treated with a base. During the transformations presented in Scheme 2, the sterically hindered radical site remains intact.[30]

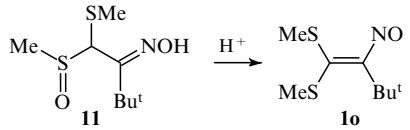
The type **3** dimers of β-chloro nitroso-compounds have also been used as precursors of some nitrosoalkenes.[31–34] Thus the reaction of Bu^n_3N with dimers of chloro nitroso-compounds prepared from styrenes affords only orange dimers of β-nitroso styrenes **9**.[33]



There are only few examples of generation of nitrosoalkenes from oximes with leaving groups other than halide ions. Thus products of the addition of nitrosyl sulfate ($NO^+HSO_4^-$) to alkenes have been used as the initial compounds for the preparation of nitrosoalkenes.[35] The nitrite ion can also serve as the leaving group.[7] Yet another interesting variant of this approach is cleavage of the oxirane rings in α-epoxy ketoximes on treatment with the cuprate reagent to give compound **10**.[36]



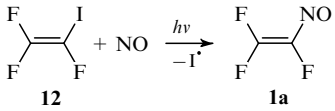
The acid-catalysed dehydration of sulfoxide **11** involves presumably the intermediate formation of the nitrosoalkene **1o**.[37]



However, as far as we know, the direct dehydration of α-hydroxy ketoximes has not been used as a method for generation of nitrosoalkenes.

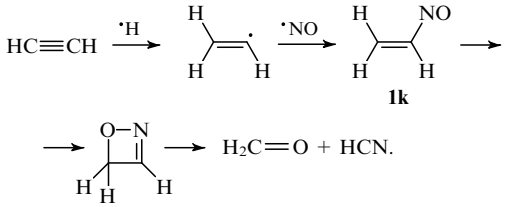
2. Reactions of nitrogen(II) oxide with vinylic radicals

Trifluoronitrosoethylene **1a** was obtained by photolysis of trifluoroiodoethylene **12** in the presence of nitrogen(II) oxide.[5]

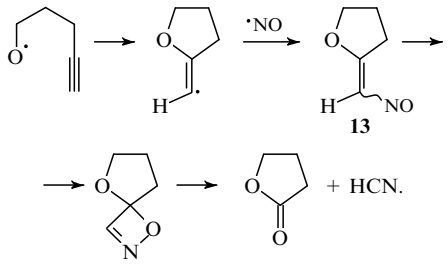


It has been assumed that the reaction product is formed upon recombination of trifluorovinyl radical with NO. To date, the compound **1a** is the only vinylic nitroso derivative prepared in a pure state using this type of reaction; however, in a number of other syntheses, nitrosoalkenes have been postulated as reaction intermediates.

Thus acetylene reacts with hydrogen atoms and NO to give HCN and formaldehyde resulting apparently from rearrangement and fragmentation of the intermediate nitroso ethylene **1k**.[38]



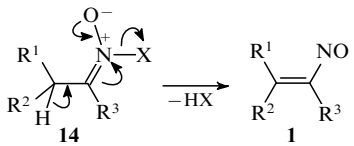
Several more reactions of this type have been reported.[38,39] For example, nitrosoalkene **13** was postulated as an intermediate in the reaction presented below:[39]



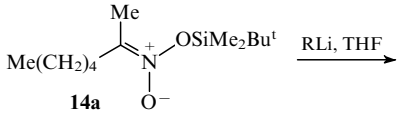
3. 1,3-N,C-elimination of trialkylsilanols from silyl nitronates

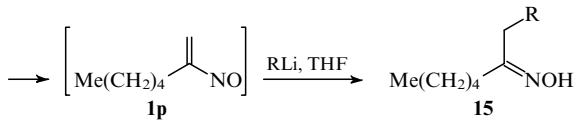
The reactions of 1,4-elimination of HX from α-substituted oximes under the action of bases is the most important and the most general method for the generation of nitrosoalkenes **1**.

It is curious to note, however, that the 'alternative' possibility of 1,3-elimination of HX from compounds like **14** as a route for generation of nitrosoalkenes has not been specially considered until recently.



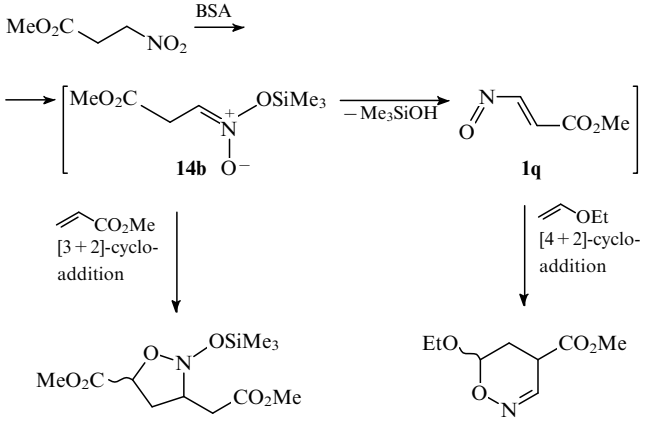
The possibility of this transformation was first hypothesised by Seebach *et al.*[40] They postulated 2-nitrosohept-1-ene **1p** as an intermediate in the reaction of *tert*-butyldimethylsilyl nitronate **14a** with excess organolithium reagent. The first equivalent of RLi reacts as a base facilitating the abstraction of *tert*-butyldimethylsilanol, and the second equivalent reacts with the resulting nitrosoalkene **1p** as a nucleophile, and this leads to the final reaction product, dialkyl ketoxime **15**.[40]





Later, in studies by Ioffe *et al.*,[41–44] β-functionally substituted nitrosoalkenes **1** have been considered as the most probable intermediates for trimethylsilylation of nitro compounds containing electron-withdrawing groups at the β-position (Scheme 3). In the authors' opinion, these substituents facilitate spontaneous fragmentation of the intermediate trimethylsilyl nitronates **14**. The fate of the resulting nitrosoalkenes **1** depends on their structure, in particular, on whether or not protons or electron-withdrawing groups are present at the γ-position of the initial nitro compound.[44] The final reaction products are either *O*-trimethylsilyl-derivatives of α,β-unsaturated oximes **16** [pathway (*a*)] or *N*,*N*-dialkenyl-*N*-trimethylsilyloxyamines **17** [pathway (*b*)]. The reaction follows pathway *a* if the molecule **1** contains two electron-withdrawing groups (R^2, R^4) such as CN or COOMe. In the latter case [pathway (*b*)], silyl nitronates **14** not only serve as the source of nitrosoalkenes **1** but also react with them according to the pattern of 1,2-addition to the nitroso group.

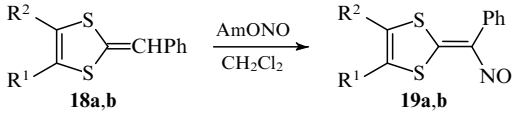
Recently, the generation of silyl nitronates **14** and then of nitoso alkenes **1** during the formation of type **17** products was confirmed by selective trapping of these intermediates in the silylation of methyl 3-nitropropionate.[45]



The above sequence of reactions confirms the possibility of generating nitrosoalkenes **1** from silyl nitronates **14**. This is fundamentally important, since the compounds **14** are readily accessible and can prove to be convenient precursors of nitrosoalkenes, especially, of β-functionally substituted ones, which have scarcely been studied.

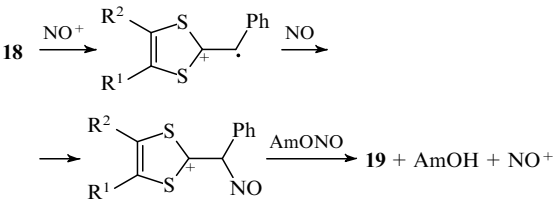
4. Nitrosation of C = C bonds enriched in electrons

When dithiafulvenes **18** are treated with amyl nitrite, nitroso-compounds of the type **19** are readily produced.[46]

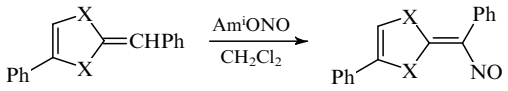


R^1 = Ph, R^2 = H (**a**); R^1 = R^2 = CO_2Me (**b**).

The ease of nitrosation is due to the presence of the electron-donating heterocyclic fragment, which efficiently stabilises the positive charge on the endocyclic C(2) atom by means of aromatisation. The reaction is accelerated by catalytic amounts of acids and inhibited by tertiary amines; therefore, it is believed that at the first stage, the nitrosonium cation is generated. However, in the opinion of the researchers cited,[46] the electrophilicity of the NO^+ cation is insufficient to accomplish nitrosation by an electrophilic mechanism; therefore, as the most probable reaction route, they proposed a scheme involving single-electron transfer.



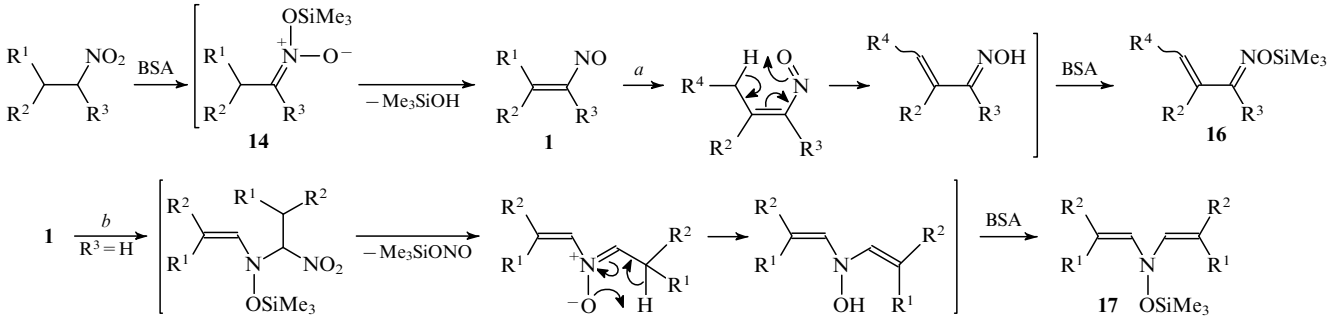
Selenium-[47] and tellurium-containing[48] analogues have been synthesised in a similar way.



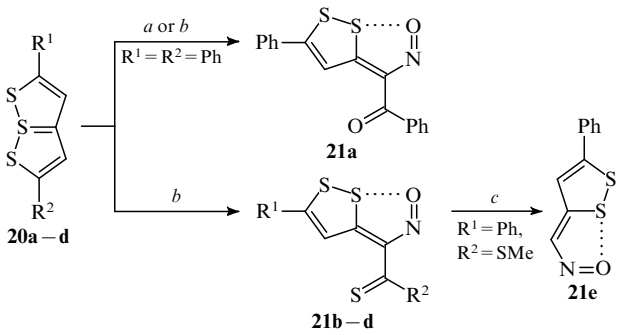
X = Se, Te.

Nitration or nitrosation of trithiapentalene **20a** has given unsaturated nitroso-derivative **21a**, the first representative of 2,4-epidithio-1-nitrosobuta-1,3-dienes.[49]

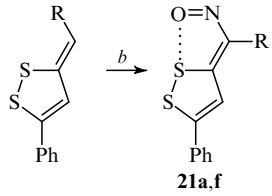
Scheme 3



BSA is *N*,*O*-bis(trimethylsilyl)acetamide;
(*a*) R^1 = CH_2R^4; R^2, R^4 are electron-withdrawing groups;
(*b*) 1,2-addition of **14**.



