

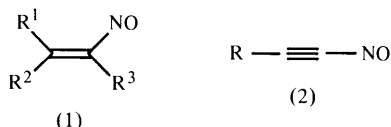
# Nitroso-alkenes and Nitroso-alkynes

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## 1 Introduction

The nitroso group has been recognized for many years as a powerful activating group for nucleophilic substitution in benzenoid aromatics,<sup>1</sup> but much of the chemistry of other types of conjugated nitroso compounds has been discovered only recently. Nitroso-carbonyl compounds (RCONO) have been generated and have been shown to participate, through the nitroso group, in Diels-Alder and ene reactions.<sup>2</sup> Nitrosyl cyanide<sup>2</sup> and C-nitroso-imines [ $R^1N=C(R^2)NO$ ]<sup>3</sup> are also excellent dienophiles. This review deals with the chemistry of two other classes of conjugated nitroso compounds, in which the nitroso group is attached to a carbon-carbon double bond, (1) or triple bond, (2).



Only a few compounds of type (1) have been isolated. The first such compound (1;  $R^1 = R^2 = R^3 = F$ ) was reported in 1960<sup>4</sup> and since then a few others, usually with bulky alkyl or halo substituents at the  $\beta$ -carbon atom, have been described. There is, however, substantial evidence for the existence of a wide range of vinyl-nitroso compounds in solution as transient intermediates. Some of these intermediates have been detected spectroscopically, or simply by the appearance of a characteristic blue colour in the solution. This group contains many  $\beta$ -alkyl- and  $\beta$ -aryl-substituted compounds, some halo-substituted derivatives, and a few with  $\beta$ -alkoxy or  $\beta$ -diakylamino substituents. Lifetimes of these compounds vary from many weeks at room temperature to short periods at low temperatures. Other types of vinyl-nitroso intermediates have not been detected directly, and the evidence for their existence is based on trapping experiments: for example, all the known intermediates  $H_2C=C(R)NO$  are in this category.

Representative examples of these different groups of vinyl-nitroso compounds, for which there is good direct or indirect evidence, are shown in Table 1.

<sup>1</sup> J. Miller and A. J. Parker, *Aust. J. Chem.*, 1958, **11**, 302.

<sup>2</sup> G. W. Kirby, *Chem. Soc. Rev.*, 1977, **6**, 1.

<sup>3</sup> T. L. Gilchrist, C. J. Harris, F. D. King, M. E. Peek, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2161.

<sup>4</sup> C. E. Griffin and R. N. Haszeldine, *J. Chem. Soc.*, 1960, 1398.

**Table 1** Representative nitroso-alkenes (1)

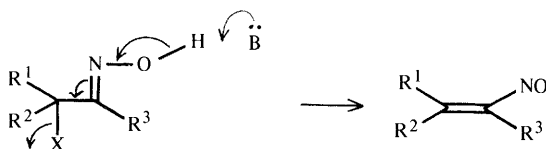
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Properties	Ref.	
(a)	F	F	F	Blue gas, stable up to 100 °C	4	
(b)*	H	C <sub>6</sub> H <sub>2</sub> Me <sub>3</sub> -2,4,6	Me	Blue solid, m.p. 47–58 °C	5	
(c)	CMe <sub>3</sub>	CMe <sub>3</sub>	H	Blue solid, m.p. 38 °C	6	
(d)	Cl	Cl	Me	Isolable at r.t.	7	
(e)	H	—(CH <sub>2</sub> ) <sub>4</sub> —		Blue solid at –50 °C, decomp. above –30 °C	8	
(f)	Cl	Cl	H	} Long-lived in solution	7	
(g)*	H	Cl	Cl		7	
(h)*	H	Ph	Me		} Detected in solution by colour	9
(i)*	Me	morpholino	COMe	10		
(j)	H	H	Ph	} Kinetic evidence for its existence; also cycloaddition reactions	11, 12	
(k)	H	H	H		} Detected only by cycloaddition reactions	13
(l)	H	H	COMe			14
(m)*	CMe <sub>3</sub>	Cl	H	} 7	7	

\* Stereochemistry about the double bond has not been established

These compounds are potentially very useful synthetic intermediates because of the presence of a double bond in conjugation with the nitroso group; there is an obvious relationship between them and other types of activated alkenes. Thus, the  $\beta$ -carbon atom is expected to be highly electrophilic, and indeed reactions with nucleophiles are the best-known features of their chemistry. In the following sections of this review, the methods of generation and characteristic physical properties of vinyl-nitroso compounds are described, and the known chemistry is then categorized according to the types of reaction involved. The final section deals with nitroso-alkynes, about which very little has so far been published, there being good evidence for the existence of only two such compounds (2; R = Bu<sup>n</sup> or Bu<sup>l</sup>) at low temperatures in solution.<sup>15</sup>

## 2 Methods of Generation of Nitroso-alkenes

**A. By 1,4-Elimination Reactions of  $\alpha$ -Halo-oximes, and Related Methods.**—The reaction of  $\alpha$ -halo-oximes with bases (Scheme 1) is by far the most important method for the generation of vinyl-nitroso compounds.

**Scheme 1**

The method has, for example, been used to generate all the compounds in Table 1, with the exception of (1a). Chloride is the most common leaving group, but other halides have also been used. Since the vinyl-nitroso compounds are very susceptible to nucleophilic attack (Section 3B) the choice of reaction conditions is important. The reaction must be carried out with poorly nucleophilic solvents and bases unless these are also to be used as nucleophiles to intercept the nitroso-alkene. For the long-lived species, the tertiary amines triethylamine<sup>5</sup> and 1,5-diazabicyclo[4.3.0]non-5-ene<sup>6</sup> have been used. Transient species are best generated from the halo-oxime in a non-nucleophilic organic solvent by means of an insoluble inorganic base such as sodium carbonate<sup>9,13</sup> or calcium hydroxide.<sup>8</sup> This allows the intermediates to be generated slowly and minimizes side reactions involving more than one molecule of the nitroso intermediates.

There are three general methods for the preparation of the required halo-oximes. The first is the reaction of the appropriate haloketone with hydroxylamine. Chloro-oximes are thus normally prepared from chloroketones and hydroxylamine hydrochloride in alcoholic solution. For bromo-oximes, hydroxylamine sulphate can be used to avoid halide exchange which can occur with the hydrochloride.<sup>16</sup> Alcoholic solvents can also interfere, as nucleophiles to displace the halide, if reaction times are prolonged.<sup>14</sup> A second method, used for some chloro-oximes, is the reaction of nitro-alkenes with metal chlorides such as tin(II)chloride<sup>17</sup> or titanium(IV)chloride.<sup>7</sup> The third method, which is also limited to chloro-oximes, is the addition of nitrosyl chloride to alkenes.<sup>18</sup> This reaction was first introduced over a century ago by Tilden and Shenstone<sup>19</sup> as a method of preparing crystalline derivatives of terpenes. More recently, the reaction has been extended to a wide range of nucleophilic and electrophilic alkenes, mainly by Ogloblin and his co-workers in the U.S.S.R. This is the method of choice for the preparation of  $\alpha$ -chloro-oximes of cyclic ketones<sup>20,21</sup> and of many other alkyl ketones.<sup>22</sup> It is also a valuable route to chloro-oximes  $\text{ClCH}_2\text{C(R)NOH}$  where

<sup>5</sup> W. Höbold, U. Prietz, and W. Pritzkow, *J. Prakt. Chem.*, 1969, **311**, 260.

<sup>6</sup> K. Wieser and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 70.

<sup>7</sup> E. Francotte, R. Merényi, V. Vandenbulcke-Coyette, and H. G. Viehe, *Helv. Chim. Acta*, 1981, **64**, 1208.

<sup>8</sup> P. Ciattoni and L. Rivolta, *Chim. Ind. (Milan)*, 1967, **49**, 1186.

<sup>9</sup> A. Dornow and H. D. Jordan, *Chem. Ber.*, 1961, **94**, 76.

