# Synthesis, Reactions, and Properties of ONO Systems

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## Contents

## *I. Introduction*

The first report (Posner, 1906)[1,2] on the preparation of compounds with ONO fragment, namely 2-hydroxy- and 2-alkoxy-5-isoxazolidinones, was disproved 80 years later.[3] The studies by Kohler[4,5] and Sokolov[6,7] on synthesis of 2-hydroxyisoxazolidines and 2-hydroxy-4-isoxazolines, respectively, also were found to be erroneous.[8–11] Knunyants and co-workers were probably the first to obtain such compounds, when in 1960 they published the synthesis of 2-hydroxydihydro-1,2,4-oxadiazete derivative.[12] In 1964, Tartakovskii et al.[13,14] found a facile and universal method of ONO systems synthesis by 1,3-dipolar cycloaddition of nitronic esters to olefins. This reaction has been studied in detail and widely applied in organic synthesis due to the easy transformation of its products, 2-alkoxy- or 2-(silyloxy)-isoxazolidines into compounds of various types.[15–23]

Some other trends in this field were successfully developed along with the above mentioned, and at the present time almost all possible types of acyclic and cyclic compounds of general formula $XN(OR)_2$, where X = alkyl, RO, H, Hal, $(RO)_2N$, RCO or unpaired electron have been synthesized. They are of special interest mainly due to the fact that, for example, the first two in this series represent the nitrogen analogues of such well-studied compounds as acetals, orthoesters of carboxylic acids or phosphonous diesters and trialkyl phosphites, respectively. They also possess some common chemical properties. The names recently suggested for them, nitroso acetals[24] or nitrosals[25] reflect the correlation between dialkoxyamines and acetals. The *O*-alkyl-*N*-alkoxyhydroxylamines are the orthoesters of nitrosyl hydride, HNO,[26] and *O*-alkyl-*N*,*N*-dialkoxyhydroxylamines are the orthoesters or nitrous acid, orthonitrites.

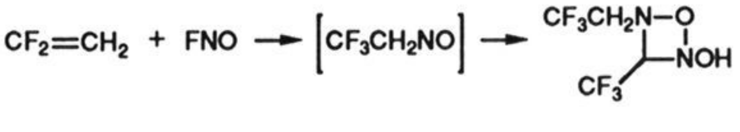
Vladimir F. Rudchenko was born in Ukraine, in 1951. He graduated from Dniepropetrovsk Institute of Chemical Technology in 1973. From 1973 to 1976 he was a postgraduate student of the Institute of Chemical Physics, Academy of Sciences of the USSR. He then served as Junior Researcher (1977–1985), Senior Researcher (1985–1989), and Principal Researcher (1989–1992) at this Institute. He is currently working at Konica Corporation in Japan. He received his Candidate Degree (Ph.D.) in 1977 and his Doctor Degree (D.Sc.) in 1986 (both from the Institute of Organic Chemistry, Academy of Sciences of the USSR). His scientific interests include the problems of an asymmetric nitrogen atom.

A high pyramidal stability is the unique feature of these compounds. The first separation of enantiomers with an asymmetric nitrogen atom in the open chain was carried out with these compounds.[27–29]

Data on all compounds containing the ONO fragment have been classified for the first time in this review, covering the literature up to the middle of 1992. Only the general aspects of the previously reviewed[15–23] material, mainly concerning 2-alkoxy- and 2-(silyloxy)-isoxazolidines, is presented here.

## *II. Synthesis*

The first compound of this type was obtained by the reaction of vinylidene fluoride with nitrosyl fluoride (eq 1).[12] However, its structure has not been strictly proved, and the reaction has not been widely used.



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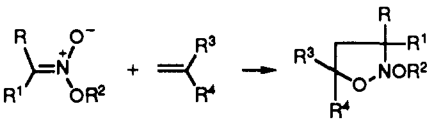
## A. [3 + 2]-Cycloadditions of Nitronic Esters

### 1. Cycloadditions of Open-Chain Nitronic Esters

Nitronic esters readily undergo 1,3-dipolar cycloaddition to alkenes (eq 2),[13,14] which proceeds regiospecifically and stereoselectively and leads to a 5-substituted isoxazolidines for monosubstituted olefins.[13,14,25,30–64] 1,2-Disubstituted alkenes such as methyl crotonate or crotonitrile give products with the electron-withdrawing group in position 5.[54,57] Trisubstituted olefins react with formation of 5,5-disubstituted products;[65,66] 1,3- and 1,4-dienes react with the participation of each double bond separately.[67–70] Nitronic esters obtained from mononitro-,[13,25,30,32,37,38,43,46,51,54–58,60–65,67,71–75] 1,1-dinitroalkanes[33] and their derivatives, as well as 1,1,1-trinitrocompounds[13,31,34,39–41,49,51–53,59,68,76,77] and tetranitromethane[35,36,42,44,45,47,48,50,66,69,70,78] have been used in this reaction. Some of them are very unstable and may be generated conveniently in situ. The reactions are conducted under mild conditions. Yields are good to excellent in most examples. The influence of the structure of the nitronic ester upon its reactivity in 1,3-dipolar cycloaddition and the stereoselectivity of the reactions have been extensively studied by Carrie and his group.[46,56,58,61,65,71–73,79]



(2)

1

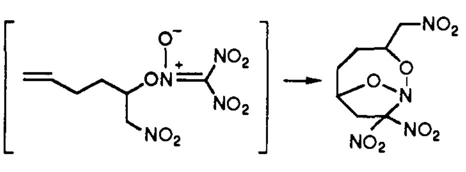
| 1 | R | R¹ | R² | R³ | R⁴ |
|---|---|---|---|---|---|
| a | $CO_2Me$ | $CO_2Me$ | Me | H | H |
| b | $CF_3$ | $CF_3$ | Me | H | $CO_2Me$ |
| c | $CO_2Me$ | $CO_2Me$ | Me | H | $NO_2$ |
| d | H | Ph | Me | H | $CO_2Me$ |
| e | H | $CO_2Et$ | Me | H | Ph |
| f | $CO_2Me$ | $CO_2Me$ | Me | H | CN |
| g | $CO_2Me$ | $CO_2Me$ | Me | $CO_2Et$ | $CO_2Et$ |

In 1972 Ioffe and co-workers[80] suggested using the silyl esters of nitronic acids as a 1,3-dipolar component, which unlike their alkyl analogues is stable and retains the ability of cycloaddition to olefins.[81–92]

The intramolecular reactions of the nitronate group with double bonds are known too. For instance, the interaction of tetranitromethane with one of the double bonds of hexa-1,5-diene gives a nitronic ester which is then added to the other double bond forming bicyclic compound **2** (Scheme 1).[70] In this case the alkene terminal carbon atom participates in C–C bond formation. However, the mode of cycloaddition is changed during cyclization of **3**[93] and nitronic ester, which is generated in situ from nitro compound **5**[94] (Scheme 2). These reactions lead to fused products **4** and **6**.

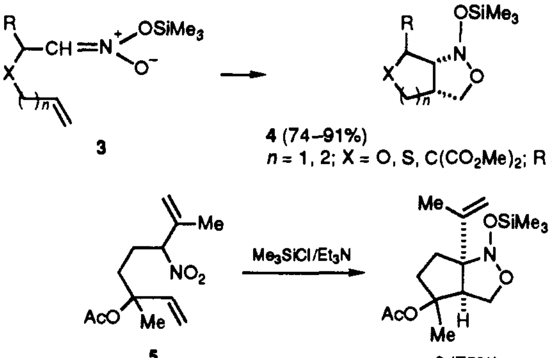
**Scheme 1**

$CH_2{=}CH(CH_2)_2CH{=}CH_2 + C(NO_2)_4 \longrightarrow$



2 (11%)

**Scheme 2**



3

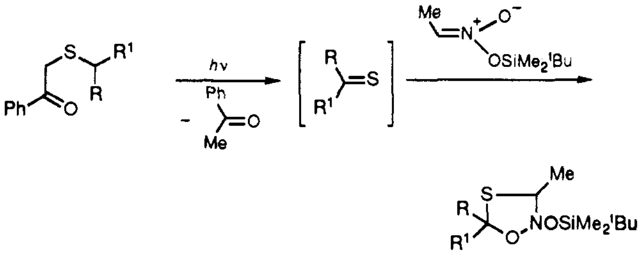
4 (74–91%)

$n$ = 1, 2; X = O, S, $C(CO_2Me)_2$; R = alkyl, Ar

5

6 (75%)

**Scheme 3**

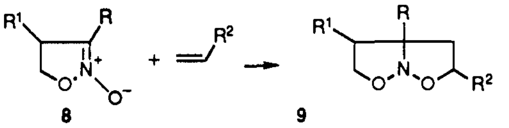


7 (34–98%)

Monomeric aliphatic thioketones and thioaldehydes have been found to behave[95–97] as 1,3-dipolarophiles toward silyl nitronates to form stable 1,4,2-oxathiazolidines **7** (Scheme 3).