R^1 = Ph: R^2 = Ph (**a**), SMe (**b**), NMe_2 (**c**); $R^1 = R^2$ = SMe (**d**).



R = PhCO (**a**), NO_2 (**f**);

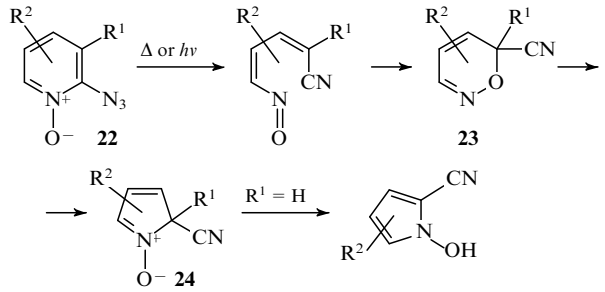
(*a*) HNO_3 – AcOH; (*b*) [HONO]; (*c*) $Hg(OAc)_2$.

At $R^1 = R^2$ = Ph, the introduction of a nitroso group is accompanied by the transformation of the thiobenzoyl substituent into benzoyl (compound **21a**).[49] The formation of 2,4-epidithio-1-nitrosobuta-1,3-dienes **21b**–**d** from the corresponding trithiapentalenes **20b**–**d** occurs with retention of the thiocarbonyl fragment.[49, 50] The CS_2Me group in the compound **21b** is removed on treatment with mercury(II) acetate.[49] The nitrosation of the corresponding 2,4-epidithiobuta-1,3-dienes yields the compounds **21a** [49] and **21f**.[51]

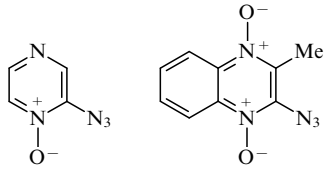
5. Other methods

Other methods are as yet of limited utility. Examples of generation of nitrosoalkenes from substrates having some specific structural features have been reported; in some cases, the arguments for the intermediate formation of nitrosoalkenes are based on the analysis of the final reaction products and, hence, they are not always convincing.

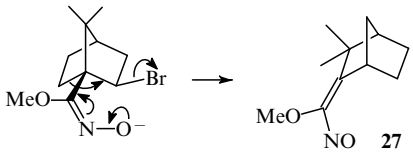
For example, 2-azidopyridine *N*-oxides **22** have been shown to undergo a number of transformations on exposure to radiation or on heating above 85 °C.[52–54] It is assumed that upon ring opening and concerted elimination of N_2, the compounds **22** can be converted into conjugated nitroso dienes, which then cyclise. When a substituent is present at the 3-position, two types of products can be formed, namely 6*H*-1,2-oxazines **23** and cyclic nitrones, 2*H*-pyrrole *N*-oxides **24**. When R^1 = Cl or Br, the compounds **23** can undergo subsequent transformations in the presence of nucleophilic solvents.[53]



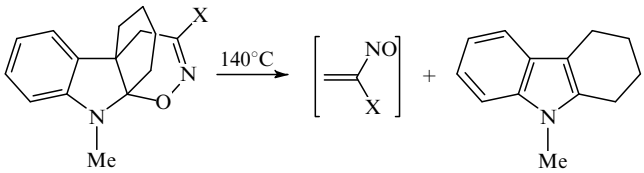
When R^1 = Me or H, the oxazines **23** are kinetically controlled products, whereas the nitrones **24** are thermodynamically controlled products of cyclisation of the intermediate nitroso dienes.[54] Similar transformations have also been observed for azidopyrazine 1-oxides **25** [52] and azidoquinoxaline 1,4-dioxides **26**.[55] In the opinion of Abramovich *et al.*,[54] in the latter case, a cyclic nitrone of type **24** is the kinetically controlled product, and 1,2-oxazine of type **23** is the thermodynamically controlled product.



The generation of nitrosoalkenes **27** is accompanied by isomerisation of the carbon skeleton of the substrate.[56]

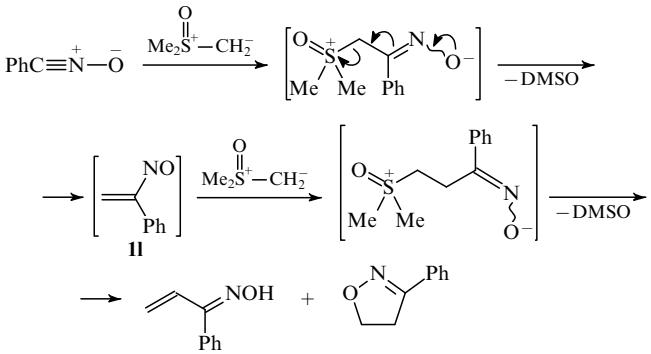


One more particular example of formation of nitrosoalkenes is retro-[2 + 4]-cycloaddition, which is facilitated by the formation of the stable aromatic structure of substituted indole.[57]

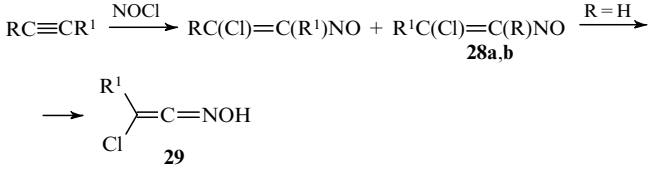


X = COMe, CO_2Et.

Apparently, the reactions of sulfonium ylides with nitrile oxides also proceed *via* nitrosoalkenes, which then react with nucleophilic ylides according to the addition–elimination reaction pattern or addition followed by cyclisation.[34, 58–61] An example of this type of reaction is presented below:

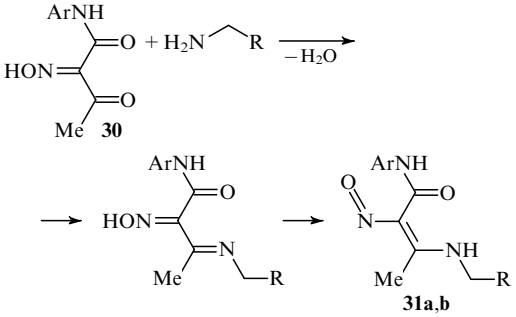


Indian researchers [62] have shown that the addition of gaseous NOCl in CH_2Cl_2 at 0 °C to the triple bonds in methyl alkynoates affords the corresponding β-chloro nitrosoalkenes. They found that nitrosoalkenes of type **28a** can isomerise to the corresponding chloro ketene oximes **29**. However, it should be mentioned that this isomerisation has never been observed for other nitrosoalkenes.



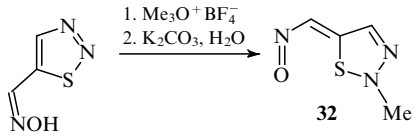
R = H (**a**), Alk (**b**); $R^1 = (CH_2)_nCO_2Me$.

Condensation of oximes **30** with allylamine[63] or benzylamine[64] makes it possible to isolate moderately stable nitrosoalkenes **31** as highly coloured crystals. The structure of the compound **31a** was confirmed by X-ray diffraction analysis.[64]

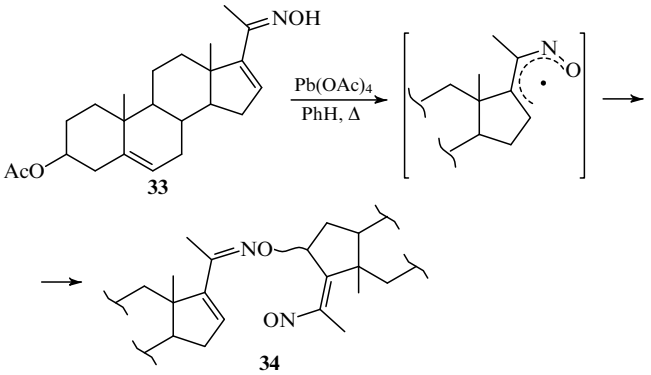


Ar = 4-ClC_6H_4: R = Ph (**a**), CH = CH_2 (**b**).

Methylation of 5-hydroxyiminomethyl-1,2,3-thiadiazole followed by treatment with a base affords a stable nitrosoalkene in a low yield.[65]

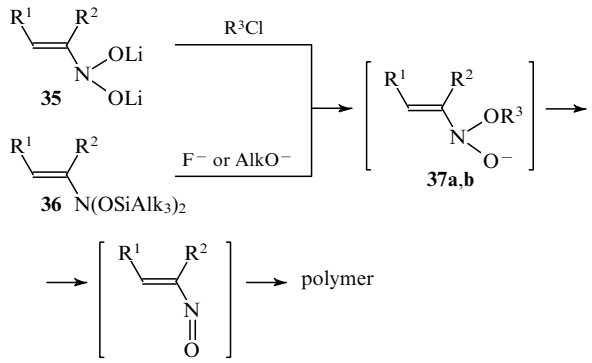


Oxidative dimerisation of α,β-unsaturated steroid oxime **33** gives rise to nitrosoalkene **34**, which is formed apparently by a radical mechanism.[66]



Deoxygenation of perchloro-2-nitrobuta-1,3-diene upon treatment with $R^1P(OR)_2$ results in the formation of perchloro-2-nitrosobuta-1,3-diene **1e** (see Table 1). The yield of this product is not indicated in the study cited.[9] Gas-phase thermolysis of nitroethylene on Fe or Ni at 883 K yields nitrosoethylene **1k**, together with MeCN.[67]

There exist two groups of compounds that can serve as close precursors of nitrosoalkenes, owing to their structural features. The first group comprises *N*,*N*-bis(lithioxy)enamines **35**, which were first described by Seebach *et al.*,[68] and the second group includes *N*,*N*-bis(trialkylsilyloxyenamines) of type **36**. It was shown[68] that treatment with benzoyl chloride of 1-[*N*,*N*-bis(lithioxy)]amino-2-phenylethylene, the product of double deprotonation of 1-nitro-2-phenylethane, gives a polymer. This was explained by assuming the generation and subsequent polymerisation of β-nitrosostyrene under the reaction conditions. However, no additional evidence supporting this hypothesis was presented.[68] Moreover, β-nitrosostyrene had been described earlier[33] as a stable crystalline dimer.



R^1 = Ph, R^2 = H, R^3 = PhCO (**37a**); $SiAlk_3$ (**37b**).

N,*N*-Bis(trialkylsilyloxy)enamines **36** were first described[69] as products of double silylation of aliphatic nitro compounds. The thermal instability of the compounds **36** (Alk = Me) observed in some cases was explained by possible easy elimination of $(Me_3Si)_2O$ giving nitrosoalkenes, which then polymerise. However, the attempt to trap nitrosoethylene **1k** as the corresponding adduct with cyclopentadiene during decomposition of the enamine **36** (R^1 = R^2 = H, Alk = Me) failed.[69]

Nevertheless, compounds **37** which have become quite available by now, are of interest as initial compounds for the generation of nitrosoalkenes *via* anionic intermediates of the semiacetal type by treatment with reagents possessing nucleophilic properties with respect to the trialkylsilyl group (see Sheme 3). Previously this route for the construction of a nitroso group has been realised during ring opening in *N*-trimethylsilyloxyisoxazolidines.[41,71]

III. Structure and physical properties of nitrosoalkenes

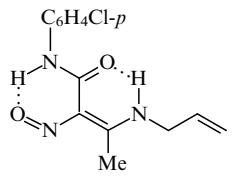
As was to be expected, stable nitrosoalkenes, the properties of which are listed in Table 1, have been characterised most comprehensively by spectroscopic data.