<sup>10</sup> P. Bravo and C. Ticozzi, *Gazz. Chim. Ital.*, 1975, **105**, 91.

<sup>11</sup> J. H. Smith, J. H. Heidema, and E. T. Kaiser, *J. Am. Chem. Soc.*, 1972, **94**, 9276.

<sup>12</sup> D. E. Davies, T. L. Gilchrist, and T. G. Roberts, *J. Chem. Soc., Perkins Trans. 1*, 1983, in press.

<sup>13</sup> R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 1979, 249.

<sup>14</sup> T. L. Gilchrist and T. G. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1983, in press.

<sup>15</sup> E. Robson, J. M. Tedder, and D. J. Woodcock, *J. Chem. Soc. (C)*, 1968, 1324.

<sup>16</sup> P. Blumbergs, C. B. Thanawalla, A. B. Ash, C. N. Lieske, and G. M. Steinberg, *J. Org. Chem.*, 1971, **36**, 2023.

<sup>17</sup> A. Dornow, H. D. Jordan, and A. Müller, *Chem. Ber.*, 1961, **94**, 67.

<sup>18</sup> L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, 1951, **48**, 319; P. P. Kadzyauskas and N. S. Zefirov, *Russ. Chem. Rev.*, 1968, **37**, 543.

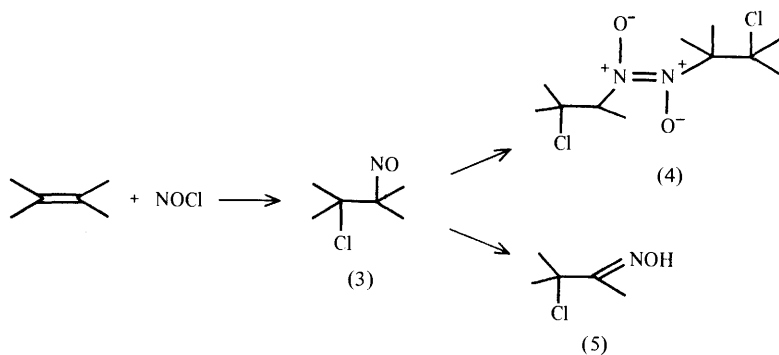
<sup>19</sup> W. A. Tilden and W. A. Shenstone, *J. Chem. Soc.*, 1877, **31**, 554.

<sup>20</sup> M. Ohno, N. Naruse, and I. Terasawa, *Org. Synth., Coll. Vol. V*, 1973, 266.

<sup>21</sup> M. Ohno, N. Naruse, S. Torimitsu, and M. Okamoto, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1119.

<sup>22</sup> M. Angermann, J. Beger, G. Collin, A. Ebenroth, R. Hellmig, H. Lunkwitz, P. Pabst, U. Prietz, W. Pritzkow, H. Schaefer, R. Siedler, and R. Weller, *Wiss. Z. tech. Hochschule Chem. Leuna-Merseburg*, 1966, **8**, 187.

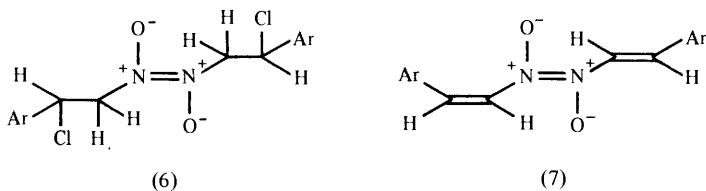
$R = \text{CHO}, \text{COMe}, \text{COPh}, \text{and CN}.$ <sup>23</sup> The reaction of alkenes with nitrosyl chloride is not always a simple one:<sup>18</sup> the major primary product is usually the  $\beta$ -chloro-nitroso compound which may dimerize, or rearrange to the chloro-oxime if the alkene bears an  $\alpha$ -hydrogen (Scheme 2).



Scheme 2

The primary adduct (3) is normally that predicted by the Markovnikov rule, and the reaction with simple alkenes is classed as an electrophilic addition.<sup>18</sup> The surprisingly rapid addition of nitrosyl chloride to some  $\alpha\beta$ -unsaturated carbonyl compounds<sup>23</sup> could be the result of the prior co-ordination of the nitrosyl cation to the carbonyl oxygen.

The nitrosochloride dimers (4) have also been used as the precursors of some vinyl-nitroso compounds,<sup>22,24-26</sup> and there is good evidence that the reactions of some dimers (4) and of the corresponding chloro-oximes (5) with nucleophilic bases go through common intermediates.<sup>22,25,27</sup> Exceptionally, the nitrosochloride dimers (6) derived from styrenes react with tri-*n*-butylamine to give orange dimers (7) of the  $\beta$ -nitrostyrenes.<sup>25</sup>



<sup>23</sup> K. A. Ogloblin and A. A. Potekhin, *J. Gen. Chem. USSR*, 1964, **34**, 2710; K. A. Ogloblin and A. A. Potekhin, *J. Org. Chem. USSR*, 1965, **1**, 1370; K. A. Ogloblin and V. P. Semenov, *J. Org. Chem. USSR*, 1965, **1**, 1378.

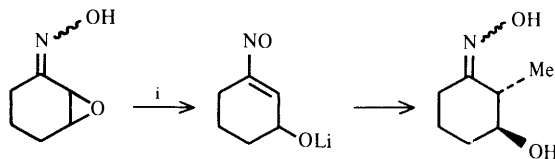
<sup>24</sup> R. U. Lemieux, T. L. Nagabhushan, and I. K. O'Neill, *Tetrahedron Lett.*, 1964, 1909.

<sup>25</sup> W. Pritzkow, H. Schaefer, P. Pabst, A. Ebenroth, and J. Beger, *J. Prakt. Chem.*, 1965, **29**, 123.

<sup>26</sup> P. Bravo, G. Gaudiano, C. Ticozzi, and A. Umani-Ronchi, *Gazz. Chim. Ital.*, 1969, **99**, 549.

<sup>27</sup> O. Wallach, *Liebigs Ann. Chem.*, 1899, **306**, 278.

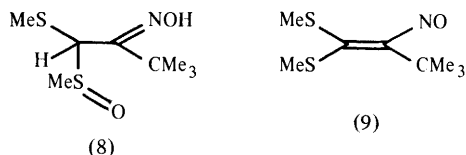
There are a few examples of the use of oximes bearing leaving groups other than halides for the generation of vinyl-nitroso compounds. Nitrosyl hydrogen-sulphate,  $\text{NOSO}_3\text{H}$ , has been added to alkenes and the adducts used as sources of vinyl-nitroso compounds.<sup>28</sup> Nitrite has also been used as a leaving group.<sup>6</sup> The ring opening of oximes of  $\alpha$ -epoxyketones<sup>29</sup> (Scheme 3) provides an interesting



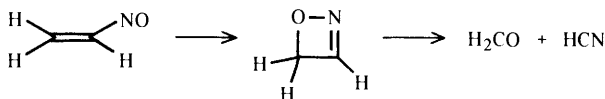
Reagent: i,  $\text{Me}_2\text{CuLi}$ ,  $\text{Et}_2\text{O}$ ,  $-25^\circ\text{C}$

Scheme 3

variant of this approach. Simple dehydration of  $\alpha$ -hydroxyketoximes does not appear to have been used as a route to these intermediates, but the acid-catalysed dehydration of the sulfoxide (8) is postulated to involve the nitroso-alkene (9).<sup>30</sup>



**B. By Combination of Nitric Oxide with Vinyl Radicals.**—Nitrosotrifluoroethylene (1a) was formed by the sensitized photolysis of iodotrifluoroethylene in the presence of nitric oxide.<sup>4</sup> It is probable that the product is formed by the combination of trifluorovinyl radicals with nitric oxide. This is the only vinyl-nitroso compound which has so far been detected directly in this type of reaction, but others have been postulated as reaction intermediates. Thus, ethyne reacts with hydrogen atoms and nitric oxide to give HCN and formaldehyde, which, it is suggested, are formed by the rearrangement and fragmentation of nitroso-ethylene (Scheme 4).<sup>31</sup> Several similar reactions have been reported;<sup>31,32</sup> for example, the sequence shown in Scheme 5.<sup>32</sup>



Scheme 4

<sup>28</sup> W. Kisan and W. Pritzkow, *J. Prakt. Chem.*, 1978, **320**, 59.