### 2. Cycloadditions of Cyclic Nitronic Esters

Isoxazoline *N*-oxides can be used as 1,3-dipoles. They add to alkenes forming bicycles **9**[13] (eq 3). The same regularities as for the cycloaddition of the open-chain nitronates are observed for this reaction.[98–105] The data on it, up to 1972, are summarized in the review of Takeuchi and Furusaki.[16] The cycloaddition of **8** to silyl-substituted alkenes,[106] styrene,[107] allylic alcohol,[108] methyl acrylate,[109] as well as the stereochemistry of 3-methyl-5-phenylisoxazoline N-oxide reaction with different mono- and disubstituted olefins has also been studied.[110]



(3)

8

9

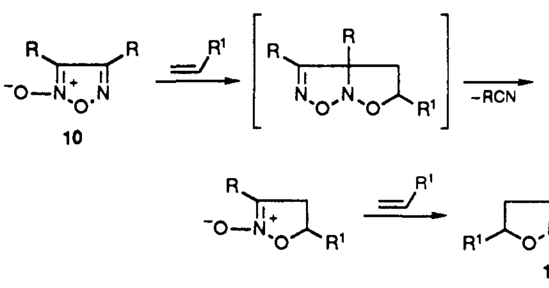
9a: R = $NO_2$, R¹ = R² = H

In 1983 Shimizu and co-workers suggested[111,112] using 1,2,5-oxadiazole *N*-oxides (furoxanes) **10** as 1,3-dipoles. Their cycloadducts with alkenes are unstable and decompose into isoxazoline *N*-oxides, the reaction of which with the second mole of olefin gives the final products **11** (Scheme 4).

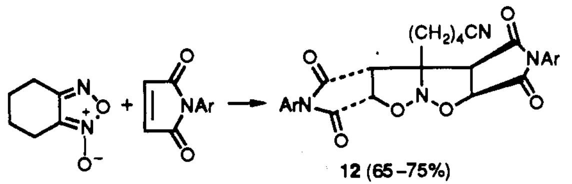
The stereospecific reaction in Scheme 5 proceeds according to similar a scheme.[113]

Furoxanes can also undergo the intramolecular cycloaddition which has been used for the synthesis of heterocyclic compound **13** (Scheme 6).[112]

**Scheme 4**

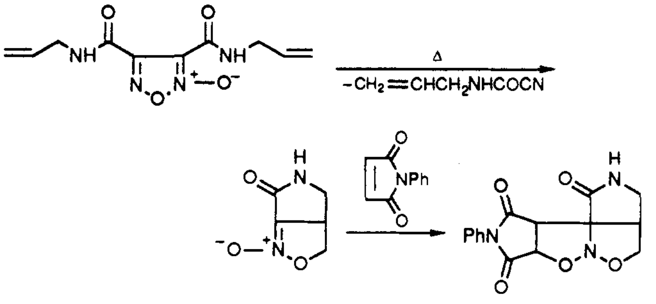


**Scheme 5**



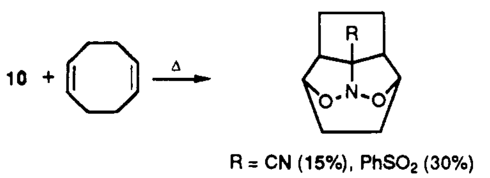
12 (65–75%)
12a: Ar = $p$-BrC$_6$H$_4$

**Scheme 6**



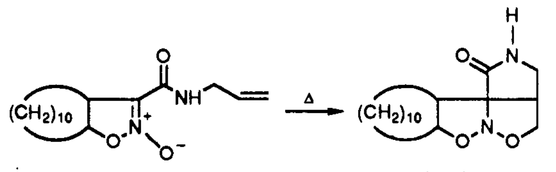
13 (88%)

The intramolecular cycloadducts are formed in the reaction of furoxanes **10** with cycloocta-1,5-diene (eq 4)[112] as well as by the cyclization of isoxazoline *N*-oxide **14** (eq 5).[111]



(4)

R = CN (15%), PhSO$_2$ (30%)

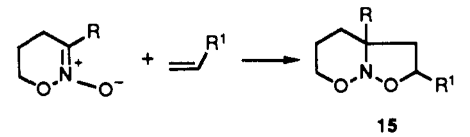


(5)

14    (29%)

The reactions with various olefins have been described for 6-membered cyclic (eq 6)[114–117] and bicyclic nitronates as well. The latter are readily available from nitro alkenes via inter-[24,118] or intramolecular[119] reactions of [4 + 2]-heterodiene synthesis (Scheme 7).

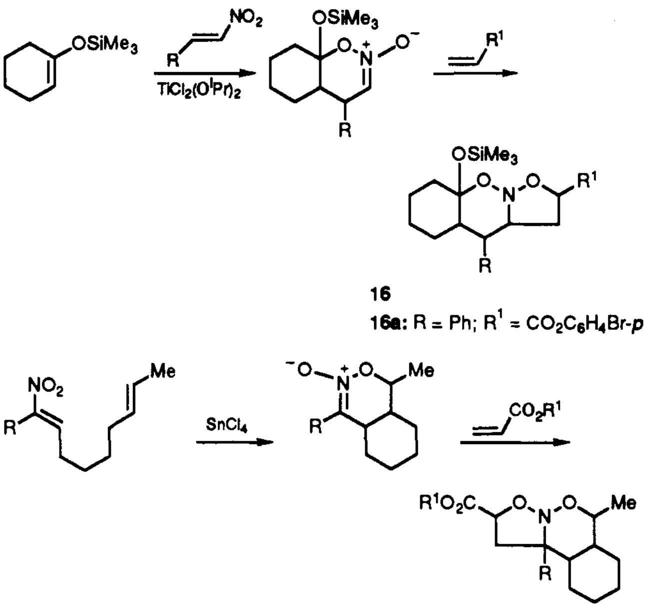
The 6-membered nitronates easily form the intramolecular [3 + 2]-cycloadducts. It has been demonstrated[120] for the synthesis of tricyclic compounds **18** (Scheme 8) via the tandem [4 + 2]/[3 + 2]-cycloadditions, which can also be effectively triggered with a chiral vinyl ether. The reactions proceed in good yield with high stereoselectivity.



(6)

| 15 | R | R$^1$ |
|---|---|---|
| a | COMe | Ph |
| b | Ph | CO$_2$Me |
| c | CO$_2$Me | Ph |
| d | Me | Ph |
| e | Me | CO$_2$Me |
| f | NO$_2$ | Ph |

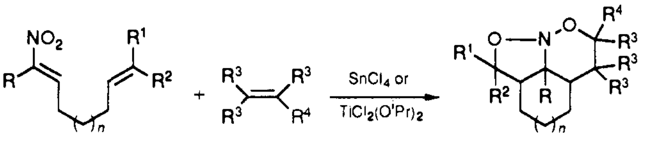
**Scheme 7**



16
16a: R = Ph; R$^1$ = CO$_2$C$_6$H$_4$Br-$p$

17
17a: R = H; R$^1$ = $p$-BrC$_6$H$_4$

**Scheme 8**



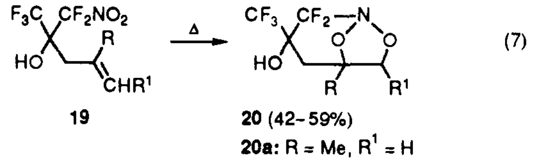
18

| 18 | $n$ | R | R$^1$ | R$^2$ | R$^3$ | R$^4$ |
|---|---|---|---|---|---|---|
| a | 0 | Me | CO$_2$Et | H | Me | Me |
| b | 1 | Me | CN | H | Me | Me |

## B. Cycloadditions of Nitro Compounds

The nitro group, according to the Huisgen's classification,[121] belongs to the allylic type 1,3-dipoles, which are well stabilized by resonance and should show little tendency to cycloadditions. The calculations predict[122] that the nitro group should participate in cycloadditions as a 2π-partner rather than 1,3-dipole. In accordance with that, the mechanism of intramolecular thermal cyclization of nitro olefins **19** and **21** was suggested,[123] which involves initial [2 + 2]-cycloaddition with formation of 2*H*-1,2-oxazete *N*-oxides followed by their rearrangement into 1,3,2-dioxazolidines **20** (eq 7) and **22** (eq 8).