Spectroscopic characteristics of long-lived nitrosoalkenes have been described systematically.[8] The blue colour of these compounds is due to absorption in the visible region (λ_{max} = 675–795 nm) with low extinction coefficients (ε = 20–60).[19] Absorption is also observed between 250 and 350 nm (in some cases, two maxima can be distinguished).

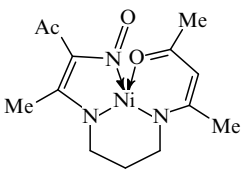
IR spectra of nitrosoalkenes contain two absorption bands in the region 1420–1660 cm^{-1}. A band in the range 1420–1480 cm^{-1} corresponds to the stretching vibrations of the N=O bond (for 2,2-di-*tert*-butylnitrosoethylene **1c**[7] this band occurs at 1485 cm^{-1}). The same region contains the absorption bands for the N=O bonds in other monomeric nitroso compounds.[72] The absorption at shorter wavelengths (1500–1600 cm^{-1}) was assigned to stretching vibrations of the C=C bond.[8]

In the ^1H NMR spectra of the compounds **1b** and **1f** (see Table 1), the vinylic protons account for signals at δ 9.13 ppm[6] and 8.68 ppm,[10] respectively. In the case of the nitrosoalkene **1c**, the signal due to the proton at the carbon atom bound to the nitroso group manifests itself in a substantially higher field (δ 6.30 ppm).[7] Thus, spectral data attest to the occurrence of appreciable π-conjugation between the C=C bond and the nitroso group.

The stability of nitrosoalkenes markedly increases in the presence of halogen atoms or bulky aryl or *tert*-alkyl groups (see Table 1), as well as upon formation of strong intramolecular hydrogen bonds (compound **31b**)[63] or complexes with transition metals (compound **38**).[73]



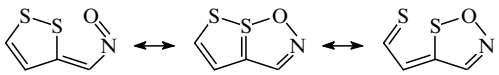
31b



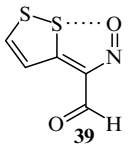
38

The high stability of 2,4-epidithio-1-nitrosobuta-1,3-dienes **21**, the nitroso compound **32**, the nitroso fulvenes **19**, and their selenium- and tellurium-containing analogues is due to the fact that the β-carbon atom of the nitrosoalkenyl fragment and the electron-donating substituents attached to it are incorporated into a common 6π-electron heterocyclic system.

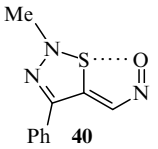
The structure of the nitrosobutadienes **21a,f** was unambiguously determined based on X-ray diffraction analysis. It was found that the S···O interatomic distance is much shorter than that expected on the basis of the van der Waals radii of the S and O atoms.[74–76] The abnormally short distance between the sulfur and oxygen in the nitrosobutadienes **21** is explained by the ability of the formally divalent sulfur atom to be involved into additional binding, which can be accomplished either with participation of the sulfur *d* orbitals or due to the formation of a three-centred electron-enriched S–S–O bond.[75] It is noteworthy that, according to X-ray diffraction data, the S···O interatomic distance formed upon coordination of the nitroso group to sulfur is markedly shorter than that arising upon coordination to a carbonyl[76] or nitro group.[74] The configuration of the C=C bond in the compounds **21** is determined by the fact that sulfur coordinates preferentially to the oxygen atom of the nitroso group rather than to other groups (C=S, C=O, or NO_2).[51] In terms of the valence-bond method, the S···O binding can be represented by the following canonical structures:



The CNDO/2-SCF-MO calculations[77] for a hypothetical structure of aldehyde **39** demonstrated the possibility of this binding. The X-ray diffraction[78] and ^{15}N NMR spectroscopy[79] data for 1,2,3-thiadiazole **40** also imply a thiapentalene character of this structure.



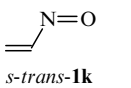
39



40

Mass spectra of 2,4-epidithio-1-nitrosobuta-1,3-dienes **21b**,**e**,**f** have been studied.[80]

Unstable nitrosoalkenes have scarcely been investigated by spectroscopy. The structure of the *s-trans*-rotamer of nitrosoethylene **1k** generated by pyrolysis of chloroacetaldoxime has been studied by microwave spectroscopy in the gas phase.[13] The molecular orbitals of **1k** have been calculated by the Hückel[56] and CNDO[81] methods. The optimised structures, bond orders, and electrostatic potentials for the compound **1k** and fluoronitrosoethylenes have been calculated by the *ab initio* (SCF-MO) method.[82] It was found[81] that the *s-trans*-rotamer of **1k** is somewhat more stable than the *s-cis*-rotamer.



s-trans-**1k**



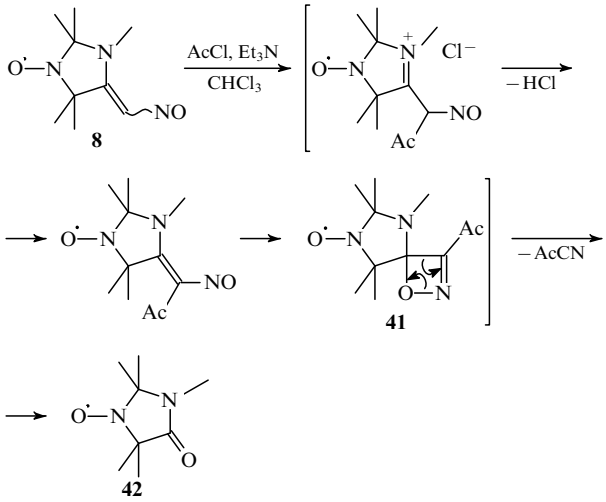
s-cis-**1k**

IV. Reactions of nitrosoalkenes

Due to the presence of the C=C–N=O fragment, nitrosoalkenes are highly reactive compounds; they readily undergo intramolecular rearrangements, react with nucleophiles, and enter into concerted cycloaddition reactions.

1. Unimolecular reactions

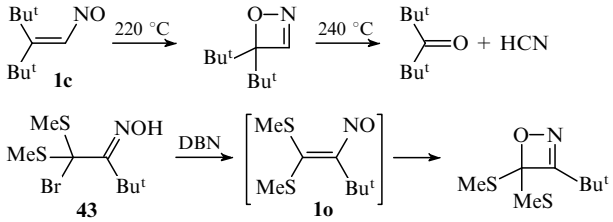
Two types of intramolecular rearrangements of nitrosoalkenes have already been mentioned here; these are cyclisation to 1,2-oxazetines followed by fragmentation (see Section II.2) and cyclisation of nitroso-dienes to 6*H*-1,2-oxazines and 2*H*-pyrrole *N*-oxides (see Section II.5). Taking into account the reaction conditions described in Ref. 30, the transformation of the nitrosoalkene **8** into the final product **42** upon treatment with acetyl chloride occurs most probably *via* an intermediate 1,2-oxazetine rather than according to the haloform decomposition pattern, as the authors cited[30] believe.



8

The intramolecular route of fragmentation of nitrosoethylene **1k** involving intermediate formation of 1,2-oxazetine was confirmed subsequently by *ab initio* (SCF-MO) calculations.[83]

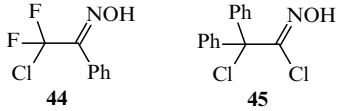
Oxazetines have also been isolated after thermal rearrangement of the nitrosoalkene **1c**[7] and after the reaction of bromo oxime **43** with bases. In the latter case, the intermediate formation of the nitrosoalkene **1o** was assumed.[37]



1c **43** **1o**

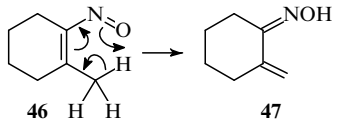
DBN is diazabicyclononane.

It has been suggested[8] that cyclisation to 1,2-oxazetines followed by fragmentation is the main route of decomposition of many other nitrosoalkenes, which do not isomerise to unsaturated oximes without external nucleophiles. The examples of formation of PhCN and Ph_2CO upon treatment of oximes **44** and **45**, respectively, with Na_2CO_3 in CH_2Cl_2 were presented as evidence supporting this hypothesis.[8]



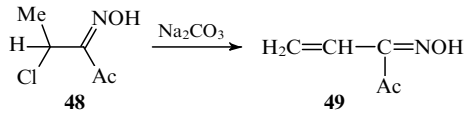
44 **45**

Yet another characteristic type of intramolecular rearrangements is [1,5]-shift of a hydrogen atom. This is the main route of transformation of internal nitrosoalkenes having allylic hydrogen atoms. This rearrangement results in the formation of the corresponding unsaturated oximes in 28% – 72% yields.[31] Thus it has been assumed[35] that the [1,5]-shift of hydrogen in 2-methyl-1-nitrosocyclohexene **46** gives unsaturated oxime, which has been identified[3] as having the structure **47**. During the reaction, the blue colour, typical of solutions of the nitrosoalkene **46**, disappears.



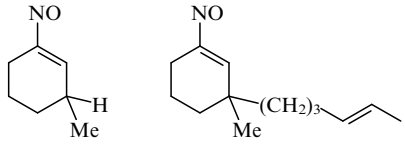
46 **47**

When chlorinated oxime **48** is treated with Na_2CO_3,[84] [1,5]-shift of hydrogen results in the formation of unsaturated oxime **49**. The same compound is formed as a side product in cycloaddition reactions of the nitrosoalkene MeCH = C(Ac)NO[16] (see Section IV.3).



48 **49**

It has been found[19] that the rearrangement giving unsaturated oximes can occur not only as an intramolecular transformation but also as a base-catalysed one. Thus nitrosoalkene **50** for which concerted hydrogen [1,5]-shift is impossible due to steric reasons, is much less stable than compound **51**, which contains no hydrogen atoms at C(3) (the half-life $\tau_{1/2}$ for the compound **50** in a dilute solution is 12 min, while that for the compound **51** is 900 min).[19]



50 **51**

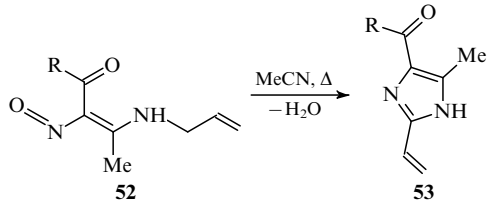
The scheme of transformation of the isoxazolinone **2** into the corresponding α,β-unsaturated oxime (see Section II.1)[21] and the synthesis of *O*-trimethylsilyl derivatives of the α,β-unsaturated oximes **16** (see Scheme 3)[44] have also been assumed to include stages involving the [1,5]-shift of hydrogen.

2. Reactions with nucleophiles

In the nitroso compounds **1**, the C = C double bond is conjugated with the nitroso group and is thus activated. The reactivity of nitrosoalkenes obviously resembles those of other activated alkenes, for example, conjugated nitroalkenes. The presence of π-conjugation accounts for the high electrophilicity of the β-carbon atom in nitrosoalkenes; therefore, these compounds are especially prone to react with nucleophiles.