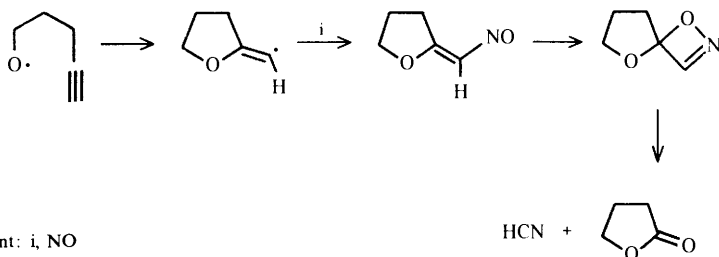
<sup>29</sup> E. J. Corey, L. S. Melvin, and M. F. Haslanger, *Tetrahedron Lett.*, 1975, 3117.

<sup>30</sup> H. G. Corkins, L. Storace, and E. R. Osgood, *Tetrahedron Lett.*, 1980, 2025.

<sup>31</sup> A. G. Sherwood and H. E. Gunning, *J. Am. Chem. Soc.*, 1963, **85**, 3506.

<sup>32</sup> J.-M. Surzur, C. Dupuy, M. P. Bertrand, and R. Nougier, *J. Org. Chem.*, 1972, **37**, 2782.

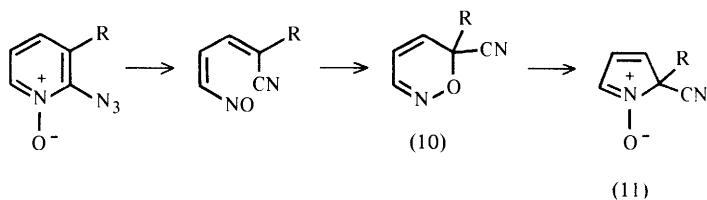
*Nitroso-alkenes and Nitroso-alkynes*



**Scheme 5**

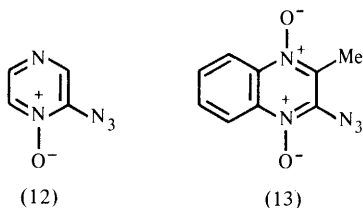
**C. Other Methods.**—Other methods are so far restricted to examples with special structural features, and the evidence for the formation of vinyl-nitroso intermediates is in all cases indirect, being based on the nature of the final products.

Abramovitch and his co-workers have shown that 2-azidopyridine 1-oxides decompose when irradiated or when heated above about 85 °C.<sup>33,34</sup> If a 3-substituent is present, two types of product can be isolated: the 6*H*-1,2-oxazines (10) and the 2*H*-pyrrole 1-oxides (11). These may undergo further transformations in the presence of a nucleophilic solvent or if there is no 3-substituent. It is suggested that the azides undergo a fragmentation to dienyl-nitroso intermediates which then cyclize (Scheme 6). The oxazines (10) are the kinetic



**Scheme 6**

products and the nitrones (11) the thermodynamic products. Similar fragmentations have been observed with the azidopyrazine 1-oxide (12)<sup>33</sup> and with the azidoquinoxaline 1,4-dioxide (13).<sup>35</sup>

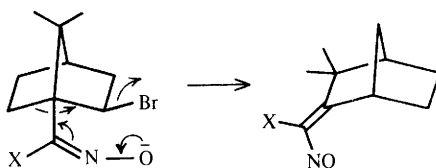


<sup>33</sup> R. A. Abramovitch and B. W. Cue, *J. Am. Chem. Soc.*, 1976, **98**, 1478.

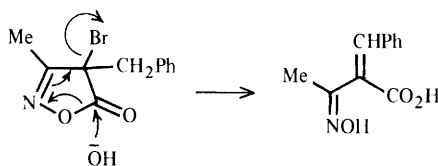
<sup>34</sup> R. A. Abramovitch, I. Shinkai, B. W. Cue, F. A. Ragan, and J. L. Atwood, *J. Heterocycl. Chem.*, 1976, **13**, 415; R. A. Abramovitch and C. Dupuy, *J. Chem. Soc., Chem. Commun.*, 1981, 36.

<sup>35</sup> J. P. Dirlam, B. W. Cue, and K. J. Gombatz, *J. Org. Chem.*, 1978, **43**, 76.

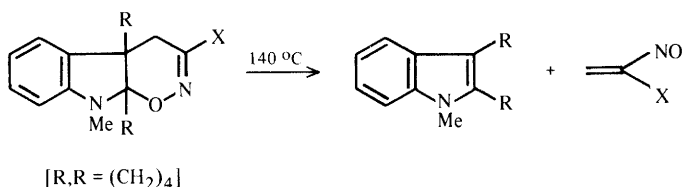
Other ring-cleavage reactions in which vinyl-nitroso compounds are postulated as intermediates are illustrated in Schemes 7,<sup>36</sup> 8,<sup>37</sup> and 9.<sup>38</sup> That shown in Scheme 9 can be regarded as a retro-Diels-Alder reaction which is facilitated by the production of an aromatic fragment (the indole).



Scheme 7



Scheme 8



Scheme 9

The nucleophilic addition-elimination reactions of sulphur ylides with nitrile oxides probably also produce nitroso-alkenes as intermediates, but these then react further with the nucleophilic ylides to give 2:1 adducts.<sup>26,39,40</sup> An example is shown in Scheme 10.

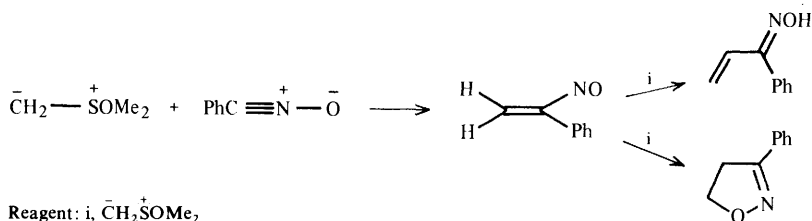
<sup>36</sup> S. Ranganathan, B. B. Singh, and C. S. Panda, *Tetrahedron*, 1977, **33**, 2415.

<sup>37</sup> A. Silveira and S. K. Satra, *J. Org. Chem.*, 1979, **44**, 873.

<sup>38</sup> D. E. Davies and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 1983, in press.

<sup>39</sup> P. Bravo, G. Gaudiano, and A. Umani-Ronchi, *Gazz. Chim. Ital.*, 1967, **97**, 1664; Y. Hayashi, T. Watanabe, and R. Oda, *Tetrahedron Lett.*, 1970, 605; R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1196.

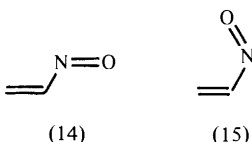
<sup>40</sup> P. Bravo, G. Gaudiano, P. P. Ponti, and C. Ticozzi, *Tetrahedron*, 1972, **28**, 3845.