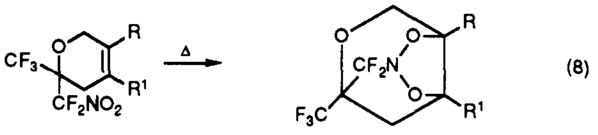
Nevertheless, it is assumed[124] that the intramolecular 1,3-cycloaddition of nitro group to the double bond is



19

20 (42–59%)

20a: R = Me, R$^1$ = H



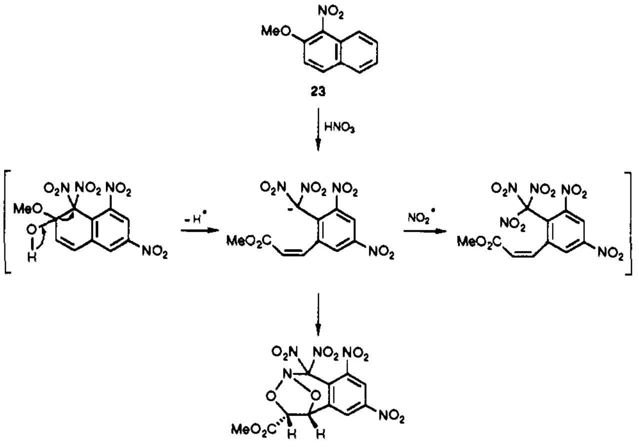
21

22 (32–84%) R = H, Me; R$^1$ = H, Me

one of the steps (Scheme 9) in the unusual nitration reaction of 1-nitronaphthalene **23** with formation of compound **24**.

There is only one example of thermal intermolecular cycloaddition of the nitro compounds to alkenes, which was carried out with nitrobenzene derivatives bearing electron-withdrawing groups and the highly reactive (*E,Z*)-cycloocta-1,5-diene (eq 9).[125]

**Scheme 9**



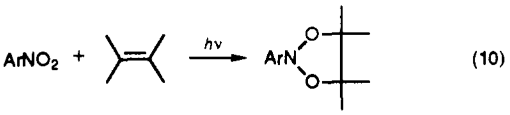
23

24 (35%)

25

Ar = 4-CNC$_6$H$_4$, 4-O$_2$NC$_6$H$_4$, 3-O$_2$NC$_6$H$_4$, 3-O$_2$N-5-MeO$_2$CC$_6$H$_3$

For the nitro compounds it is more common to undergo the photochemical cycloaddition to olefins (eq 10)[126] via a biradical intermediate with formation of unstable adducts **26**.



26

## C. Nucleophilic Substitution of Chlorine in ONCl Compounds

The high anionic mobility of chlorine is the characteristic feature of *N*-chloro-*N*-alkoxy-substituted nitrogen-containing compounds. It is caused by $n_{\pi(O)}-\sigma^*_{N-Cl}$ interaction, which kinetically destabilizes the N–Cl bond and facilitates its heterolysis. Thus, *N*-chloro-*N*-alkoxyamines **27**[127] readily react with a number of alcohols under mild conditions, giving the stable dialkoxyamines **28** (yields 21–88%), which are in most cases the only reaction products (eq 11).[28,127,128]

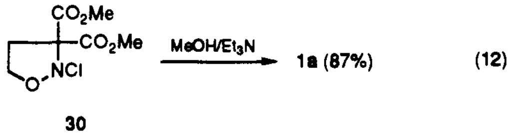
$$\underset{27}{\text{RN(Cl)OMe}} \xrightarrow{\text{R}^1\text{OH/B}} \underset{28}{\text{RN(OR}^1\text{)OMe}} + \underset{29}{\text{RN(O)=NR}} \qquad (11)$$

B = Et$_3$N, R$^1$ONa

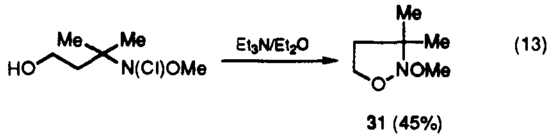
| 28 | R | R$^1$ |
|---|---|---|
| a | MeO$_2$CCMe$_2$ | Me |
| b | MeO$_2$CCMe$_2$ | PhCH$_2$ |
| c | MeO$_2$CCH$_2$CMe$_2$ | Me |
| d | MeO$_2$CCH$_2$CMe$_2$ | Et |
| e | MeO$_2$CCH$_2$CMe$_2$ | PhCH$_2$ |
| f | MeO$_2$CCH$_2$C(CF$_3$)Me | Me |

However, reactions of **27** with sterically hindered alcohols ($^i$PrOH, $^t$BuOH) in the presence of triethylamine also yield diazene oxides **29** due to the reduction of **27** into *N*-alkoxy aminyl radicals and their further transformations.[129] This method is suitable only for preparation of *N*-*tert*-alkyl-substituted compounds, because *N*-chloroamines **27** with primary and secondary *N*-alkyl substituents are unstable and are easily dehydrochlorinated.[28]

This reaction has been used in two of its modifications for synthesis of isoxazolidines **1a** (eq 12)[130–132] and **31** (eq 13).[28,133]



30



31 (45%)

The nucleophilic substitution of chlorine in **27a** also proceeds under the action of sodium acetate, leading to *N*-acetoxy-*N*-methoxyamine **32** and its decomposition products **33** and **28a** (eq 14).[134]

$$\textbf{27a} \xrightarrow{\text{NaOAc/MeCN}} \underset{\textbf{32}\ (36\%)}{\text{RN(OAc)OMe}} + \underset{\textbf{33}}{\text{RN=O}} + \textbf{28a} \qquad (14)$$

The N–Cl bond in chloro compounds **34** more likely undergoes heterolysis than in **27** due to two-electron-donating *N*-alkoxy substituents. For this reason **34** are highly unstable. Their reaction in situ with sodium methylate remains so far the only method of orthonitrites **35** synthesis (eq 15).[135–137]

$$\underset{\textbf{34}}{{}^t\text{BuON(Cl)OR}} \xrightarrow{\text{MeONa}} {}^t\text{BuON(OMe)OR} \qquad (15)$$

**35a**: R = Me (64%)
**b**: R = Et (50%)

The nucleophilic substitution of chlorine proceeds in *N*-chloro-*N*-alkoxyureas under the action of alcohols (eq 16)[138–141] and in *N*-chloro-*N*-alkoxybenzamides when treated by silver acetate (Scheme 10).[142,143]

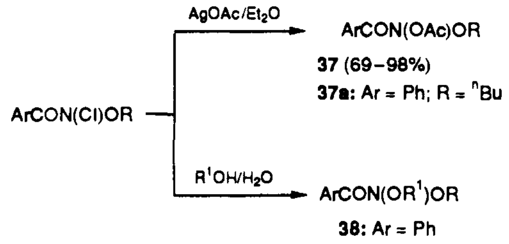
The solvolysis of the latter compounds in aqueous alcohols with the formation of dialkoxyamides 38 has

$$Me_2NCON(Cl)OR \xrightarrow{R^1OH/B} Me_2NCON(OR^1)OR \qquad (16)$$

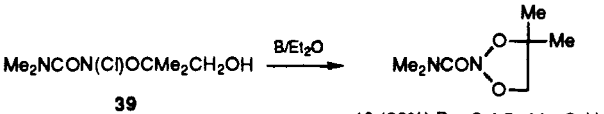
**36** (14–85%) B = $R^1ONa$, 2,4,5-$Me_3C_5H_2N$
**36a**: R = $R^1$ = Me

also been reported (Scheme 10).[142] Although, these products have not been characterized in this paper.