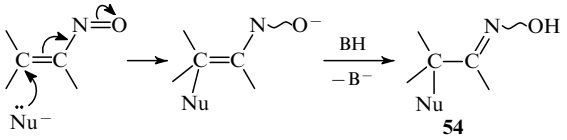
The reactions of nitrosoalkenes with nucleophiles can be conventionally divided into two groups: (1) 1,2-addition at the N = O bond and (2) conjugate 1,4-addition.

Only two examples of reactions of the former type are known. These are addition of silyl nitronates to the nitroso group in β-substituted vinyl nitroso compounds [see Scheme 3, pathway (*b*)] and intramolecular condensation of substituted nitrosoalkenes **52** to the corresponding vinylimidazoles **53**.[63]



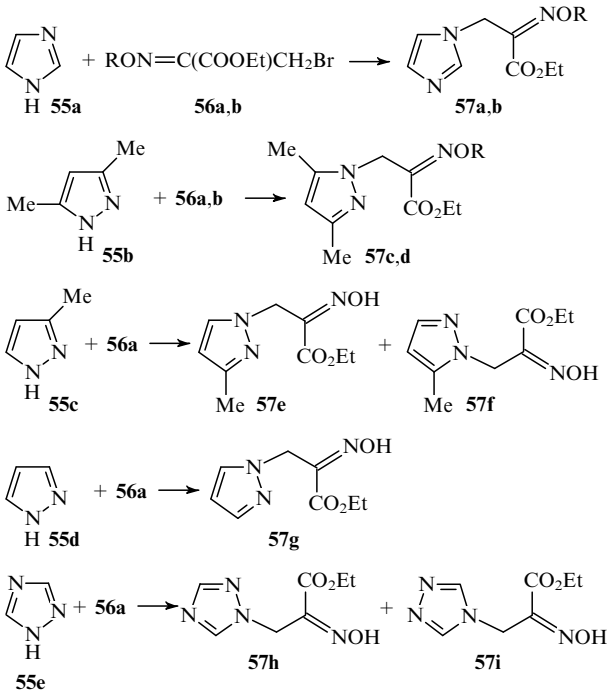
52 **53**

Conjugate 1,4-nucleophilic addition is much more typical of vinyl nitroso compounds and largely determines their synthetic value.



54

When α-halo oximes are used as synthetic precursors of the substituted oximes **54**, two routes are, in principle, possible: (1) 1,4-elimination–addition with intermediate formation of nitrosoalkenes and (2) direct substitution of the halogen by a nucleophile by the S_N2 mechanism. Is it possible to determine which of the mechanisms is realised in each particular case? This important question has been answered[55] based on a semiquantitative study of the rates of *N*-alkylation of azoles **55a**–**e** by model α-bromo oximes **56a,b**. The results of this study are presented in Table 2.



R = H (**56a**, **57a**), CMe_2OMe (**56b**, **57b**).

It can be seen from the data of Table 2 that imidazole **55a** and 3,5-dimethylpyrazole **55b** react with α-bromo oxime **56a** much faster than their less basic analogues. On passing to the bromo oxime **56b**, the rate of the reaction with the compounds **55a**,**b**

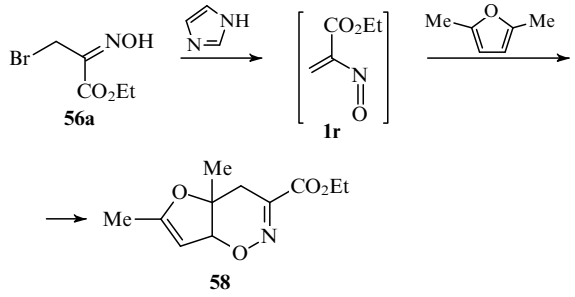
Table 2. Effect of the basicity of the azoles **55a**–**e** on the duration of *N*-alkylation with α-bromo oximes **56a**,**b**.

Substrate **55**	pK_a[a]	Duration of the reaction (h) with the oximes	
		56a	**56b**
a	7.10	0.2	24
b	4.12	0.5	48
c	3.32	24[b]	–
d	2.52	72	–
e	2.27	72	–

Note. An azole (2.0 mmol) and a bromo oxime (1 mmol) in 25 ml of MeCN, 20 °C. [a] For aqueous solutions of conjugated acids. [b] The ratio **57e** : **57f** = 2 : 1.

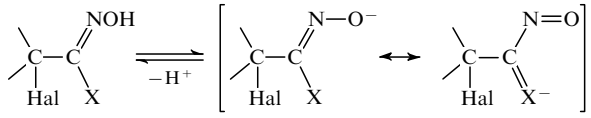
markedly decreases and becomes comparable with the rates of reactions of weakly basic azoles.

Evidently, the azoles **55a**,**b** are sufficiently basic to react with the oxime **56a** *via* the 1,4-elimination – addition pattern involving intermediate formation of the corresponding nitrosoalkene, acting simultaneously as bases and as nucleophiles. Bromo oxime **56b** cannot react according to the elimination – addition scheme. In this case, the reaction occurs as direct S_N2 substitution. The conclusion about the formation of ethyl α-nitrosoacrylate **1r** during this reaction was confirmed [85] by its trapping. The product of reaction of the nitrosoalkene **1r** with 2,5-dimethylfuran **58** was obtained in 50% yield.

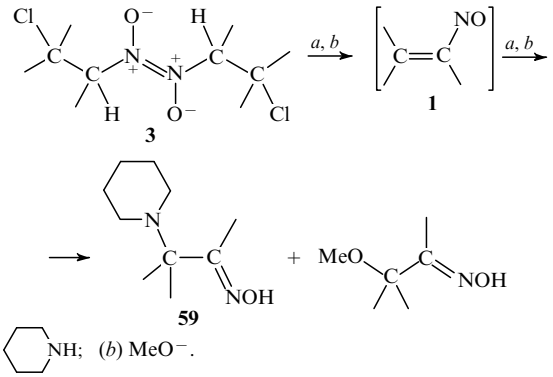


The reaction of the oxime **56a** with a weaker base, pyrazole **55d**, in the presence of 2,5-dimethylfuran yields only the corresponding *N*-alkylation product, cycloadduct of type **58** being totally missing. When Na_2CO_3 is added to a solution of pyrazole **55d** and bromo oxime **56a** under standard conditions, the reaction is completed over a period of 10 min giving the corresponding *N*-alkylation product in a high yield.[85] Based on these data, it was concluded that the reactions of the azoles **55c** – **e** with the oxime **56a** and of the compounds **55a**,**b** with the oxime **56b** occur as direct S_N2 substitution.

The facts presented in the study cited [85] to justify the assumption that the mechanism of *N*-alkylation changes upon a decrease in the azole basicity seem quite convincing. However, in our opinion, the reaction mechanism depends not only on the basicity of the nucleophile but also on the acidity of the preceding oxime, which varies as a function of the substituent X at the C = N bond.



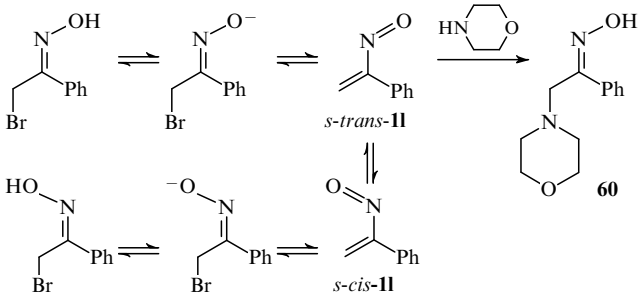
There are weighty arguments that the reactions of the dimers of β-chloro nitroso compounds **3** with nucleophilic bases occur by the elimination – addition mechanism. These compounds react with MeONa faster than with piperidine; however, when both bases are present, α-piperidino oximes **59** are the major reaction products.[33]



(*a*) NH; (*b*) MeO^-.

The experimental results rule out the direct substitution mechanism. It is obvious that the ratio of the reaction products is determined by the fact that at a fast reaction step, piperidine which possesses stronger nucleophilic properties, adds preferentially to the nitrosoalkene **1**.

Study of the reactions of *syn*- and *anti*-α-bromoacetophenone oximes with morpholine in an aqueous buffer solution also points to the intermediate formation of 1-nitroso-1-phenylethylene **1l**. Reactions with both bromo oximes give *anti*-α-morpholino oxime **60**.[15]



Presumably, bromo oximes undergo fast deprotonation and then eliminate Br^- in the rate-determining step yielding the intermediate 1-nitroso-1-phenylethylene **1l**. Morpholine adds to the nitrosoalkene **1l**, which occurs in the transoid conformation.

In the majority of other cases, the mechanisms of reactions of nucleophiles with α-halo oximes and with dimers of β-chloro nitroso compounds have not been studied. Alkylation of the anions derived from 1,1-dinitroalkanes [86] or tertiary phosphines [87,88] with α-halo oximes proceeds apparently as the direct S_N2 substitution of the halogen atom. In view of the relatively low basicity of these nucleophiles, the intermediate formation of nitrosoalkenes during their alkylation seems unlikely.

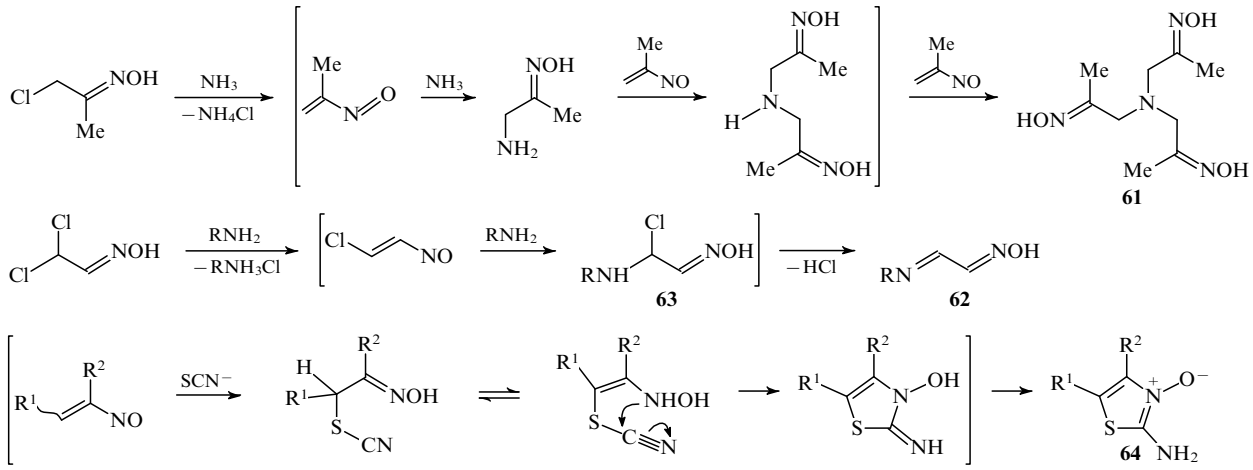
Below we discuss only those examples in which either the reaction conditions strongly imply the occurrence of the elimination – addition mechanism or independent evidence for the intermediate formation of nitrosoalkenes exists.

Examples of interaction of *N*-, *O*-, and *S*-nucleophiles with nitrosoalkenes are presented in Table 3.

Table 3. Addition of N-, O-, and S-nucleophiles with nitrosoalkenes.