Scheme 10

### 3 Structure and Physical Properties

No X-ray or microwave structure determinations have so far been carried out on the isolable nitroso-alkenes. Molecular orbital calculations, using the Hückel<sup>36</sup> and CNDO<sup>41</sup> methods, have been carried out on nitrosoethylene, and *ab initio* (STO-3G) calculations have been reported for 2- and 3-nitrosobutene.<sup>42</sup> For nitrosoethylene the *transoid* structure (14) is calculated to be of slightly lower energy than the *cisoid* (15).<sup>41</sup> In the nitrosfurans the planar structures are



calculated to be much more stable than forms with the nitroso groups out of the plane, the barriers to rotation being high ( $29\text{--}36\text{ kJ mole}^{-1}$ ).<sup>42</sup>

The spectroscopic properties of the long-lived vinyl-nitroso compounds have been tabulated by Viehe *et al.*<sup>7</sup> The blue colour is due to a  $n \rightarrow \pi^*$  absorption band ( $\lambda_{\text{max}} 675\text{--}795\text{ nm}$ ) with a small extinction coefficient ( $\epsilon 20\text{--}60$ ). A higher energy absorption band is also observed (sometimes showing two maxima) in the  $250\text{--}350\text{ nm}$  region; this may be due to an excitation involving considerable transfer of charge to the nitroso group.<sup>41</sup> Infra-red spectra normally show two bands in the region  $1420\text{--}1660\text{ cm}^{-1}$ , a region in which the  $\text{N}=\text{O}$  stretching frequencies of other monomeric nitroso compounds lie.<sup>43</sup> An absorption at  $1485\text{ cm}^{-1}$  ( $\text{CCl}_4$ ) for the di-*t*-butyl compound (1c) is assigned as the  $\text{N}=\text{O}$  stretching band,<sup>6</sup> and the absorption in the  $1420\text{--}1480\text{ cm}^{-1}$  region of other vinyl-nitroso compounds has also been assigned as the  $\text{N}=\text{O}$  stretching band, the higher frequency band ( $1500\text{--}1660\text{ cm}^{-1}$ ) being the  $\text{C}=\text{C}$  stretching absorption.<sup>7</sup> In the  $^1\text{H}$  n.m.r. spectra, the  $\beta$ -hydrogen atoms of compounds (1b) and (1e) are deshielded and appear respectively at  $\delta 9.13^5$  and  $8.68$ .<sup>8</sup> The  $\alpha$ -hydrogen atom in compound (1c) appears at much higher field ( $\delta 6.30$ ).<sup>6</sup>

<sup>41</sup> V. Bhujle, U. P. Wild, H. Baumann, and G. Wagnière, *Tetrahedron*, 1976, **32**, 467.

<sup>42</sup> I. G. John and L. Radom, *J. Am. Chem. Soc.*, 1978, **100**, 3981.

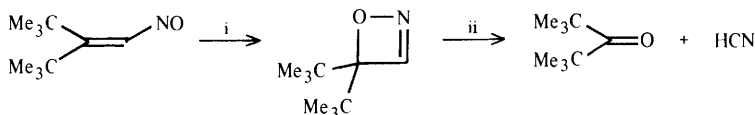
<sup>43</sup> C. N. R. Rao and K. R. Bhaskar, in 'The Chemistry of the Nitro and Nitroso Groups' Part 1, ed. H. Feuer, Interscience, New York, 1969, p. 137.



The limited physical data are consistent with structures for vinyl-nitroso compounds in which there is strong conjugative interaction between the carbon-carbon double bonds and the nitroso groups.

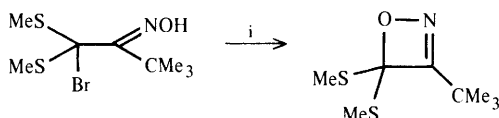
#### 4 Reactions

**A. Unimolecular Reactions.**—Two types of intramolecular rearrangement have already been referred to: cyclization to oxazetes (Schemes 4 and 5), and the cyclization of dienyl-nitroso compounds to 6*H*-1,2-oxazines (Scheme 6). Oxazetes have also been isolated from the thermal rearrangement of the nitroso-alkene (1c)<sup>6</sup> (Scheme 11) and from the reaction of the bromo-oxime (16) with base, in which the vinyl-nitroso compound (9) is proposed as an intermediate<sup>30</sup> (Scheme 12). Viehe and his co-workers have suggested that this is the major



Reaction conditions: i, 220 °C; ii, 240 °C

Scheme 11

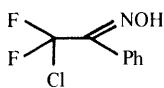


(16)

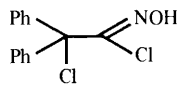
Reagent: i, DBN

Scheme 12

decomposition pathway of many other nitroso-alkenes in the absence of added nucleophiles, and they cite the additional examples of the formation of benzonitrile from the oxime (17), and of benzophenone from the oxime (18), when these oximes are treated with sodium hydrogen carbonate in dichloromethane.<sup>7</sup>

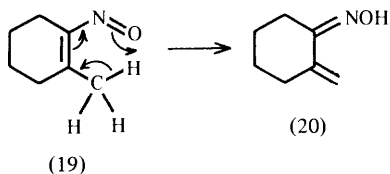


(17)



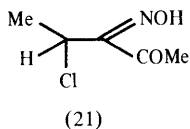
(18)

Another possible mode of rearrangement of appropriately substituted vinyl-nitroso compounds is a [1,5] hydrogen shift. An example is provided by the rearrangement of 2-methyl-1-nitrosocyclohexene (19) (Scheme 13). The presence of the nitroso-alkene in solution is revealed by a blue colour which disappears within 30 min, and the unsaturated oxime (20) can be isolated from the solution.<sup>28</sup>

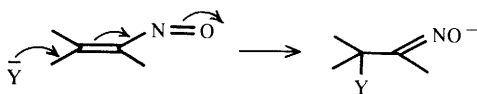


Scheme 13

This is a major mode of decomposition of other nitroso-alkenes bearing two  $\beta$ -alkyl substituents,<sup>22</sup> the unsaturated oximes being isolated in fair yields (28–72%). A similar unsaturated oxime is isolated when the chloro-oxime (21) is treated with sodium carbonate.<sup>3</sup>



**B. Reactions with Nucleophiles.**—Conjugate addition of nucleophiles to vinyl-nitroso compounds takes place as shown in Scheme 14. Thus, when halo-oximes are used as the precursors, the overall reaction with nucleophiles is displacement



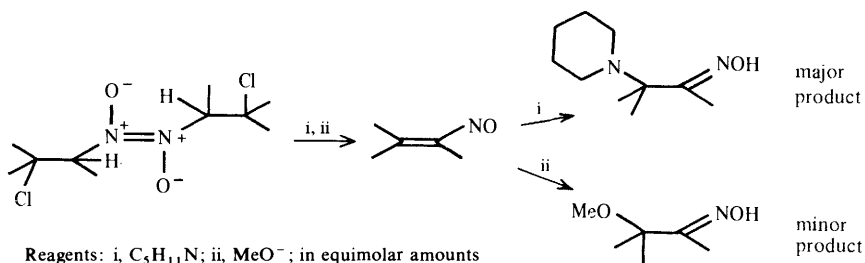
Scheme 14

of the halide anion by the nucleophile. It is likely that many reactions of halo-oximes with weakly basic nucleophiles such as cyanide<sup>44</sup> or phosphines<sup>16,45</sup> do involve a direct displacement of the halide, but with more strongly basic nucleophiles, or in the presence of an external base, an elimination–addition mechanism is preferred.

There is good evidence that nitrosochloride dimers derived from alkenes also react with nucleophilic bases by an elimination–addition mechanism. These compounds react faster with sodium methoxide than with piperidine, but in the presence of both bases, the major products are the piperidino-oximes (Scheme 15).<sup>25</sup> This rules out a direct displacement and indicates that the products are derived by addition of the better nucleophile, piperidine, to the nitroso-alkenes in a step which is not rate-determining.

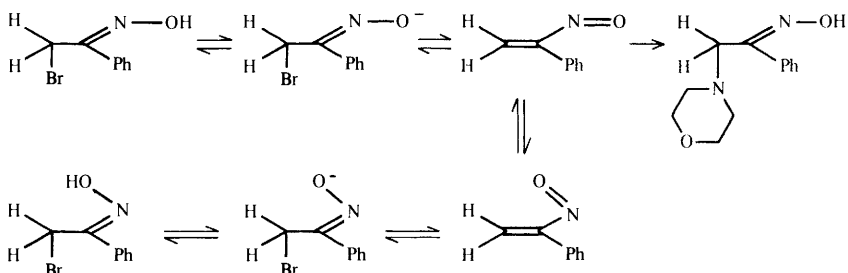
<sup>44</sup> M. Ohno and N. Naruse, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1125.