**Scheme 10**



The intramolecular cyclization of N-chlorourea 39 is a simple method for 1,3,2-dioxazolidine 40 synthesis (eq 17).[144]



(17)

**39**

**40** (68%) B = 2,4,5-$Me_3C_5H_2N$

## D. Other Synthetic Methods

In 1965, a patent was registered on the preparation of perfluorinated dialkoxyamines 41 (eq 18) and 42 (eq 19) by a photochemical reaction with difluoroamines.[145]

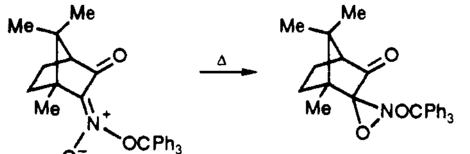
$$(CF_3O)_2 + RNF_2 \xrightarrow{h\nu} RN(OCF_3)_2 + RN(F)OCF_3 \qquad (18)$$

**41** R = $CF_3$(5%), $^nC_3F_7$(4%), $^iC_3F_7$(1%)

$$(CF_3O)_2 + CF_3ONF_2 \xrightarrow{h\nu} (CF_3O)_2NF \qquad (19)$$

**42** (3%)

So far, the only known N-alkoxyoxaziridine 44 has been synthesized by the thermal isomerization of nitronic ester 43 (eq 20).[146]



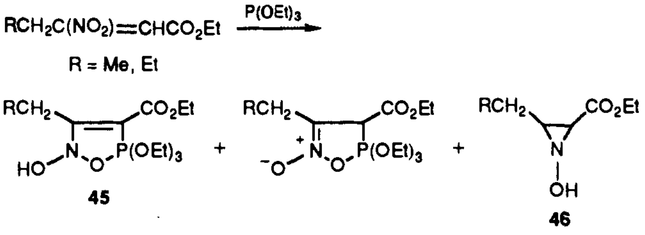
(20)

**43**

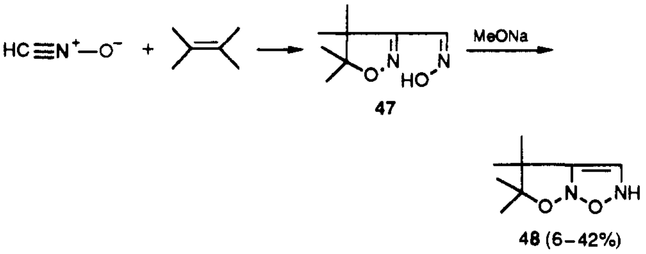
**44** (33%)

The reaction of ethyl α,β-unsaturated-β-nitrocarboxylates with triethyl phosphite gives an N-hydroxy derivative of a O,N,P-containing heterocycle 45 as one of the products (Scheme 11).[147] Unfortunately, its structure has not been strictly proved, while it was shown[148] that N-hydroxyaziridine structure of 46 was erroneous.

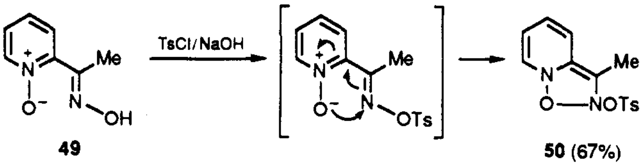
**Scheme 11**



**Scheme 12**



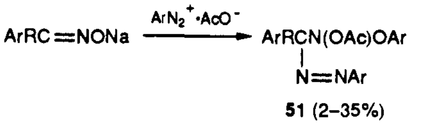
**Scheme 13**



The cyclization of *anti*-oximes 47, produced in the reaction of formonitrile oxide with olefins (ethylene, cyclopentene, 1-acetylcyclopent-1-ene, 3β-acetoxy-5,6-pregnadiene-20-one), leads to a new heterocyclic system 48 (Scheme 12).[149]

The tosylation of the *E* form of oxime 49 gives the corresponding oxime *O*-ester which undergoes an unusual intramolecular cyclization producing bicycle 50 (Scheme 13).[150]

*N*-(Acyloxy)-*N*-(aryloxy)amines 51 were obtained by the arylation of benzaldoxime and ketoximes salts with aryl diazonium salts (eq 21).[151,152] A wide range of other products is also formed. However, in this paper there is no evidence for structure 51.



$$ArRC{=}NONa \xrightarrow{ArN_2^+ \cdot AcO^-} ArR\underset{\displaystyle N{=}NAr}{\underset{|}{C}}N(OAc)OAr \qquad (21)$$

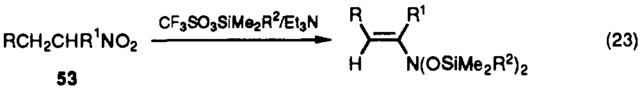
**51** (2–35%)

The first amides with a nitrogen atom covalently bounded with two oxygen atoms were obtained by reaction of perfluorocarboxylic acids with peroxydisulfuryl difluoride (eq 22).[153] The low yields of compounds 52 may be interpreted by their instability under the reaction conditions at −20 to −30 °C.

$$R_fCONH_2 \xrightarrow{2S_2O_6F_2} R_fCON(OSO_2F)_2 + 2HSO_3F \qquad (22)$$

**52** $R_f$ = $CF_3$ (17%), $C_3F_7$ (21%), $C_6F_{13}$ (25%)

The *N*,*N*-bis[(trialkylsilyl)oxy]-1-alken-1-amines were synthesized predominantly (95%) in the form of *E* isomers 54 by the complete silylation of nitro compounds 53 (eq 23).[154]

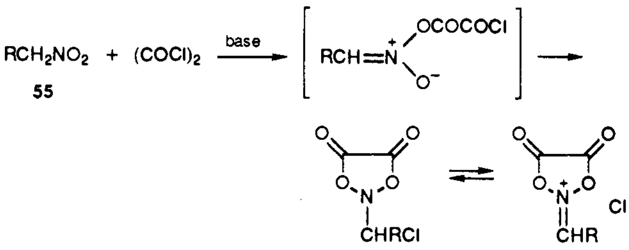


53 (23)

54 R = H, Me, Ph, c-$C_6H_{11}$, $R^1$ = H, Me, $PhCH_2$, $R^2$ = Me, ${}^tBu$

The reaction of nitro compounds **55** with oxalyl chloride gives N-substituted 4,5-diketo-1,3,2-dioxazolidines **56**, which exist in the equilibrium with anionic form (Scheme 14).[155] However, there is no evidence proving the structure of these products.

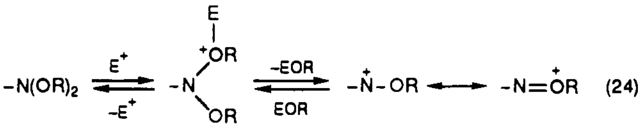
### Scheme 14



56 R = H, c-$C_5H_{11}$

## III. Reactions

The presence of a triad of heteroatoms with lone electron pairs in the compounds in question is responsible for their tendency to react with electrophilic reagents. The electrophilic attack at one of the oxygen atoms leads to the weakening and further cleavage of its N–O bond. The vicinal $n_{\pi(O)}$–$\sigma^*_{N-O}$ interaction facilitates this process, which proceeds under a stereoelectronic control[156,157] and is accompanied by various transformations. It is assumed[129,137,156,158] that resonance-stabilized N-alkoxy nitrenium ions (eq 24) take part in such reactions. However, only in two cases was this hypothesis strictly proved experimentally.[143,159,160] On the other hand the data supporting the synchronous mechanism of some electrophilically initiated reactions of dialkoxyamines were obtained.[161]

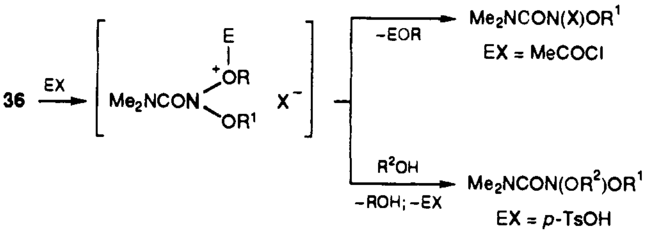


## A. RCON(OR)2 Systems

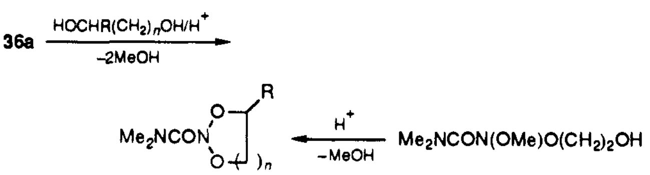
Among such compounds, the properties of *N,N*-dialkoxyureas **36** were studied more thoroughly. It was found they can be cleaved by acetyl chloride to give *N*-chloro-*N*-alkoxyureas[162] and undergo acid-catalyzed "transesterification" under the action of alcohols (Scheme 15).[140,162,163] The latter reaction has been used for the synthesis of *N*-carbamoyl-substituted heterocycles **57** (Scheme 16).[162–164]