Nitrosoalkenes	Types of nucleophiles	Ref.
$CH_2=C(Me)NO$	NH_3, R_2NH	4
$CH_2=C(Pr)NO$	$RCH(NH_2)CO_2Et$	89
$CH_2=C(Ph)NO$ (**1l**)	NH_3	90
	R_2NH	15
	SCN^-	91
$CH_2=C(Ac)NO$ (**1m**)	$(H_2N)_2CS$, H_2NCH_2CN	91
	$RCH(NH_2)CO_2Et$	92
	$Me(CH_2)_4OH$	57
$CH_2=C(CO_2Et)NO$ (**1r**)	ArSH	93
$R^1R^2C=C(R^3)NO$	NH_3, RNH_2, R_2NH,	94
R^1 = H, Alk;	NH_2OH, NO_2^-, N_3^-	
R^2, R^3 = Alk, cyclo-Alk	R_2NH, ROH, ArSH	31, 33, 35, 95
	R_3N	11
$ClCH=CHNO$	RNH_2, $ArNH_2$	96
$Cl_2C=CHNO$ (**1h**)	$ArNH_2$	97
$ArCH=C(R)NO$	R_2NH, ROH, ArSH	31, 33
	R_3N	11
	SCN^-, $EtOCS_2^-$	98
$CH_2=C(CF_3)NO$ (**1n**)	Et_2NH, H_2O	17

Scheme 4

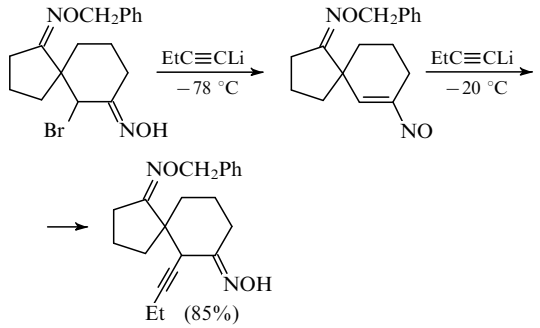


The reaction follows the general Scheme 4; however, the primary adducts often undergo subsequent transformations. For example, treatment of chloroacetone oxime with aqueous ammonia affords tertiary amine **61**.[4] Reactions of this type have also been observed for 1-haloalkyl phenyl ketoximes.[90] The dichloroacetaldehyde oxime reacts with primary amines to give imines **62** resulting from elimination of HCl from the primary adduct **63**;[96] the chloral oxime reacts in a similar way.[96] The reactions with thiocyanate ions yield 2-aminithiazole *N*-oxides **64** formed upon cyclisation of the primary adducts.[31, 91, 98]

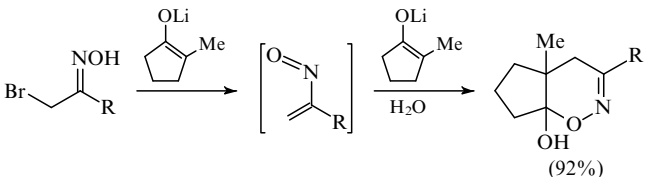
The interaction of nitrosoalkenes with enamines and other electron-donating alkenes will be considered in Section IV.3.b among cycloaddition reactions. In this section, we shall discuss reactions of nitrosoalkenes with carbanions and also electrophilic substitution in aromatic substrates.

Vinyl nitroso compounds are convenient reagents for alkylation of nucleophilic carbon atoms under mild conditions. Reactive carbanions or their equivalents serving as nucleophiles in these reactions are taken in a twofold (or larger) molar excess. The first mole of a nucleophilic compound reacts as a base with liberation of an intermediate nitrosoalkene, and the second mole acts as the nucleophile. A typical example of these reactions is the generation of nitrosoalkenes followed by nucleophilic addition of organometallic substrates to them, which gives rise to the compounds **10** [36] and **15**.[40]

EtMgBr,[11] PhMgBr,[94] and EtC≡CLi [99] have also been used in similar reactions.



α-Bromo oximes have been used to alkylate lithium enolates prepared from substituted cyclopentanones.[100, 101]

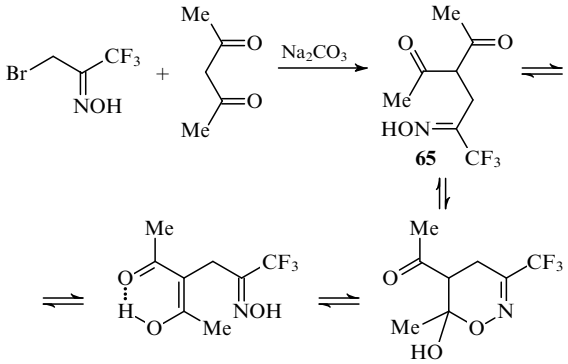


R = $(CH_2)_3CH=CH_2$.

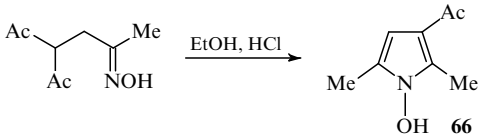
The reactions of nitrosoalkenes with other stabilised carbanions are presented in Table 4. In many cases, EtONa and EtOH are used as the base and the solvent, respectively; in some cases, Na_2CO_3 in CH_2Cl_2 [93] or in Bu^tOMe [17] or piperidinium acetate in THF [96] are also employed.

The reaction products are 1 : 1 adducts; they exist in solutions as mixtures of linear tautomers and five- or six-membered cyclic species, as for example, the adduct **65** (Scheme 5).[17]

Scheme 5



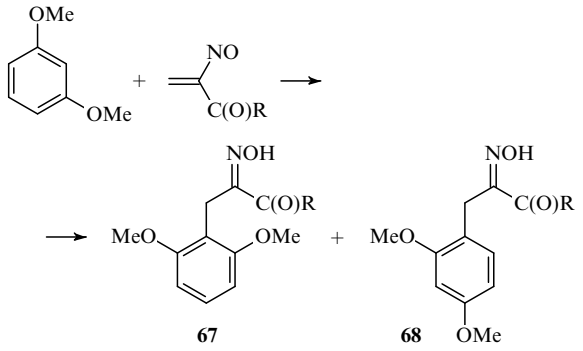
Some of the addition products can undergo subsequent transformations. Thus the adducts obtained from the nitrosoalkene ClCH=CHNO eliminate HCl under the reaction conditions giving rise to α,β-unsaturated oximes $R^1R^2C=CHCH=NOH$.[96] Some of the adducts can be converted into the corresponding 1-hydroxypyrroles by treatment with an acid.[102–105, 107] An example is provided by the formation of 3-acetyl-1-hydroxy-2,5-dimethylpyrrole **66** from the adduct of chloroacetone oxime and acetylacetone.[102]



Reactions of sulfonium ylides yielding isoxazolines and α,β-unsaturated oximes have been described above (Section II.5).[34, 58–61]

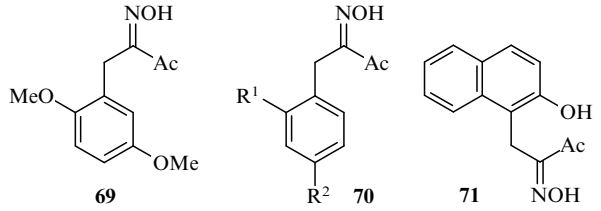
It seems very attractive to use nitrosoalkenes as electrophiles in aromatic substitution reactions, because they are generated under mild conditions in the absence of acids. This reaction would permit introduction of various functional groups. However, in practice, only highly electrophilic nitrosoalkenes in combination with highly nucleophilic aromatic and heteroaromatic systems are suitable for this purpose. Thus alkylation of 1,3-dimethoxybenzene with electrophilic nitrosoalkenes is one of the few

reported examples of this type of reaction.[16] The ratio of the isomers **67** and **68** formed in this process is 1 : 4.



R	H	Me	OEt
Yield of **67** + **68** (%)	41	63	11

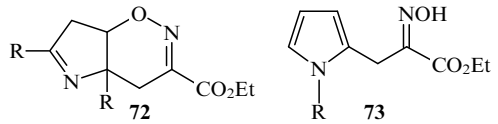
Alkylation of 1,4-dimethoxybenzene, *N*,*N*-dimethylaniline, and 2-naphthol with 3-nitrosobut-3-en-2-one 1**m** gives the corresponding products **69**–**71** in low yields; less electrophilic ethyl α-nitrosoacrylate **1r** does not alkylate 2-naphthol.



R^1, R^2 = H, NMe_2.

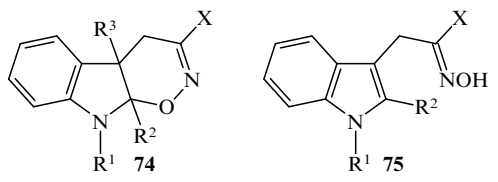
The reactions of nitrosoalkenes with heteroaromatic systems (furans, benzofurans, pyrroles, and indoles) are more general. In this review, we classify these reactions as electrophilic substitution. However, this classification is quite arbitrary (see, for example, Refs 16, 17, and 108), because for these heterocycles it is often difficult to decide between electrophilic substitution and [4 + 2]-cycloaddition reaction mechanisms.

The reactions of pyrroles with ethyl α-nitrosoacrylate **1r** involve only the 2-position.[108, 109] The data about the formation of 3-substituted pyrroles[3, 16] as side products have not been supported later.[108] Depending on the presence and the positions of substituents, pyrroles give 1 : 1 adducts of two types, **72** and **73**. This is apparently due to proton migrations in the adducts formed initially. Unfortunately, the attempt to involve ethyl α-nitrosoacrylate **1r** in the reaction with 1,2,5-trisubstituted pyrroles, which would rule out the possibility of these migrations, was unsuccessful. Ethyl α-nitrosoacrylate also did not react with less electron-donating *N*-(toluene-4-sulfonyl)pyrroles and pyrrole-2-carbaldehyde.[108]

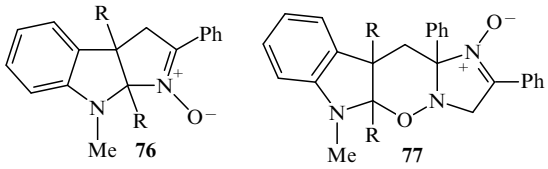


R = Me, Ph (**72**); R = H, Me (**73**).

Unlike pyrroles, indoles are alkylated by nitrosoalkenes; the reaction involves the 3-position and yields two types of adducts, **74** and **75**, depending on whether or not this position contains substituent.



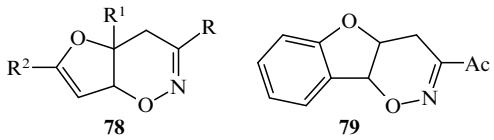
In the case of electron-deficient nitrosoalkenes — $CH_2=C(CO_2Et)NO$ (**1r**),[16, 93, 110] $CH_2=C(Ac)NO$ (**1m**),[16] and $CH_2=C(CF_3)NO$ (**1n**)[17] — the corresponding adducts are formed in high yields (65% – 88%) even from equimolar amounts of bromo oxime and indole.[16] However, at elevated temperatures, the yields decrease, because the reaction becomes noticeably reversible.[57] When 1-nitroso-1-phenylethylene **1l** reacts with *N*-methyltetrahydrocarbazole, cyclic nitrone **76** and 2 : 1 adduct **77** are formed together with the main product **74**.[57]



R, R = $(CH_2)_4$.