<sup>45</sup> M. Masaki, K. Fukui, and M. Ohta, *J. Org. Chem.*, 1967, **32**, 3564; G. Gaudiano, R. Mondelli, P. P. Ponti, C. Ticozzi, and A. Umami-Ronchi, *J. Org. Chem.*, 1968, **33**, 4431.



Scheme 15

An investigation of the reaction of *syn*- and *anti*- $\alpha$ -bromo-acetophenone oximes with morpholine in aqueous buffer also implicated a vinyl-nitroso compound,  $\alpha$ -nitrosostyrene, as an intermediate.<sup>11</sup> Both bromo-oximes gave the *anti*-morpholino-oxime as the product. It is suggested that the bromo-oximes are rapidly deprotonated and that  $\alpha$ -nitrosostyrene is then formed by loss of bromide in a rate-determining step. This preferentially adds morpholine when in the *transoid* conformation (Scheme 16).



Scheme 16

The mechanisms of many of the other reactions of nucleophiles with halo-oximes and with bis-chloronitroso compounds have not been established. The following discussion includes examples for which the elimination–addition mechanism appears to be likely, either because of independent evidence for the intermediacy of nitroso-alkenes, or because of the reaction conditions employed.

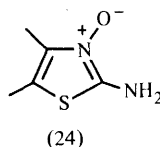
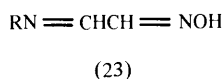
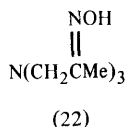
(i) *Nitrogen, Oxygen, and Sulphur Nucleophiles.* There are many and diverse examples of these nucleophiles reacting with vinyl-nitroso compounds, as Table 2 shows. The reactions go by the general route shown in Scheme 14 but further reactions may follow. For example, chloroacetone oxime and aqueous ammonia gave the tertiary amine (22)<sup>46</sup> and similar reactions were observed with oximes

<sup>46</sup> G. Matthaiopoulos, *Ber.*, 1898, **31**, 2396.

**Table 2** Addition of Nitrogen, Oxygen, and Sulphur nucleophiles to nitroso-alkenes

Nitroso-alkenes	Types of nucleophiles	Ref.
H <sub>2</sub> C=C(Me)NO	NH <sub>3</sub> , R <sub>2</sub> NH	46
H <sub>2</sub> C=C(Pr)NO	RCH(NH <sub>2</sub> )CO <sub>2</sub> Et	51
H <sub>2</sub> C=C(Ph)NO	NH <sub>3</sub>	47
	R <sub>2</sub> NH	11
	$\bar{S}CN$	49
H <sub>2</sub> C=C(COMe)NO	(H <sub>2</sub> N) <sub>2</sub> CS, H <sub>2</sub> NCH <sub>2</sub> CN,	49
	RCH(NH <sub>2</sub> )CO <sub>2</sub> Et	52
H <sub>2</sub> C=C(CO <sub>2</sub> Et)NO	ArSH	53
R <sup>1</sup> R <sup>2</sup> C=C(R <sup>3</sup> )NO (R <sup>1</sup> = alkyl or H; R <sup>2</sup> , R <sup>3</sup> = alkyl or cycloalkyl)	NH <sub>3</sub> , RNH <sub>2</sub> , H <sub>2</sub> NOH,	54
	NO <sub>2</sub> <sup>-</sup> , N <sub>3</sub> <sup>-</sup>	
	R <sub>2</sub> NH, ROH, ArSH,	21, 22, 25, 28
	$\bar{S}CN$ , $\bar{O}COR$	
	R <sub>3</sub> N	9
ClCH=CHNO	RNH <sub>2</sub> , ArNH <sub>2</sub>	48
Cl <sub>2</sub> C=CHNO	ArNH <sub>2</sub>	55
ArCH=C(R)NO	R <sub>2</sub> NH, ROH, ArSH,	22, 25
	R <sub>3</sub> N	9
	$\bar{S}CN$ , $\bar{S}C(=S)OEt$	50
	RNH <sub>2</sub> , R <sub>2</sub> NH,	24
	MeOH, MeCO <sub>2</sub> H, RSH	

of phenacyl halides.<sup>47</sup> Dichloroacetaldehyde oxime reacts with primary amines to give imines (23) derived from the initial adducts by further loss of HCl;<sup>48</sup> chloral oxime reacts in a similar way. Reactions with thiocyanate ions leads to the formation of 2-aminothiazole 3-oxides (24) by cyclization.<sup>22,49,50</sup>



(ii) *Carbon Nucleophiles.* Under this heading, only the reactions of carbanions, and electrophilic substitutions of aromatic substrates, will be considered. Reactions with enamines and other electron-rich alkenes are described separately, as cycloadditions, in Section 4C.

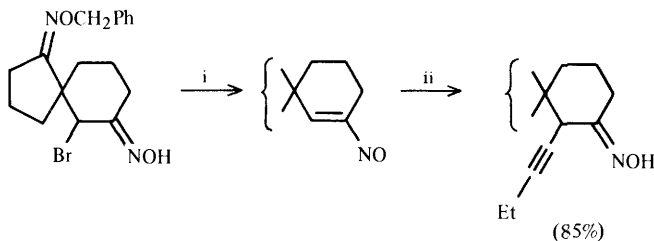
<sup>47</sup> H. Korten and R. Scholl, *Ber.*, 1901, **34**, 1901.

<sup>48</sup> H. Lerche, J. Treiber, and T. Severin, *Chem. Ber.*, 1980, **113**, 2796.

<sup>49</sup> M. Masaki, M. Sugiyama, S. Tayama, and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2745.

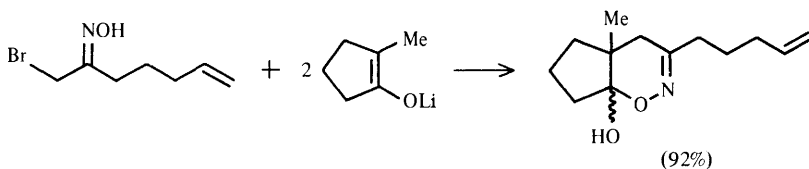
<sup>50</sup> A. Dornow, H.-H. Marquardt, and H. Paucksch, *Chem. Ber.*, 1964, **97**, 2165.

Vinyl-nitroso compounds are useful for the alkylation of nucleophilic carbon centres under mild conditions. With highly reactive carbanions or their equivalents, two moles or more are normally used, the first to generate the vinyl-nitroso intermediate and the second to act as the nucleophile. The generation and subsequent methylation of the nitrosocyclohexene by  $\text{Me}_2\text{CuLi}$  illustrated in Scheme 3 provides an example.<sup>29</sup> Ethyl-<sup>9</sup> and phenyl-<sup>54</sup> magnesium bromide have been used in a similar manner, as base and nucleophile, as has 1-lithiobutynyl (Scheme 17).<sup>56</sup> Oppolzer and his co-workers have used bromo-oximes as alkylating agents for lithium enolates derived from substituted cyclopentanones;<sup>57,58</sup> one such reaction is shown in Scheme 18.<sup>58</sup>



Reagents: i,  $\text{EtC}\equiv\text{CLi}$ ,  $-78^\circ\text{C}$ ; ii,  $\text{EtC}\equiv\text{CLi}$ ,  $-20^\circ\text{C}$

Scheme 17



Scheme 18

Reactions of nitroso-alkenes with other stabilized carbanions are summarized in Table 3. Sodium ethoxide and ethanol have been used as the base-solvent system in many of these reactions, but sodium carbonate in dichloromethane<sup>14</sup> and piperidinium acetate in tetrahydrofuran<sup>48</sup> have also been used. The products are 1:1 adducts which may exist in solution as open-chain tautomers or in five- or six-membered cyclic forms.