The alkaline hydrolysis or methanolysis of acyclic **36** (eq 25) or cyclic dialkoxyureas **57** (eq 26) leads to a new type of ONO systems, *O*-alkyl-*N*-alkoxyhydroxylamines **58**[138,140,141,165] and **59**,[162–164] respectively. In these reactions the dialkoxyamine function is a pseudohaloide, easily leaving group. However, transamidation with loss of dimethylamine occurs during interaction of **36a** with methylamine.[162]

### Scheme 15



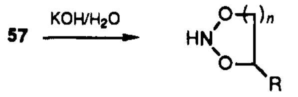
### Scheme 16



57 (27–55%)
57a: n = 1, R = H
57b: n = 2, R = H
57c: n = 2, R = Me

$$36 \xrightarrow{KOH/H_2O} RONHOR^1 \qquad (25)$$

58 (25–74%)
58a: R = $R^1$ = Me
58b: R = Et, $R^1$ = (S)-PhCHMeNHCOCMe$_2$



(26)

59 (34–61%)
59a: n = 1, R = H
59b: n = 2, R = H
59c: n = 2, R = Me

Moreover, the decomposition of **36a** under the action of TsOH,[162] as well as thermolysis of **52**[153] and acid hydrolysis of **37a**[143] have been studied.

## B. O-Alkyl-N-alkoxyhydroxylamines

The electronegative substituents in these compounds significantly decrease the p character of the nitrogen lone pair.[166] Therefore, *O*-alkyl-*N*-alkoxyhydroxylamines are characterized by a weaker nucleophilicity[165,167] compared to common amines and *O*-alkylhydroxylamines. Nevertheless, they readily undergo the reactions typical for secondary amines; hydroxymethylation[165] and aminomethylation,[165] acylation,[168] carbamoylation,[168] and *N*-chlorination.[137] They are also easily oxidized, forming dialkoxyaminyl radicals **60** stable in solution and inert toward oxygen (eq 27),[141,169]

$$\mathbf{58}\text{ or }\mathbf{59} \xrightarrow[-H^\cdot]{} \underset{\mathbf{60}}{2RO\dot{N}OR^1} \rightleftarrows \underset{\mathbf{61}}{RO(R^1O)NN(OR^1)OR}$$
$$\mathbf{61a}:\ R = R^1 = Me \qquad (27)$$

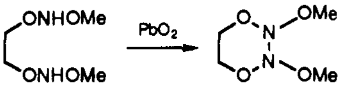
the stability of which is mainly caused by delocalization of the unpaired electron with participation of the neighbouring oxygen atoms (eq 28).[141,170,171]

$$\mathbf{60} \longleftrightarrow R\overset{+\bullet}{O}-\bar{\ddot{N}}-OR^1 \longleftrightarrow RO-\bar{\ddot{N}}-\overset{\bullet+}{\ddot{O}}R^1 \qquad (28)$$

Radicals **60** exist in solution in an equilibrium with their diamagnetic tetraalkoxyhydrazine dimers **61** (eq

27), which can be isolated in a pure state.[141] These radicals can recombine with the 2-cyanoisopropyl radical as well.[141]

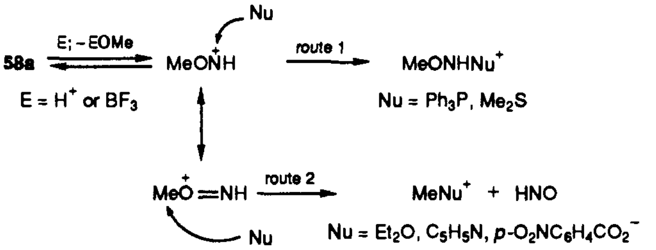
The oxidation of 1,2-bis[(methoxyamino)oxy]ethane (**62**) leads to a new heterocycle **63**, for which no equilibrium with the corresponding diradical has been observed (eq 29).[172]



**62** **63** (95%) (29)

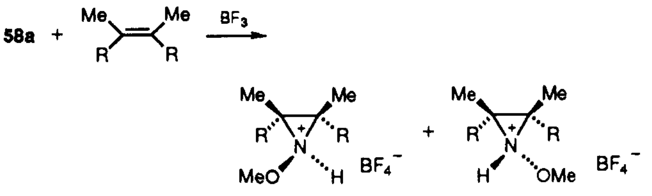
*O*-Methyl-*N*-methoxyhydroxylamine (**58a**) easily undergoes electrophilically initiated cleavage of the N–O bond, affording *N*-methoxy nitrenium ion, which is an ambident cation and takes part in reactions with nucleophiles as methoxyaminating or methylating agent (Scheme 17).[159,160]

**Scheme 17**



This ion can be added to alkenes producing 1-methoxyaziridinium salts **64** (Scheme 18).[159,160] The stereospecifity of *N*-methoxy nitrenium ion cycloaddition to *cis*-but-2-ene was considered as evidence of its singlet ground electronic state.

**Scheme 18**



**64** R = H (95%), Me (31%)

## C. *N,N*-Dialkoxy-*N*-alkylamines

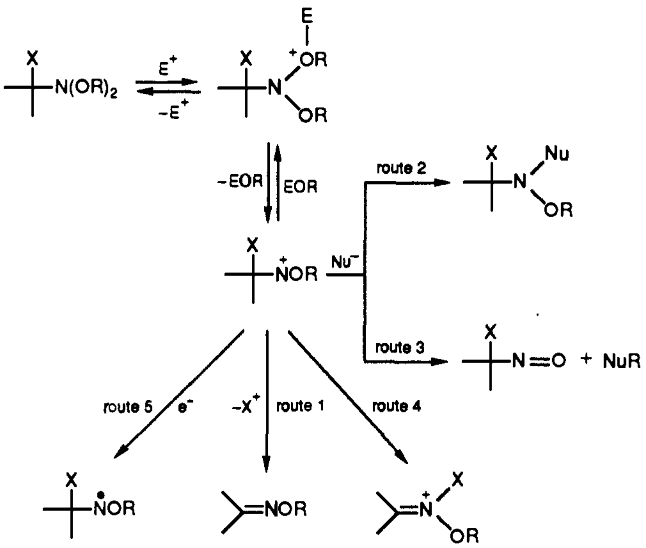
The properties of acyclic and cyclic compounds of this series are considered here.

### 1. Reactions with Electrophilic Reagents

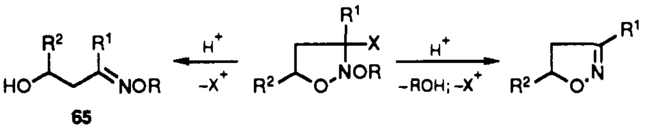
The main directions of these reactions are presented in Scheme 19.[173]

*a. Route 1.* This type of transformations predominates if there is electrofuge (H, $NO_2$, CONHMe, Ac) at the $\alpha$-carbon atom in N-substituent of isoxazolidines **1**,[30-33,36,37,41,62,67,83,85-92,156] 1,4,2-oxathiazolidines **7**,[96] as well as bicyclic dialkoxyamines **4**,[93] **9**,[98,101,106,174] and **15**.[175,176] HCl, $H_2SO_4$, *p*-TsOH, $ZnCl_2$, $BF_3$, and HOAc were used as electrophiles. The acid hydrolysis of isoxazolidines **1** has been investigated most thoroughly (see also reviews found in refs 15, 20, and 22). It was found to proceed under the stereoelectronic control,[156,157] and the preference of one of its directions

**Scheme 19**



**Scheme 20**

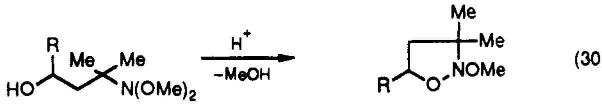


**65**

(Scheme 20) depends on the acid used[32,33] and the nature[32,37] and mutual orientation[37] of $R^1$ and $R^2$ substituents. The $\beta$-imino alcohols **65**[32,37] under some reaction conditions are transformed further into $\beta$-hydroxy ketones,[30] $\beta$-hydroxy acids (for compounds with $R^1$=$NO_2$),[31,33] or $\alpha,\beta$-unsaturated acids.[31,36,41,51]

The hydrolysis of 2-(silyloxy)isoxazolidines gives exclusively 2-isoxazolines.[83,85-92]

*b. Route 2.* This includes the substitution of *N*-alkoxy group for chlorine during interaction of dialkoxyamines **28**[129,130] with MeCOCl, $CF_3COCl$, $SOCl_2$, $Me_3SiCl$, HCl, or isoxazolidine **1a**[130,131] with $SOCl_2$ as well as acid-catalyzed "transesterification" of these compounds under the alcohols action.[156,158] The latter reaction is used for synthesis of isoxazolidines **66** (eq 30)[158] as well as *N*-alkyl-substituted heterocycles with endocyclic fragment ONO **67**[158,177-179] and **68**[180] (Scheme 21).