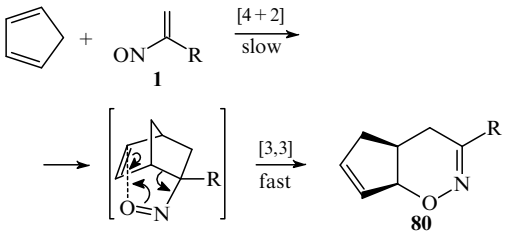
Alkylation of 2-substituted indoles by the nitrosoalkene $CH_2=C(CO_2Et)NO$ (**1r**) is the key stage in the synthesis of several tryptophan derivatives.[111, 112] A series of studies[113–115] have been devoted to alkylation of 3-substituted indoles with ethyl α-nitrosoacrylate aimed at the synthesis of biologically active tryptophan derivatives. In some cases, the primary adducts were found to be unstable and to rearrange readily.[113–115]

The reactions with less aromatic substrates such as furan,[16, 18, 93] 2-metyl-,[116] 2,5-dimethyl-,[16, 18, 116, 117] and benzofuran[16] always afford cycloadducts **78** and **79**, which readily undergo selective cleavage on treatment with acids[16, 118] or bases[116] to give either products of oxazine ring opening or products of more extensive transformations.[116, 118]



3. Cycloaddition reactions

Nitrosoalkenes can participate in cycloaddition reactions either as 2π-electron systems (the reaction involves the nitroso group) or as 4π-electron conjugated heterodienes (1,2-dihetero-1,3-diene systems). No examples of reactions involving only the C=C bond have been found yet. However, some researchers[119, 120] have suggested that nitrosoalkenes enter into [4 + 2]-cycloaddition reactions with 1,3-dienes as $2\pi_{C=C}$ components, which are followed by fast [3,3]-sigmatropic rearrangement of the resulting adducts into the final products. For example, cycloaddition of nitrosoalkenes to cyclopentadiene to give adduct **80** can be considered within the framework of this hypotheses; however, no facts supporting it have been obtained.



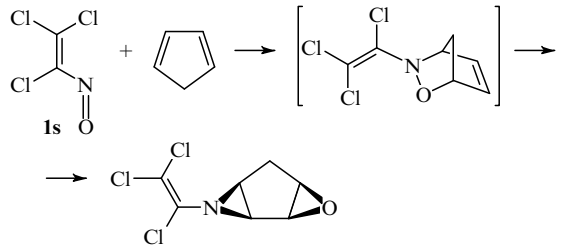
R = Ar, C(O)R.

a. Nitrosoalkenes as 2π systems in cycloaddition reactions

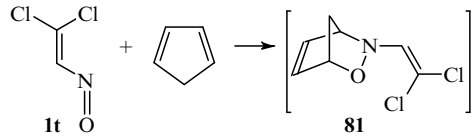
Cycloaddition to a nitroso group acting as a 2π-electron system is typical of nitroso compounds of many classes.[121–123] In the case of nitrosoalkenes, this type of reaction is limited to β,β-dihalo- and β-halo-β-alkyl-derivatives.[8] For example, trichloronitrosoethylene **1s** reacts as heterodienophile with various cyclic and

acyclic nucleophilic dienes including butadiene,[8] 1-methoxybutadiene,[8] cyclopentadiene,[8] cyclohexadiene,[8] and benzene oxide.[124]

Adducts formed from cyclic dienes are thermally unstable and readily rearrange at room temperature to epoxyaziridines, similarly to the [4 + 2]-cycloadducts of 1,3-dienes with singlet oxygen, which are converted into 1,3-diepoxides.[125, 126]



The structure of the adduct derived from β,β-dichloronitrosoethylene **1t** and cyclopentadiene **81** was confirmed by recording its low-temperature NMR spectrum.[127]

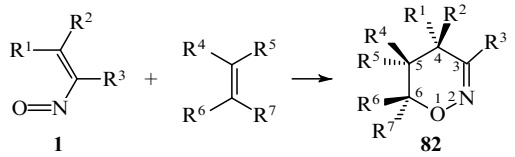


It should be emphasised that the rearrangement to epoxyaziridines is typical only of adducts of halo-substituted nitrosoalkenes with cyclic dienes. Cycloadducts of nitrosoalkenes with acyclic dienes,[8] as well as the products of [4 + 2]-cycloaddition of cyclic 1,3-dienes to the nitroso groups of other types of nitroso compounds,[121, 127] do not undergo this rearrangement. This regularity has not been explained yet.

It has been shown that tetrafluoroethylene and chlorotrifluoroethylene add to the nitroso group of trifluoronitrosoethylene **1a** according to the [2 + 2]-cycloaddition pattern to give 1,2-oxazetidines.[5]

b. Nitrosoalkenes as conjugated heterodienes in the cycloaddition to C = C bonds

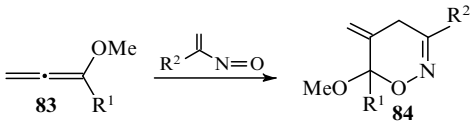
The [4 + 2]-cycloaddition to alkenes is perhaps the most important reaction of nitrosoalkenes, which has mainly determined the vigorous development of the chemistry of these compounds in the last decade. In this reaction, nitrosoalkenes **1** act as electron-withdrawing 4π-components (conjugated heterodienes) and give rise to 5,6-dihydro-4*H*-1,2-oxazines **82**, which are valuable intermediate compounds in the synthesis of various cyclic and linear polyfunctional compounds.



This type of addition was observed for the first time in the reaction of cyclopentadiene [18] with 1-nitroso-1-phenylethylene **1l**. Later, this reaction route has been extended to other alkenes and nitrosoalkenes; as a rule, the latter contain unsubstituted β-carbon atoms ($R^1 = R^2 = H$),[8, 14, 16] although this type of cycloaddition is also possible[8, 16, 45, 128] for some β-substituted nitrosoalkenes, for instance, MeCH = C(Ac)N = O (**1u**) [16] and $MeO_2CCH = CHN = O$ (**1q**).[45]

The reaction is highly regio- and stereoselective; in the adducts of type **80** derived from cyclopentadiene, the oxygen atom of the nitroso group is always attached to the allylic carbon atom of the cyclopentene fragment. Other linear and cyclic conjugated dienes add to nitrosoalkenes of the general type $CH_2 = C(R)NO$ in a similar way.[8, 14, 18, 120, 129]

Another type of nucleophilic dienes, methoxyallenes **83**, readily react with nitrosoalkenes to give 6-methoxy-substituted cycloadducts **84** with high regioselectivity.[130, 131] The successful synthesis of these compounds opened up new opportunities for using the oxazine ring in various transformations.[132 – 136]



Unfortunately, the attempt to extend cycloaddition to allene, phenylallene, and trimethylsilylallene was unsuccessful, indicating that the electronic requirements to allenes are stricter than those to alkenes.[131]

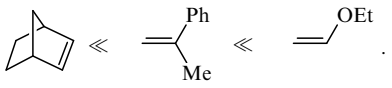
Electron-deficient alkenes, diethyl fumarate,[16] *trans*-1,2-dichloroethylene,[16] and maleic anhydride [137] do not form [4 + 2]-cycloaddition products with nitrosoalkenes.

Simple alkenes, oct-1-ene,[14, 16] *cis*-cyclooctene,[16, 138] and cyclohexene,[16] react only with highly electrophilic nitrosoalkenes **1** ($R^1 = R^2 = H$), containing substituents such as Ac, CHO, or 4-$NO_2C_6H_4$ at the α-position; these reactions can give mixtures of regioisomers. Thus 1-nitroso-1-(4-nitrophenyl)ethylene **1v** reacts with oct-1-ene giving rise to a mixture of 6- and 5-n-hexyl-substituted 1,2-oxazines **82** in a ratio of 85 : 15.[14] However, the reactions of nitrosoalkenes with conjugated terminal mono- and disubstituted alkenes result in the formation of only 6-mono- and 6,6-disubstituted regioisomers **82** ($R^4 = R^5 = H$; $R^6 = NR_2$, OR or Ar; R^7 = H, Alk, or Ar).[14, 18, 120] The interaction with 1,2-disubstituted alkenes follows a more complex route. Thus the reaction of *trans*-1-phenylpropene with nitrosoalkenes affords both regioisomers with low regioselectivity. The introduction of an electron-donating methoxy group into the *para*-position of *trans*-1-phenylpropene markedly increases the regioselectivity of this reaction; in this case, regioisomers containing the aryl group at the 6-position are formed predominantly.[14]

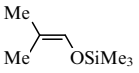
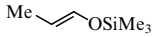
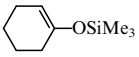
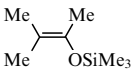
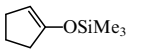
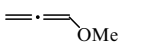
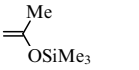
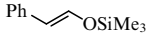
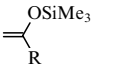
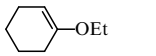
The cycloaddition of nitrosoalkenes to 1,2-disubstituted alkenes, containing an OR or NR_2 group as one of the substituents at the C = C bond, always yields 6-alkoxy(or silyloxy-) or 6-dialkylamino(or disilylamino)-substituted 1,2-oxazines, respectively.[117, 120, 139 – 144] The versatility and high regioselectivity of the cycloaddition of nitrosoalkenes to vinyl ethers or enamines have stimulated investigations of the synthetic potential of the reaction products, namely, 5,6-dihydro-4*H*-1,2-oxazines containing OR or NR_2 groups at the 6-position.[93, 107, 117, 118, 138 – 140, 145 – 152]

It is noteworthy that allylsilanes proved to be convenient ene components for [4 + 2]-cycloaddition to nitrosoalkenes (triallylbutylstannane reacts in a similar way [120]). The reaction is highly regioselective and results in the formation of 6-(1-trimethylsilylalkyl)-1,2-oxazines,[120, 151, 152] which can be converted into valuable compounds by modification of the oxazine ring [155] and also proved to be convenient starting compounds for the synthesis of γ,δ-unsaturated ketones and amines.[120, 153 – 155]

Using the method of competing reactions, it has been found [16] that the rate of [4 + 2]-cycloaddition of alkenes to 3-nitrosobut-3-en-2-one **1m** increases with increase in the electron-donating capacity of the substituents at the C = C bond in the alkenes; in terms of the reaction rate, the alkenes studied can be arranged in the following sequence:



Reissig *et al.*[128] studied the relative reactivities of various alkenes in more detail. They used mainly trimethylsilyl ethers of enols and chose 1-nitroso-1-phenylethylene **1l** as the model nitrosoalkene.[128] The following relative rate constants (k) were obtained for cycloaddition of various alkenes to 1-nitroso-1-phenylethylene:[128, 156]

Alkene	k	Alkene	k
	17		0.33
	11.5		0.2
	8.5		0.19
	3.5		0.13
	2.2		
	1.2		0.11
	1.0		0.09
	0.95		
	0.6		< 0.01

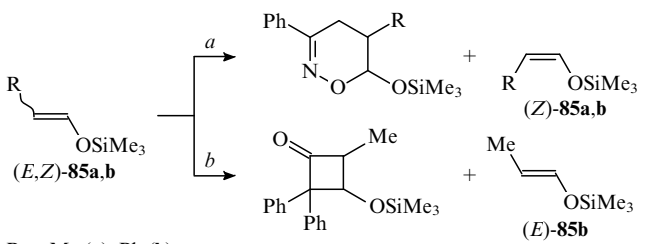
(R = Pr^i, Ph, Bu^t)