<sup>51</sup> M. Masaki and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 922, 1177.

<sup>52</sup> M. Sugiyama, M. Masaki, and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2517.

<sup>53</sup> T. L. Gilchrist, D. A. Lingham, and T. G. Roberts, *J. Chem. Soc., Chem. Commun.*, 1979, 1089.

<sup>54</sup> M. Ohno, S. Torimitsu, N. Naruse, M. Okamoto, and I. Sakai, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1129.

<sup>55</sup> T. Sandmeyer, *Helv. Chim. Acta*, 1919, **2**, 234.

<sup>56</sup> E. J. Corey, M. Petrzilka, and Y. Ueda, *Helv. Chim. Acta*, 1977, **60**, 2294.

<sup>57</sup> W. Oppolzer, M. Petrzilka, and K. Bättig, *Helv. Chim. Acta*, 1977, **60**, 2964.

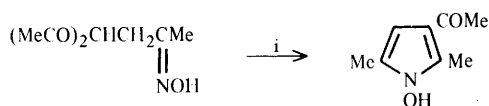
<sup>58</sup> W. Oppolzer, K. Bättig, and T. Hudlicky, *Tetrahedron*, 1981, **37**, 4359.

**Table 3** Addition of stabilized carbanions to nitroso-alkenes

Nitroso-alkenes	Substrates	Ref.
$H_2C=C(Me)NO$	1,3-diketones } $\beta$ -keto-esters } malonic esters }	59
$H_2C=C(CMe_3)NO$	$Me_3CCOCH_2CO_2Et$	60
$H_2C=C(Ph)NO$	$\beta$ -keto-esters	61
	dinitroalkanes	62
$H_2C=C(COMe)NO$	1,3-diketones	63
$H_2C=C(CO_2Et)NO$	$CH_2(CO_2Et)_2$	53
	$MeNO_2$	14
$PhCH=C(Me)NO$	$MeCOCH_2CO_2Et$ } $MeCOCH_2COPh$ }	9
$RCH=C(R)NO$	$CH_2(COMe)_2$ } $CH_2(CO_2Et)_2$ }	54
$ClCH=CHNO$	1,3-dicarbonyl compounds }*	
	$CH_2(CO_2Me)_2$ }	48
	$EtO_2CCH_2CN$ }	
	$CH_2(CN)_2$ }	

\* Adducts have the structure  $XYC=CH=NOH$

Several of the adducts have been converted, by treatment with acid, into 1-hydroxypyrrroles.<sup>59-61,63</sup> An example is the formation of 3-acetyl-2,5-dimethyl-1-hydroxypyrrrole from the adduct of chloroacetone oxime and acetylacetone (Scheme 19).<sup>59</sup>



Reagent: i, HCl, EtOH

**Scheme 19**

The reactions of sulphur-carbon ylides with nitroso-alkenes to give isoxazolines and  $\alpha$ -methylene-oximes have been illustrated earlier (Scheme 10).

Nitroso-alkenes are potentially very attractive reagents for electrophilic aromatic substitution because of the mild, non-acidic conditions in which they

<sup>59</sup> V. Sprio and P. Madonia, *Ann. Chim. (Rome)*, 1960, **50**, 1627.

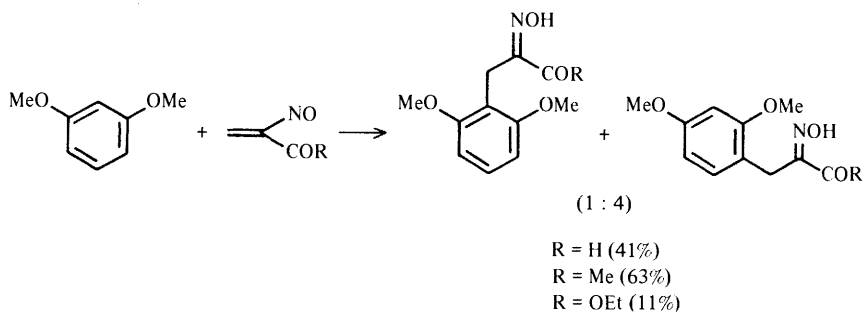
<sup>60</sup> R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, 1970, 4330.

<sup>61</sup> V. Sprio and G. C. Vaccaro, *Ann. Chim. (Rome)*, 1959, **49**, 2075; V. Sprio and J. Fabra, *ibid.*, 1960, **50**, 1635.

<sup>62</sup> S. A. Shevelev, V. I. Erashko, and A. A. Fainzilberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2725.

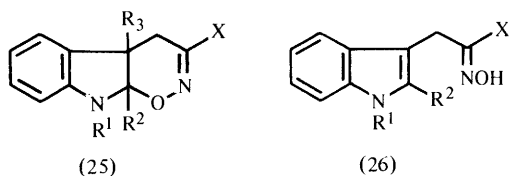
<sup>63</sup> T. L. Gilchrist, G. M. Iskander, and A. K. Yagoub, *J. Chem. Soc., Chem. Commun.*, 1981, 696.

are generated and because of the variety of functional groups which they can introduce. In practice, the reaction is limited to the most nucleophilic aromatic and heteroaromatic systems and the most electrophilic nitroso-alkenes. Of the simple benzenoid aromatics, only 1,3- and 1,4-dimethoxybenzene and *NN*-dimethylaniline have been alkylated, and only by the highly electrophilic intermediates  $\text{H}_2\text{C}=\text{C}(\text{COR})\text{NO}$ .<sup>14</sup> The reactions with 1,3-dimethoxybenzene are illustrated in Scheme 20. 3-Nitrosobut-3-en-2-one also alkylates 2-naphthol at the 1-position.<sup>14</sup>

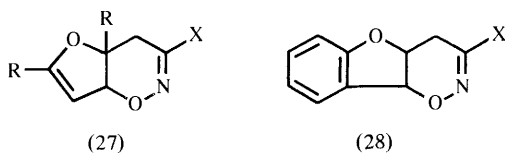


Scheme 20

Reactions with electron-rich heterocyclic compounds are more successful. Pyrrole and 1-methylpyrrole have been alkylated by ethyl bromopyruvate oxime in the presence of sodium carbonate, giving mixtures of the 2- and 3-substitution products.<sup>14</sup> Indole and simple alkyl-substituted indoles react particularly well with vinyl-nitroso compounds of this type. Alkylation invariably takes place at the 3-position, so that if a 3-alkylindole is the substrate, the product is a cycloadduct (25) rather than a substitution product (26). Yields of adducts are



good (60–85%) even when equimolar amounts of bromo-oxime and indole are used.<sup>14,38</sup> With the less aromatic systems furan, dimethylfuran, and benzofuran, the initial products are always cycloadducts (27) and (28)<sup>13,14</sup> although they



**Table 4** Alkylation of aromatic heterocycles by nitroso-alkenes

Heterocyclic compounds	Nitroso-alkene X in $\text{H}_2\text{C}=\text{C}(\text{X})\text{NO}$	Type of product	Ref.
Pyrrole	$\text{CO}_2\text{Et}$	2-substituted	86:14 14
		3-substituted	
1-Methylpyrrole	$\text{CO}_2\text{Et}$	2-substituted	80:20 14
		3-substituted	
Indole	Ph	(26)	38
	$\text{CO}_2\text{Et}$	(26)	14
	COMe	(26)	14
1-Methylindole	$\text{CO}_2\text{Et}$	(26)	64
2-Methylindole	COMe	(26)	14
3-Methylindole	$\text{CO}_2\text{Et}$	(25)	14
	COMe	(25)	14
N-Methyltetrahydrocarbazole	Ph	(25)	38
	$\text{CO}_2\text{Et}$	(25)	38
	COMe	(25)	38
Furan	Ph	(27)	13
	COMe	(27)	14
	$\text{CO}_2\text{Et}$	(27)	14
2,5-Dimethylfuran	Ph	(27)	13
	COMe	(27)	14
Benzofuran	COMe	(28)	14

are readily isomerized to the open-chain oximes by heat or by treatment with acid. The products isolated result from attack only at the 2-position, even with 2,5-dimethylfuran.