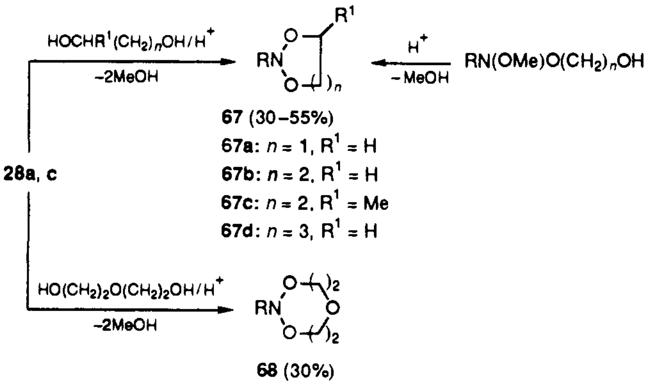
(30)

**66** R = H (36%), $CH_2OH$ (58%)

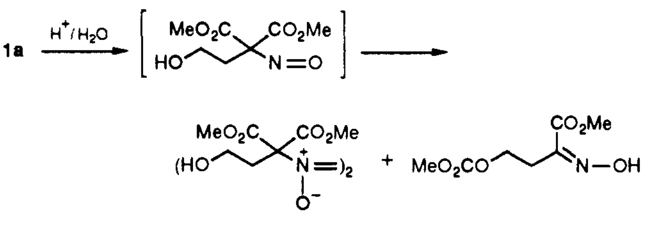
*c. Route 3.* The nitroso compounds are formed by acid-catalyzed alcoholysis[158] or hydrolysis[25,64] of dialkoxyamines **28a,c,f**. The acid hydrolysis of isoxazolidine **1b** leads to the corresponding $\gamma$-nitroso alcohol.[25,64] Isoxazolidine **1a** gives a nitroso alcohol dimer and the product of its rearrangement (Scheme 22).[25,64]

*d. Route 4.* Dialkoxyamines readily undergo a $BF_3$-induced 1,2-rearrangement with migration of various groups to the nitrogen atom. The 1,2-shift of the ester group was observed in the dialkoxyamine **28a**[129,158] and isoxazolidine **1a**[156,161] as well as the methyl group in dialkoxyamine **28c**.[158] The 1,2-rearrangement of bicycles **15** with migration of acetyl (in **15a**[175,176]) or phenyl (in **15b**[181]) groups leads to spirocyclic products. In the

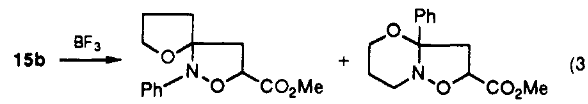
**Scheme 21**



**Scheme 22**

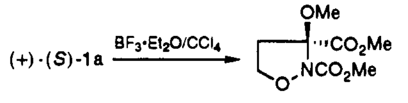


latter case a competitive 1,2-shift of the alkyl group has also been observed (eq 31).[181]



(31)

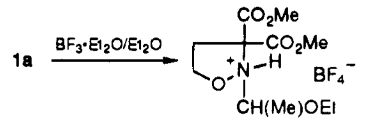
It is assumed that the rearrangement of isoxazolidine **1a** proceeds according to synchronous mechanism. The isolation of optically active product (+)-**69** of isoxazolidine (+)-(*S*)-**1a** rearrangement (eq 32) was considered as one of the evidences of that.[131,161]



(+)-**69** (73%)

(32)

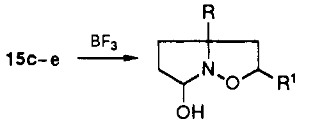
*e. Route 5.* This direction is realized if dialkoxyamines are treated by an electrophile in the presence of a reducing reagent. The intermediately formed *N*-alkoxy aminyl radicals undergo further transformations. Thus, in reactions of **28a,c** with triethylamine hydrochloride they are dimerized into 1,2-dialkoxyhydrazines, fragmentation of which gives the final products, 1,2-dialkyldiazene oxides.[129,158] In the reaction of isoxazolidine **1a** with $BF_3$ etherate (eq 33),[161] the diethyl ether acts as a reducing agent and product **70** is formed by recombination of aminyl radical and the radical produced by oxidation of ether.



**70** (69%)

(33)

The red-ox mechanism is proposed[161] for the following rearrangement (eq 34) of bicycles **15c–e** which leads to products **71**.[181-183]



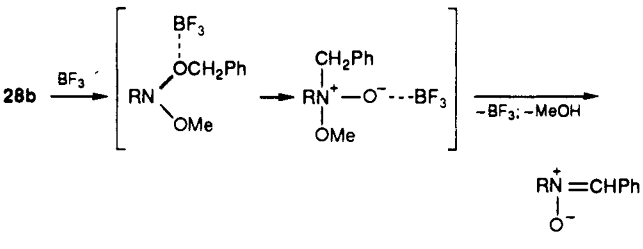
**71**

(34)

Besides the above-discussed reactions, which were summarized in Scheme 19, the electrophilically initiated addition of **28a**[129] and **1a**[161] to isobutylene, the acid-catalyzed reduction of **28a** by cathehole,[158] acid hydrolysis of oxaziridine 44,[146] and 2-(2-nitro-1-arylethoxy)isoxazolidines[184] with formation of 2-isoxazoline *N*-oxides were also studied.

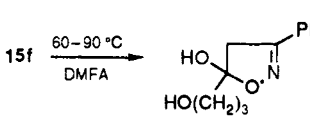
It should be mentioned that reactions of dialkoxyamines according to routes 1–3 (Scheme 19) are also typical for their carbon analogues, acetals. At the same time there is an obvious difference in the properties of dialkoxyamines and their phosphorous analogues, phosphonous diesters, in the reactions of which an electrophilic attack at the phosphorous atom is realized.[185] The dialkoxyamines are inert under the conditions of Arbuzov reaction and are converted according to routes 3 or 4 (Scheme 19) when treated by methyl triflate.[173] Nevertheless, to explain the formation of nitrone **72** in the reaction of **28b** with $BF_3$[158] Scheme 23 was suggested.[173] It involves the isomerization of **28b** into derivative of *O*-methylhydroxylamine *N*-oxide, which is similar to Arbuzov rearrangement.

**Scheme 23**



**72** (37%)

It is assumed[173] that such a type of isomerization might also be one of the steps of the acid-catalyzed or thermal rearrangement of bicycles **15** (R = OH, OMe; $R^1$ = Ph)[181,186] or **15f**,[186-188] respectively (eq 35).