The rate constant (k) values presented above indicate that the EtO group possesses higher activating ability than the Me_3SiO group. It is also noteworthy that the reactivity of 1,1-disubstituted trimethylsilyl enol ethers is much lower than that of 1,2-disubstituted derivatives. For example, the relative reactivity of *E*-(1-trimethylsilyloxy)propene is ~100 times higher than that of (2-trimethylsilyloxy)propene, and the enol silyl ethers containing Pr^i, Ph, or Bu^t groups at the α-position do not react with the nitrosoalkene **1l** at all. The absence of the reaction in the latter case is due to the steric influence of substituents and, hence, it confirms indirectly the concerted mechanism of [4 + 2]-cycloaddition of nitrosoalkene. If the reaction occurred by a stepwise mechanism, these substituents would efficiently stabilise the positive charge or the radical site in an intermediate.[128]

The substantially higher reactivity of the *E*-isomers of vinyl ethers compared to that of the *Z*-isomers also deserves attention.[128] The ratios of the reaction rates for *E*- and *Z*-isomers [$k(E)/k(Z)$] are the following:

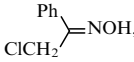
Compound	The $k(E)/k(Z)$ ratio
MeCH = CHOSiMe$_3$	26
Pr^{i}CH = CHOSiMe$_3$	25
PhCH = CHOSiMe$_3$	> 50
Me$_3$SiOCH = CHOSiMe$_3$	> 50
MeCH = CHOEt	6

This relationship has found application in the development of an elegant method for the kinetic resolution of mixtures of the *E*- and *Z*-isomers of trimethylsilyl vinyl ethers,[157] based on the difference between the rates of their cycloaddition to 1-nitroso-1-phenylethylene **1l** and diphenyl ketene.[157] 1-Nitroso-1-phenylethylene **1l** generated *in situ* reacts selectively with the *E*-isomers of the silyl ethers **85a,b**, whereas diphenyl ketene reacts with the *Z*-isomers; as a consequence, the initial mixtures of trimethylsilyl enolates become enriched in the less reactive isomers.



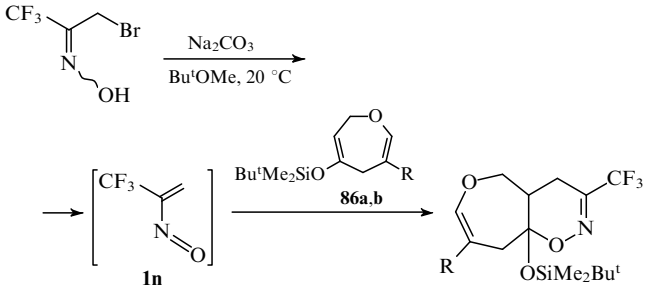
(*E*,*Z*)-**85a**,**b** (*Z*)-**85a**,**b** (*E*)-**85b**

R = Me (**a**), Ph (**b**);

(*a*) , Na_2CO_3, Et_2O; (*b*) $Ph_2C=C=O$.

Compound	(*E*)-**85a**	(*Z*)-**85a**	(*Z*)-**85b**
Yield (%)	66	43	99
Degree of enrichment (%)	> 98	> 99	> 99

Although alkyl ethers of enols are generally more reactive towards nitrosoalkenes than silyl ethers,[128] the reaction of dihydrooxepines **86a,b** with the nitrosoalkene **1n** gives fused 1,2-oxazines **87a,b** as the only reaction products. This unexpected result has been explained by assuming that specific conformational features of the dihydrooxepine ring prevent the lone electron pair of the endocyclic oxygen atom from overlapping efficiently with the C(5) = C(6) double bond, and hence, the C(2) = C(3) bond becomes more reactive.[158]



1n **86a,b** **87a,b**

R = H (**a**), R = Me (**b**).

The high stereospecificity of cycloaddition confirms its concerted mechanism. It has been established reliably that the formation of mixtures of *cis*- and *trans*-1,2-oxazines from *cis*-alkenes, observed in some cases, is due to some amounts of *trans*-isomers present in the initial alkenes. Since the rate of cycloaddition of nitrosoalkenes to *trans*-alkenes is markedly higher, and the typical experimental procedure involves the use of a large excess of the alkene, the content of *trans*-substituted 1,2-oxazines in the reaction products can be quite noticeable.[14, 16, 17, 128]

The nitrosoalkenes **1** with R^1 = R^2 = H are extremely unstable (see Table 1); therefore, their relative reactivities can hardly be estimated. Nevertheless, some qualitative conclusions have been drawn.

For example, the yields of cycloaddition products obtained from 1-nitroso-1-(4-nitrophenyl)ethylene **1v** were generally higher than those obtained from 1-nitroso-1-phenylethylene **1l**. Therefore, it was concluded that the former is more reactive.[14] 3-Nitrosobut-3-en-2-one **1m**, which is more reactive, forms adducts with cyclohexene and benzofuran, whereas ethyl α-nitrosoacrylate **1r** does not react with these substrates. This reflects the general tendency of the reactivity to decrease upon replacement of the acetyl group by CO_2Et.[16] As noted above, sterically hindered alkenes like $CH_2=C(R)OSiMe_3$ (R = Pr^i, Ph, Bu^t) do not react with 1-nitroso-1-phenylethylene **1l** or ethyl α-nitrosoacrylate;[120, 128] however, more reactive 1,1,1-trifluoro-2-nitrosopropene **1n** does form cycloadducts with these alkenes, although in low yields.[17] The higher reactivity of the nitrosoalkene **1n** compared to 1-nitroso-1-phenylethylene **1l** was also confirmed by MNDO calculations.[17]

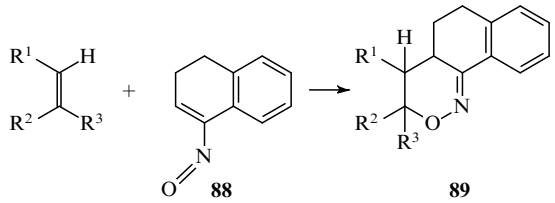
Nitrosoethylene,[18] 2-nitrosopropene,[8, 120] and some other 1-alkylnitrosoethylenes [120] form cycloadducts in extremely low yields or do not react at all even with the most reactive dienophiles, cyclopentadiene and ethyl vinyl ether.

Recently, calculations have been carried out for some cycloaddition reactions of nitroso ketene [159] and nitrosoethylene.[160, 161]

It is of interest that trichloronitrosoethylene **1s** readily reacts with various alkenes as a conjugated heterodiene,[162] although as has been noted above, it behaves as a typical dienophile towards conjugated dienes.

The reactions of 1-nitroso-1-phenylethylene **1l** with norbornene and norbornadiene yield mainly *exo*-adducts.[120]

The diastereoselectivity of cycloaddition of alkenes to 3,4-dihydro-1-nitrosonaphthalene **88** has been studied.[128]

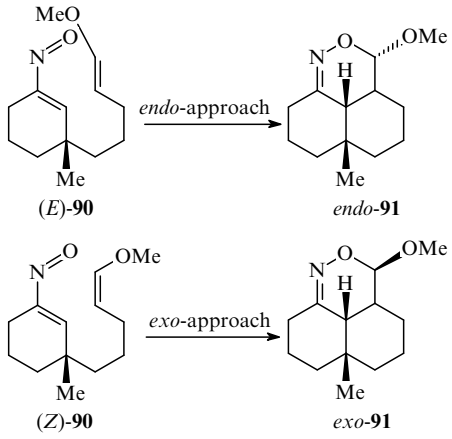


88 **89**

Ratio *exo*-**89** : *endo*-**89**	R^1	R^2	R^3
> 97 : 3	H	H	$OSiMe_3$
64 : 36	Me	H	$OSiMe_3$
18 : 82	$(CH_2)_3$		$OSiMe_3$
1 : 1	H	H	CH_2SiMe_3

It was found that trimethylsilyloxyethylene affords almost exclusively the *exo*-adduct. When there are one or two alkyl substituents at the double bond, the proportion of the *endo*-adduct increases. In the case of 1-trimethylsilyloxycyclopentene, the *endo*-adduct **89** predominates among the reaction products. Evidently, in this case, the *exo*-approach in the transition state is sterically hindered. For methoxyallene, the steric obstacles to the *exo*-approach prove to be insignificant, and consequently, this alkene, like trimethylsilyloxyethylene, forms predominantly the *exo*-adduct (the *exo* : *endo* ratio is 92 : 8).[131] The fact that the reaction of 1-nitroso-3,4-dihydronaphthalene **88** with allyltrimethylsilane is less diastereoselective than its reaction with trimethylsilyloxyethylene has been explained [128] by different reactive conformations of these molecules.

Intramolecular [4 + 2]-cycloaddition of the nitroso-alkene fragment to the vinyl-ether fragment in compound **90** has been studied.[20] An equimolar mixture of the *E*- and *Z*-isomers of **90** was converted into a mixture of *endo*- and *exo*-adducts **91** in a ratio of 3.4 : 1 (total yield 35%). Based on these data, it was concluded that the *endo*-approach is preferable.

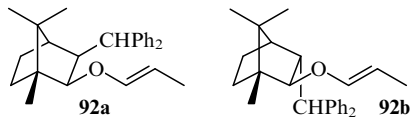


(*E*)-**90** *endo*-**91**

(*Z*)-**90** *exo*-**91**

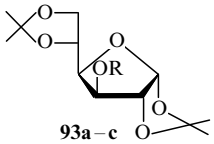
However, in our opinion, this selectivity is actually due to the fact that the *Z*-alkene fragment is much less reactive than the *E*-fragment.

Arnold and Reissig [163] were the first to use nitrosoalkenes in enantioselective synthesis. They studied [4 + 2]-cycloaddition to optically active vinyl ethers with various optically active fragments and alkenyl residues. The highest diestereoisomeric excess (up to 90%) was observed for the reaction of 1-nitroso-1-phenylethylene **1l** with isomeric bulky norbornane derivatives **92a**,**b**.[163]



92a **92b**

Further studies along this line have shown [164] that readily available diacetone glucosyl is the most versatile optically active fragment. Compounds with the general formula **93**, where R are various alkenyl groups (including the allenyl group) ensure high diastereoisomeric yields in [4 + 2]-cycloaddition to terminal nitrosoalkenes.



93a–c

R = CH = CHMe (*E*, *Z*) (**a**); CH = CMe_2 (**b**); CH = C = CH_2 (**c**).

The above characteristic features of the cycloaddition of nitrosoalkenes to alkenes lead to the clear idea that this is a concerted Diels–Alder reaction with inverse electron demand.[165–168] The concept of this reaction, first proposed by Gilchrist,[3, 14] is based on interaction of the lowest unoccupied molecular orbital (LUMO) of nitrosoalkene, acting as an electron-withdrawing conjugated heterodiene, with the highest occupied molecular orbital (HOMO) of the alkene, which serves as the electron-donating dienophile. The regioselectivity of this reaction is determined by the HOMO coefficients of the atoms in the alkene (the greatest coefficient characterises the β-C atom) and the LUMO coefficients of the atoms in the nitrosoalkene (the greatest coefficient belongs again to the β-C atom) (Fig. 1); the greater these coefficients, the higher the cycloaddition rate.

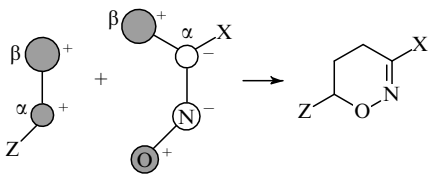


Figure 1. Reaction of nitrosoalkenes with alkenes in terms of the MO LCAO method.[3, 14]

It should be emphasised that no examples of participation of nitrosoalkenes in any Diels–Alder reactions of the standard type have been found so far. The attempts to carry out their cycloaddition to alkenes with electron-withdrawing substituents [16, 137] failed.