Published examples of alkylation of heterocycles by vinyl-nitroso compounds are summarized in Table 4. There is plenty of scope for extending this type of alkylation.

**C. Cycloaddition Reactions.**—Nitroso-alkenes can participate in cycloaddition reactions either as  $2\pi$ -electron systems, through the nitroso group, or as  $4\pi$ -electron (heterodiene) systems. There are, so far, no examples of cycloadditions involving only the carbon-carbon double bond.

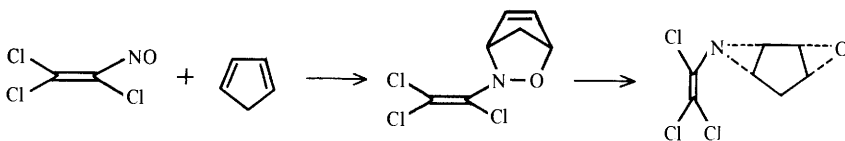
Addition to the nitroso group is a reaction which also occurs with many other classes of nitroso compounds.<sup>2,65</sup> This type of cycloaddition of nitroso-alkenes is restricted to compounds which bear at least one, and usually two, halogen substituents on the vinyl group.<sup>7</sup> For example, trichloronitrosoethylene undergoes such reactions with several acyclic and cyclic nucleophilic dienes

<sup>64</sup> H. C. J. Ottenheijm, R. Plate, J. H. Noordick, and J. D. M. Herscheid, *J. Org. Chem.*, 1982, **47**, 2147.

<sup>65</sup> J. H. Boyer, in ref. 43, p. 215.

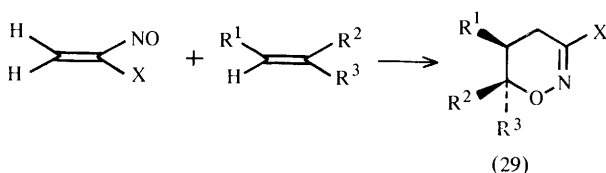


including butadiene,<sup>7</sup> 1-methoxybutadiene,<sup>7</sup> cyclopentadiene,<sup>7</sup> cyclohexadiene,<sup>66</sup> and benzene oxide.<sup>66</sup> The adducts derived from cyclic dienes are thermally unstable and rearrange above room temperature to epoxy-aziridines (Scheme 21) in a manner analogous to that of the corresponding cyclic peroxides derived from singlet oxygen addition. Trifluoronitrosoethylene (1a) has also been shown to undergo cycloaddition at the nitroso group, with tetrafluoroethylene and with chlorotrifluoroethylene, to give 1,2-oxazetines.<sup>4</sup>



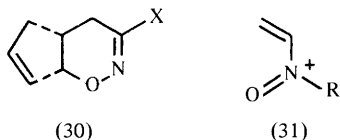
Scheme 21

The other important type of cycloaddition reaction of nitroso-alkenes involves reaction at the terminal carbon and oxygen atoms with nucleophilic alkenes, to give 5,6-dihydro-4*H*-1,2-oxazines (29) (Scheme 22). This mode of addition



Scheme 22

was first observed between  $\alpha$ -nitrostyrene (1j) and cyclopentadiene.<sup>13</sup> It is in contrast to other reactions of nitroso compounds with cyclopentadiene, in which the diene adds as a  $4\pi$ -electron system across the N=O bond, and also to the reactions of most other activated alkenes in which addition takes place at the electrophilic double bond. The reaction has since been extended to several other nitroso-alkenes, most of which are unsubstituted at the  $\beta$ -carbon atom.<sup>7,13,14</sup> These intermediates are highly electrophilic, and, in frontier orbital terms, have a large coefficient on the  $\beta$ -carbon atom in the lowest unoccupied molecular orbital (LUMO).<sup>13,36</sup> Reactions with cyclopentadiene are highly regio- and stereo-selective, the isolated adducts having the structures (30). Other acyclic



<sup>66</sup> E. Francotte, R. Merényi, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 1978, 17, 936.

and cyclic conjugated dienes add in the same way to nitroso-alkenes of the general type  $H_2C=C(X)NO$ .<sup>7,13,14,67</sup>

$\alpha$ -Nitrostyrene has not been intercepted by simple alkenes, but it will form adducts in low yields with indene,  $\alpha$ -methylstyrene, and other conjugated alkenes. When the substituent X in the nitroso-alkene  $H_2C=C(X)NO$  is also a conjugatively electron-withdrawing group, however, addition occurs even with simple alkenes.<sup>12,14</sup> More nucleophilic alkenes, such as enol ethers<sup>14,58</sup> and enamines,<sup>13,68</sup> add very well to these intermediates and give high yields of the adducts (29). These reactions show the general characteristics expected for Diels–Alder cycloadditions ‘with inverse electron demand’; that is, with electron-deficient heterodienes and electron-rich alkenes. Since all the nitroso-alkenes are transient species, no direct rate measurements are possible, but the reactions are most efficient for alkenes with a high-lying HOMO and with vinyl-nitroso compounds with a low-lying LUMO. Competition experiments with the addition of pairs of alkenes to 3-nitrosobut-3-en-2-one showed that adducts are formed preferentially with the more nucleophilic alkenes.<sup>14</sup> The reactions show high stereoselectivity, and the observed regioselectivity of the additions is also in accord with that expected on the basis of the HOMO coefficients of the alkenes. No examples of addition with ‘normal electron demand’, that is, between a nucleophilic nitroso-alkene and an electrophilic alkene, have been observed; an attempt to perform such a reaction between nitrosocyclohexene and maleic anhydride was unsuccessful.<sup>69</sup>

Typical examples of cycloadditions of this type, following the general pattern of Scheme 22, are shown in Table 5. These reactions thus represent a simple method of functionalization of alkenes. The closest analogies to these reactions are the cycloadditions of vinyl-nitrosonium salts (31) which have been extensively studied by Eschenmoser and his co-workers.<sup>70</sup> Conjugated nitro-alkenes can also add in this manner to highly nucleophilic alkenes such as enamines.<sup>71</sup>

The 1,2-oxazines (29) can be cleaved reductively at the N–O bond<sup>53,68</sup> and thermally or by acid at the C–O bond.<sup>58,72,73</sup> These reactions make the oxazines potentially useful for the synthesis of pyrroles,<sup>58,68</sup> pyridines,<sup>58,72</sup>  $\gamma$ -lactones,<sup>73</sup> and esters of  $\alpha$ -amino-acids.<sup>53</sup>

Analogous adducts have not been isolated from other nucleophilic multiple bonds. No adduct could be isolated from a reaction between 3-nitrosobut-3-en-2-one and phenylacetylene, or with (diethylamino)propyne, although the ynamine did undergo a reaction.  $\alpha$ -Nitrostyrene has been shown to add to the C=N

<sup>67</sup> G. M. Iskander and V. S. Gulta, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1891.

<sup>68</sup> P. Bravo, G. Gaudiano, P. P. Ponti, and A. Umani-Ronchi, *Tetrahedron*, 1970, **26**, 1315; S. Nakanishi, Y. Shirai, K. Takahashi, and Y. Otsuji, *Chem. Lett.*, 1981, 869.

<sup>69</sup> G. Just and W. Zehetner, *Chem. Commun.*, 1971, 81.

<sup>70</sup> U. M. Kempe, T. K. DasGupta, K. Blatt, P. Gygax, D. Felix, and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 2188; M. Riediker and W. Graf, *Helv. Chim. Acta*, 1979, **62**, 205; M. Riediker and W. Graf, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 481.