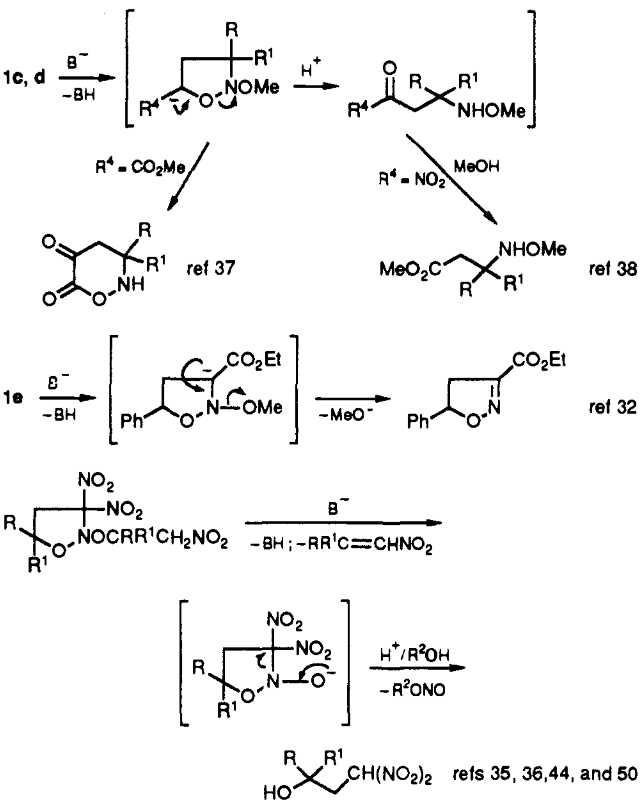
(35)

### 2. Reactions with Nucleophiles

These reactions can proceed either with retention or with cleavage of dialkoxyamine ONO fragment. This fragment is not affected by the nucleophilic substitution of nitro group in bicycles **15** (R = $NO_2$) for OH,[189] OR,[190,191] $N_3$,[192] or CN[193,194] as well as by amidation or alkaline hydrolysis of some isoxazolidines **1**[38,74,195-197] and dialkoxyamines **28**[27-29] or **67**.[179,198]

The reactions of the second type are observed for isoxazolidines **1** with an electron-withdrawing ($NO_2$ or $CO_2Me$) substituent in the cycle or the *N*-alkoxy group, which promotes the formation of an anion at the carbon atom bearing that substituent. Further transformations of this carbanion depend on its location and are

**Scheme 24**

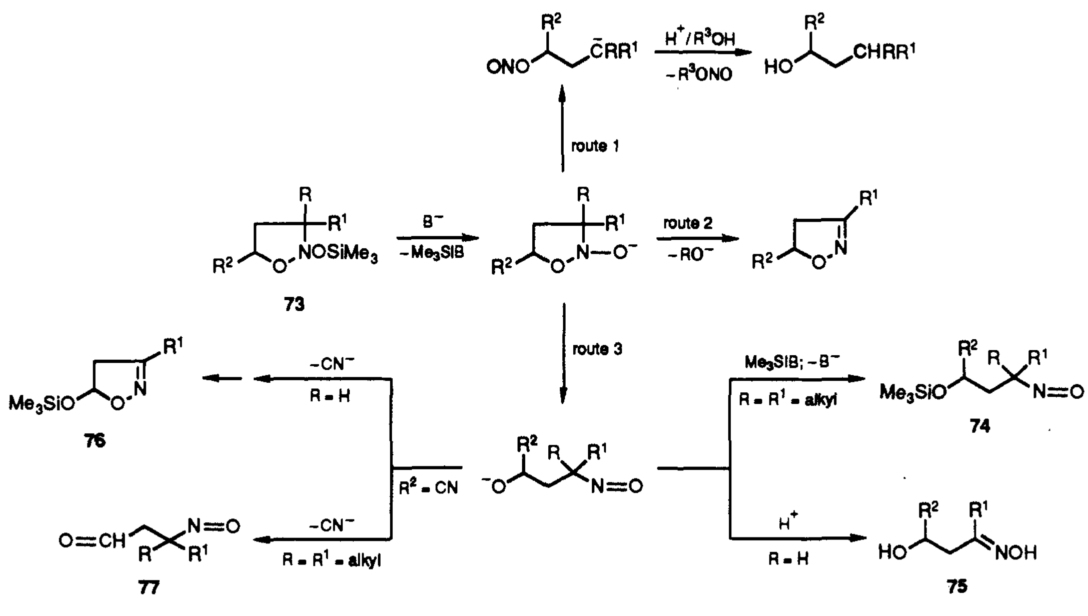


accompanied by cleavage of one of the nitrogen atom bonds (Scheme 24).[32,35-38,44,50]

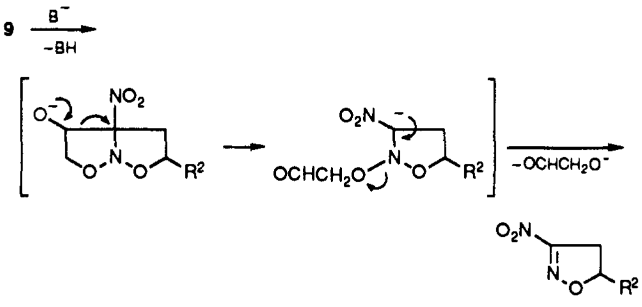
The reactions of 2-(silyloxy)isoxazolidines **73** with nucleophiles (see also the reviews found in refs 22 and 23) always occur via the cleavage of the Si–O bond. The anion formed can be then transformed according to the three routes in Scheme 25.

3,3-Dinitro-substituted isoxazolidines **73** react with alcoholic solution of alkali or alcoholates by route 1.[49,81,82] For some of them[81] route 2 is also partially realized, which becomes the main one for isoxazolidines **73**, where R = R$^1$ = CO$_2$Me.[80] In all of the rest of cases the reactions proceed with the cleavage of the cyclic N–O bond (route 3). Depending on the type of substituents in the cycle and the nucleophile used, the final products are nitroso compounds **74**,[88] oximes **75**,[83,85,86] 2-isoxazolines **76**,[87,89] and nitroso aldehydes **77**.[88]

**Scheme 25**



**Scheme 26**



The F$^-$-induced transformation of 1,4,2-oxathiazolidines **7** into carbonyl compounds[96] and the fragmentation of bicycle **9** (R = NO$_2$, R$^1$ = OH) according to the Scheme 26[100] are related to this reaction type as well.

### *3. Other Reactions*

Reduction of isoxazolidines **6** and **73** (B$_2$H$_6$,[85] Li/NH$_3$,[94] H$_2$/Raney Ni[86-88]) as well as of bicycles **16**[24] and **18**[120] (H$_2$/Raney Ni) is accompanied by the cleavage of the cyclic N–O bond and formation of corresponding amino alcohols, which in some cases may undergo further transformations. Reduction of 3-phenyl-substituted isoxazolidines **1** by LiAlH$_4$ leads to isoxazolines.[30] However, ONO fragment remains intact with LiAlH$_4$ reduction of **28**,[158] KMnO$_4$ oxidation of **1**,[68] and bromination of **9**.[102]

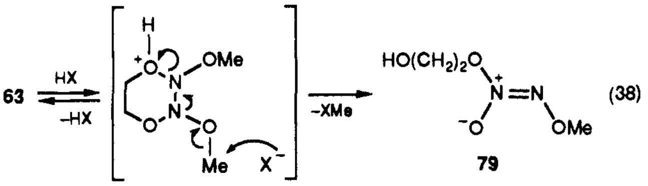
## D. Miscellaneous ONO Systems

Chemical properties of compounds considered in this section are presented by some certain reactions. Thus, hydrogenation of **25**[125] and **26**[126] on Pd–C produces corresponding 1,2-diols. Enamines **54** undergo thermal or BF$_3$-catalyzed rearrangement to silyl esters **78** (eq 36).[154] They can also add amines to their double bond with the loss of one molecule of trialkylsilanol (eq 37).[154]

$$\mathbf{54} \xrightarrow{\Delta \text{ or } BF_3 \cdot Me_2O} \underset{\mathbf{78}}{Me_2R^2SiOCHRC(R^1){=}NOSiMe_2R^2} \quad (36)$$

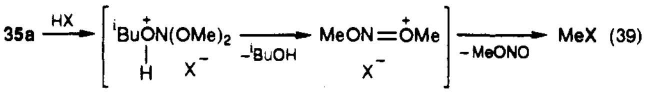
$$\mathbf{54} \xrightarrow[-Me_2R^2SiOH]{R^3_2NH} R^3_2NCHRC(R^1){=}NOSiMe_2R^2 \quad (37)$$

Regio- and stereospecific stereoelectronically controlled reaction of hydrazine **63** with *p*-nitrobenzoic acid produces an equimolar mixture of methyl *p*-nitrobenzoate and dialkoxydiazene oxide **79** in the form of the *E* isomer (eq 38),[172] which is the first representative of this type compounds.