It would be expedient to systematise the available arguments supporting the concerted mechanism of cycloaddition of nitrosoalkenes to alkenes:

(1) there are no indications of formation of any long-lived dipolar [14] or diradical [128] intermediates;

(2) the process is highly stereospecific;

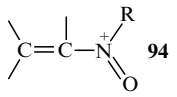
(3) the relative rate constants for the cycloaddition of *E*- and *Z*-isomers of alkenes are substantially different;

(4) the rates of cycloaddition substantially decrease on passing to alkenes like $CH_2 = C(R)OSiMe_3$;

(5) there are no rearrangements during cycloaddition to strained alkenes: norbornadiene,[120] norbornene,[120 128, 156] and benzvalene.[128, 156]

In a more detailed investigation of the reaction mechanism, it was noted [128] that, despite the concerted character of the reaction, the transition state can be asymmetrical; in particular, the formation of the C–O bond can lag behind the formation of the C–C bond. This assumption was confirmed by PM3 calculations. It has also been suggested [131] that in special cases, this reaction can follow a two-step mechanism involving formation of 1,6-zwitterion intermediates. This occurs, for instance, when 1-nitroso-1-phenylethylene **1l** adds to highly sterically strained 1-(hydroxydiphenylmethyl)-1-methoxypropa-1,2-diene.[131]

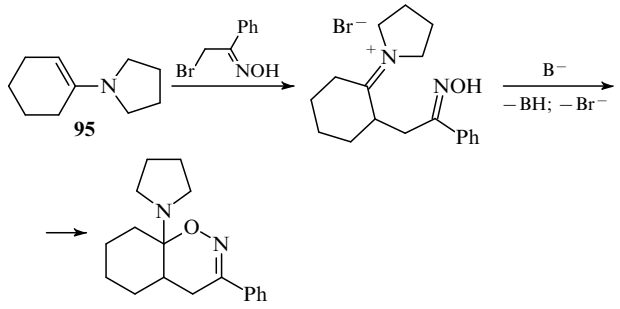
The closest analogues of nitrosoalkenes in [4 + 2]-cycloaddition reactions are vinylnitrosonium cations **94**[169–172] and conjugated nitro alkenes.[173–177]



94

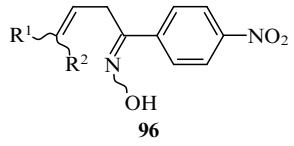
Apparently, the range of cycloaddition reactions of nitrosoalkenes to C = C bonds is not exhausted by the data presented above. Thus Gilchrist *et al.*[18,93] believe that the reaction of α-halo oximes with enamines in the presence of Na_2CO_3 involves generation and subsequent [4 + 2]-cycloaddition of nitrosoalkenes to electron-rich C = C bonds.[18,93]

However, the alkylation of enamines with α-bromo oximes[152,153] in the absence of bases should apparently be regarded as direct S_N2 substitution of bromine, because the intermediate immonium salts can be isolated. The structures of these intermediates have been established by IR, UV, and ^1H NMR spectroscopy.[151] It was found that on treatment with bases, the immonium salts cyclise to 6-(*N*,*N*-dialkylamino)-5,6-dihydro-4*H*-1,2-oxazines. This sequence of reactions is considered below in relation to the alkylation of 1-pyrrolidinocyclohexene **95** with α-bromoacetophenone oxime.[151]



95

[4 + 2]-Cycloaddition of nitrosoalkenes can be accompanied by the formation of side products. Thus the reactions of 1-nitroso-1-(*p*-nitrophenyl)ethylene with styrene, α-methylstyrene, and α-phenylstyrene, in addition to 1,2-oxazines, affords β,γ-unsaturated oximes **96**[14] (the formation of similar products has also been reported in another study[152]).



96

R^1 = Ph: R^2 = H, Me, Ph; R^1 = Me, R^2 = Ph.

c. [3 + 2]-cycloaddition of nitrosoalkenes to alkenes

[4 + 2]-Cycloaddition of 1-nitroso-1-phenylethylene **1l** and 1-nitroso-1-(4-nitrophenyl)ethylene **1v** to 2-methoxypropene giving rise to the corresponding 1,2-oxazines is accompanied by [3 + 2]-cycloaddition, which yields cyclic nitrones **97** as minor products[14] (see also Section IV.2, compound **76**). It was shown in special experiments that the ratio of the [4 + 2]- to [3 + 2]-cycloadducts does not depend on the *E*- or *Z*-configuration of the α-bromo oximes, precursors of nitrosoalkenes.[14]

In Gilchrist's opinion,[3] for concerted [3 + 2]-cycloaddition to occur, the nitrosoalkene molecule should assume a reactive conformation in which the lone electron pair of the nitroso-group nitrogen atom lies in a plane parallel to the plane of the $\pi_{C=C}$ bond, according to the 1,3-dipole type (Fig. 2).

At the same time, it was noted[14] that the minor products **96** and **97** are formed in those cases where the possible dipolar intermediates are efficiently stabilised. However, in both cases, the product ratio proved to be insensitive to an increase in the polarity of the solvent.[14]

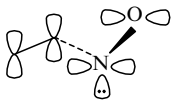
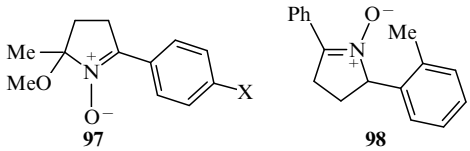


Figure 2. Conformation of nitrosoalkene during [3 + 2]-cycloaddition.

The [3 + 2]-cycloaddition of 1-nitroso-1-phenylethylene **1l** to *o*-methylstyrene gives nitrone **98**.[178]



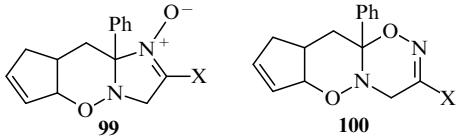
97 **98**

X = H, NO_2.

The reaction of nitrosoalkenes considered in this Section resembles the known [3 + 2]-cycloaddition of azines to multiple bonds.[179]

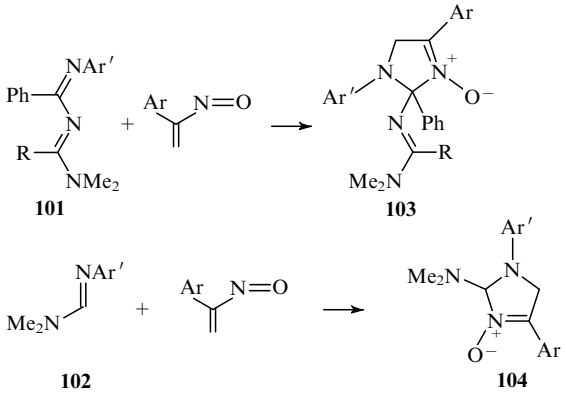
d. Nitrosoalkenes in cycloaddition to C = N, C = S, and C ≡ C bonds

[4 + 2]-Cycloaddition of nitrosoalkenes is a general method for functionalisation of alkenes. However, cycloaddition to nitrosoalkenes is not restricted to the reactions with carbon–carbon double bonds. Nitrosoalkenes are able to add to C = N bonds in some cyclic 1,2-oxazines to give nitrones **99**[119,180] (see also Section IV.2, compound **77**) and fused 1,2,5-oxadiazines **100**,[181] their yields ranging from low to moderate. This reaction is not a general transformation of the oximine fragment.[180]



99 **100**

Recently, it has been shown that nitrosoalkenes react smoothly with amidines of type **101** and **102** according to the [3 + 2]-cycloaddition fashion giving rise to the corresponding imidazoline *N*-oxides **103** and **104**.[182]

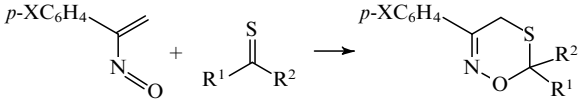


101 **103**

102 **104**

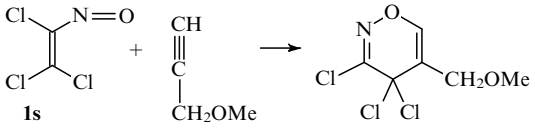
This reaction is general and, in the opinion of the researchers cited,[181] occurs *via* formation of a stabilised dipolar intermediate.

The use of the C = S bonds of thiocarbonyl compounds as a heterodienophilic 2π-component in [4 + 2]-cycloaddition to substituted α-nitrosostyrenes has been reported.[182] The reaction of trichloronitrosoethylene **1s** with $Ph_2C=S$ is an example.[162]



X = H, OMe, NO_2; R^1, R^2 = Ar, PhS, R_3Si.

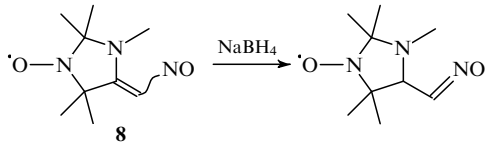
Trichloronitrosoethylene is capable of reacting with methyl propargyl ether to afford 4*H*-1,2-oxazine **105**;[162] however, the attempts to involve various alkynes in cycloaddition to nitroso alkynes of the type $CH_2=C(R)NO$ were unsuccessful.[3, 17, 120]



1s **105**

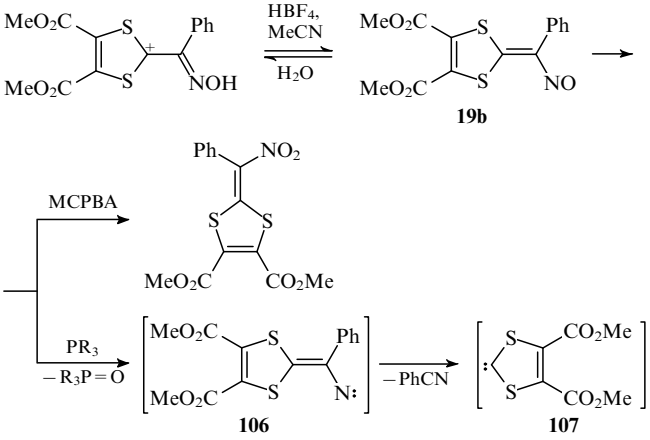
e. Other reactions

The known chemistry of nitrosoalkenes is virtually exhausted by the information presented here. At present, there are no reliable data concerning radical addition or ene reactions of these compounds, although these are typical reactions of other types of nitroso derivatives. It can only be added that 1-nitrosocyclohexene **1f**[10] and trifluoronitrosoethylene **1a**[5] can undergo electrophilic addition. The addition of HCl to some nitrosoalkenes has been reported.[10] Trifluoronitrosoethylene **1a** is able to polymerise by a radical mechanism in solution.[5] The reduction of the nitrosoalkene **8** with $NaBH_4$ gives rise to the corresponding oxime.



8

Several reactions have been reported for the nitrosofulvene **19b**, namely, reversible *O*-protonation, oxidation to nitrofulvene by *m*-chloroperbenzoic acid, and deoxygenation by tertiary phosphines followed by fast fragmentation of the intermediate nitrene **106**, resulting in the generation of carbene **107**.[46]



19b **106** **107**

MCPBA = 3-ClC_6H_4COOOH.

Nitrosoalkenes (nitrosodithiofulvenes and nitrosodiselenofulvenes) form coordination compounds with $PdCl_2$.[183]

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