<sup>71</sup> A. Risaliti, M. Forchiassin, and E. Valentin, *Tetrahedron*, 1968, **24**, 1889.

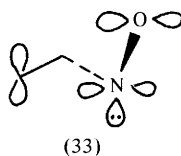
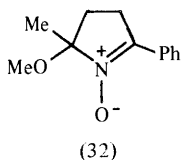
<sup>72</sup> R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 1979, 258.

<sup>73</sup> T. L. Gilchrist and T. G. Roberts, *J. Chem. Soc., Chem. Commun.*, 1979, 1090.

**Table 5** Examples of cycloaddition of nitroso-alkenes to alkenes

Alkene	Nitroso-alkene X in H <sub>2</sub> C=C(X)NO	Adduct (29)			% Yield	Ref.
		R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>		
$\alpha$ -Methylstyrene	Ph	H	Me	Ph	26	12
	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -4				83	12
	COMe				43	14
	CHO				39	14
	CO <sub>2</sub> Et				43	14
<i>(E)</i> -Stilbene	Ph	Ph	H	Ph	5	12
	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -4				57	12
	COMe				46	14
	CHO				13	14
Oct-1-ene	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -4	H	H	C <sub>6</sub> H <sub>13</sub>	(85:15)	12
		C <sub>6</sub> H <sub>13</sub>	H	H		
		COMe	H	H	C <sub>6</sub> H <sub>13</sub>	31
Ethyl vinyl ether	Ph	H	H	OEt	87	58
	COMe				82	14, 58
1-Morpholino-cyclohexene	Ph	—(CH <sub>2</sub> ) <sub>4</sub> —	NR <sub>2</sub>		91	68
	CO <sub>2</sub> Et				86	68

bonds of some 1,2-oxazines,<sup>74</sup> although this is not a general reaction of C=N bonds. The products are [3 + 2] rather than [4 + 2] cycloadducts, addition having taken place at the nitrogen atom of the nitrostyrene. Similar adducts are also found as minor products in the addition of some electron-rich alkenes to  $\alpha$ -nitrostyrene:<sup>12,38</sup> for example, 2-methoxypropene gives the nitrone (32) (10%) as well as the expected dihydro-oxazine.<sup>12</sup> The ratio of adducts is insensitive to the polarity of the solvent or to the stereochemistry of the halo-oxime precursor. If concerted, these [3 + 2] additions would require the nitrostyrene to add through a twisted conformation, (33), as a type of 1,3-dipole.

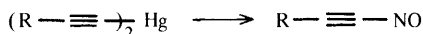


**D. Other Reactions.**—There are few other well-established reactions of these compounds. Nitrosocyclohexene<sup>8</sup> and trifluoronitroso-ethylene<sup>4</sup> have been observed to undergo electrophilic addition by chlorine; hydrogen chloride also adds to some nitroso-alkenes.<sup>8,9</sup> There are no well authenticated examples of radical additions or of ene reactions which are common with other types of nitroso compounds. Some nitroso-alkenes<sup>22</sup> and trifluoronitrosoethylene<sup>4</sup> are claimed to polymerize in solution, the latter by a radical mechanism.

<sup>74</sup> D. Mackay and K. N. Watson, *J. Chem. Soc., Chem. Commun.*, 1982, 775.

### 5 Nitroso-alkynes

The preparation of several nitroso-alkynes was attempted by Robson, Tedder, and Woodcock,<sup>15</sup> who treated metal alkynides with nitrosyl chloride. Better results were obtained with mercury alkynides than with magnesium alkynides. Green solutions containing several nitroso-alkynes (2) were obtained at low temperatures. The spectroscopic properties observed for two of these intermediates (a, R = Bu<sup>n</sup> and b, R = Bu<sup>t</sup>) are summarized in Scheme 23. The t-butyl compound (2b) has also been obtained by reaction of the corresponding trimethylstannylalkyne with dinitrogen tetroxide.<sup>75</sup>



(2) a; R = Bu  
b; R = CMe<sub>3</sub>

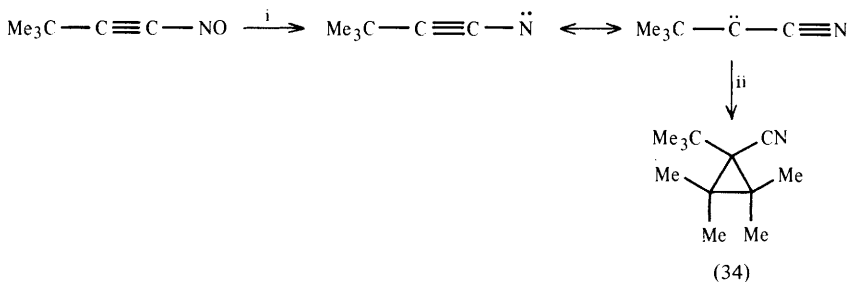
Reagent: i, NOCl, -60 °C

(2a):  $\nu_{\max}$  2290 (C≡C) and 1580 (N=O) cm<sup>-1</sup>;  $\lambda_{\max}$  640 nm

(2b):  $\nu_{\max}$  2320–2280 (C≡C) and 1560 (N=O) cm<sup>-1</sup>;  $\lambda_{\max}$  654 nm

Scheme 23

Compound (2b) rearranges in ether (4h, -30 °C) to pivaloyl cyanide, Me<sub>3</sub>CCOCN,<sup>15,75</sup> and can be oxidized by hydrogen peroxide to the corresponding nitro-alkyne.<sup>75</sup> Deoxygenation by triethyl phosphite in the presence of 2,3-dimethylbut-2-ene gave the adduct (34) (Scheme 24):<sup>75</sup> the nitrene formed by deoxygenation apparently adds to the alkene through a mesomeric carbene structure.



Reagents: i, P(OEt)<sub>3</sub>, -40 °C; ii, Me<sub>2</sub>C=CMe<sub>2</sub>

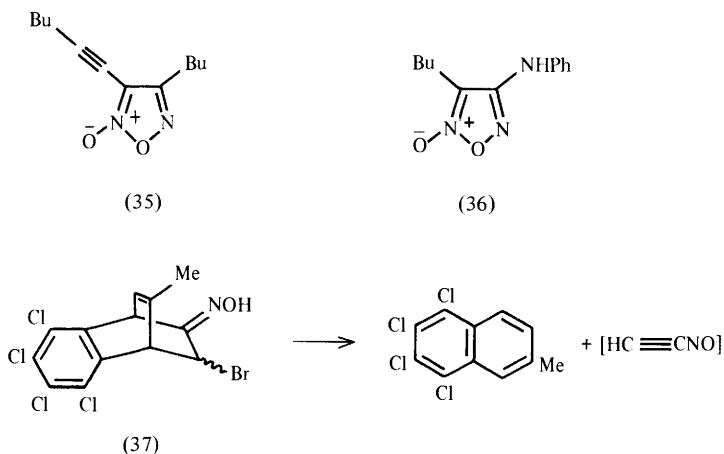
Scheme 24

The less hindered 1-nitrosohexyne (2a) dimerizes in the presence of base to the furoxan (35),<sup>15</sup> and forms a different furoxan, (36), in the presence of nitrosyl chloride and aniline.<sup>76</sup>

<sup>75</sup> J.-C. Motte and H. G. Viehe, *Chimia*, 1975, **29**, 515.

<sup>76</sup> J. M. Tedder and D. J. Woodcock, *J. Chem. Res. (S)*, 1978, 356; *J. Chem. Res. (M)*, 1978, 4356.

A reaction in which nitroso-acetylene itself may have been generated is illustrated in Scheme 25: the bromo-oxime (37) gave the naphthalene (38) on heating with base, probably by a retro-Diels–Alder process.<sup>77</sup> Attempts to intercept the nitroso-acetylene were unsuccessful.



Reagent: i, Et<sub>3</sub>N, d.m.f., 100 °C

**Scheme 25**

<sup>77</sup> P. C. Buxton, H. Heaney, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2695.