HX = $p$-$O_2NC_6H_4CO_2H$

The decomposition of orthonitrite **35a** occurs on *p*-nitrobenzoic acid treatment and leads to the methyl ester of this acid in 74% yield (eq 39).[137] This product is also obtained in 91% yield by reaction of **35a** with *p*-nitrobenzoic acid chloride.[137] These two reactions obviously demonstrate the similar properties of orthonitrites and their carbon analogues, orthoesters of carboxylic acids.



HX = $p$-$O_2NC_6H_4CO_2H$

## IV. Properties

### A. Structure and Stereochemistry

Topomerization of ONO systems as well as of some other compounds with an N–O bond[199] is an inversion–rotation process. However, while, for instance, the acyclic trialkyl-substituted hydroxylamines have close values of barriers to nitrogen inversion and N–O bond rotation ($\Delta G^{\neq}$ 9–12 kcal/mol),[199] for compounds with ONO fragment the inversion of the nitrogen pyramid is the rate-determining step in their topomerization. The latter has been related to the effect of oxygen atoms and might be explained as in the following.[43,200] The nitrogen inversion proceeds via a planar transition state in which its lone electron pair occupies the $p_z$ orbital. Electronegative ligands increase the s character of nitrogen nonbonding orbital and thereby destabilize the inversion transition state, increasing the inversion barrier. The 6-electron interaction of lone electron pairs of heteroatoms provides a considerable contribution into destabilization of this state as well.[43,201] It has been suggested[157] that the pyramidal state might be stabilized due to vicinal $n_{\pi(O)}$–$\sigma^*_{N-O}$ interaction.

Configurational stability of acyclic compounds XN(OR)OR$^1$ (Table I) to a great extent depends on the nature of the substituent X. *N,N*-Dialkoxy-*N*-alkylamines **28** and *O*-alkyl-*N*-alkoxyhydroxylamines **58** have close values of inversion barriers. It is assumed[165] that the $n_N$–$\sigma^*_{C-R}$ interaction, stabilizing the planar transition state of inversion, affects the pyramidal stability of compounds with X = $CH_2R$, where R = OH, $Me_2N$, or $Me_3N^+$. The conjugation of dialkoxyamine nitrogen atom with carbonyl group leads to a considerable decrease of its configurational stability. Therefore low inversion barriers have been found for dialkoxyureas **36** (Table I). The restricted rotation around the $Me_2N$–CO bond ($\Delta G^{\neq}$ 13.3–14.5 kcal/mol) has been observed for these compounds as well.[140–202]

An extremely high configurational stability among acyclic nitrogen-containing compounds is expected for orthonitrites **35**, although it cannot be evaluated because of their low thermostability.[137] The pyramidal configuration of the nitrogen atoms was found in hydrazines **61**, which, however, undergo homolytic cleavage of N–N bond already at room temperature.

Configurational stability of the nitrogen pyramid increases when an ONO fragment is incorporated into the cycle because that destabilizes the planar inversion transition state to a great extent.[200] Thus, inversion barriers in isoxazolidines **1** ($\Delta G^{\neq}$ 26.9–29.3 kcal/mol)[43,58,73,74] are ca. 5 kcal/mol higher (all data are collected in ref 157) than in their acyclic analogues **28**. Anomalous low inversion barriers among isoxazolidines **1** ($E_a$ 14.6[203] and 16.1 kcal/mol[204]) were found for their 3,3-dinitro derivatives, which were interpreted[204] by the increase of the ground-state energy due to nonvalent interactions in *hem*-dinitro groups. Inversion barriers for 1,3,2-dioxazines **57b** (9.8 kcal/mol) and **59b** (21.9 kcal/mol) as well as 1,3,2-dioxazolidine **57a** (15.9 kcal/mol) have also been estimated.[164]

It is assumed[73,156,157,198,205,206] that the stereochemical properties of ONO systems are mainly caused by the existence of $n_{\pi(O)}$–$\sigma^*_{N-O}$ vicinal interaction. That is why such compounds adopt the most favorable for n–$\sigma^*$ overlapping geometry (anomeric effect[207]). They also display a tendency to populate the rotamers with a maximum number of gauche interactions between adjacent electron pairs and polar bonds ("gauche" effect[208]). In accordance with that, *O*-methyl-*N*-methoxyhydroxylamine **58a** exists[205] in the crystalline and gaseous state as well as in solution in (+sc, +sc) conformation (symmetry $C_2$) with dihedral angles CONO (Figure 1) of 78.7° (X-ray). A substantial shortening of the N–O bonds in **58a** (1.384 Å) in comparison, for instance, with MeONHMe (1.496 Å),[209] is considered to be the second geometrical consequence of n–$\sigma^*$ overlapping. It is interesting that ab initio calculations[210] of dihydroxylamine $(HO)_2NH$ predict an energy minimum for its (+ac, –ac) conformer.

The advantage of synclinical conformations around N–O bonds is preserved upon incorporation of one of these bonds into a 5-membered cycle. Thus, by NMR[46,55,58,61,71–73,75,105,203,204,211,212] and X-ray analysis[74,90b,156,157,197,201,213–216] it has been established that isoxazolidines **1** exist both in solution and in the crystalline state as anomers with a pseudoaxial orientation of *N*-alkoxy group. Isoxazolidine ring has the envelope type conformation. The values of dihedral angles CONO for *endo*- and *exo*-CON fragments equal to 65.5–79.4° and 81.4–98.8°, respectively. (Selected structural parameters of isoxazolidines **1** are collected in ref 157.)

**Table I. Inversion Barriers (kcal/mol) in XN(OR)OR$^1$ Compounds**

| X | R | R$^1$ | solvent | *T*, °C | $\Delta G^{\ddagger}$, T | ref |
|---|---|---|---|---|---|---|
| H | $^{i}$Bu | Me | toluene-$d_8$ | 25 | 20.4 | 165 |
| H | $^{i}$Bu | Et | toluene-$d_8$ | 25 | 20.0 | 165 |
| H | PhCH(Me)NHCOCMe$_2$ | Et | toluene-$d_8$ | 64 | 18.9 | 140 |
| $MeO_2CCMe_2$ | Et | Me | $Ph_2O$ | 20 | 23.6 | 28 |
| $MeO_2CCMe_2$ | $CF_3CH_2$ | Me | toluene-$d_8$ | 20 | 22.6 | 28 |
| $MeO_2CCMe_2$ | $^{i}$Pr | Me | $Ph_2O$ | 20 | 21.9 | 28 |
| $MeO_2CCMe_2$ | $HO(CH_2)_2$ | Me | $Ph_2O$ | 20 | 22.4 | 28 |
| $MeO_2CCH_2CMe_2$ | Et | Me | toluene-$d_8$ | 20 | 24.6 | 28 |
| $MeO_2CCH_2CMe_2$ | $^{i}$Pr | Me | $Ph_2O$ | 20 | 21.7 | 28 |
| $MeO_2CCH_2CMe_2$ | $PhCH_2$ | Me | $Ph_2O$ | 20 | 22.6 | 28 |
| $MeO_2CCH_2CMe_2$ | $PhCH_2$ | Me | MeOH | 20 | 23.5 | 28 |
| $(EtO_2C)_2CHCMe_2$ | $^{i}$Pr | Me | $Ph_2O$ | 20 | 22.2 | 28 |
| $HOCH_2$ | $PhCH_2$ | Me | DMSO-$d_6$ | 25 | 20.7 | 165 |
| $Me_2NCH_2$ | $PhCH_2$ | Me | DMSO-$d_6$ | 25 | 21.2 | 165 |
| $Me_3N^+CH_2$ | $PhCH_2$ | Me | DMSO-$d_6$ | 25 | 15.4 | 165 |
| $Me_2NCO$ | $^{i}$Bu | $CF_3CH_2$ | toluene-$d_8$ | 25 | 10.5 | 202 |
| $Me_2NCO$ | $CH_2{=}CHCH_2$ | $CF_3CH_2$ | toluene-$d_8$ | 25 | 9.8 | 202 |
| $Me_2NCO$ | PhCH(Me)NHCOCMe$_2$ | Et | toluene-$d_8$ | −30 | 12.8 | 140 |

**Figure 1.** Newman projections along N–O bonds of *O*-methyl-*N*-methoxyhydroxylamine (**58a**).

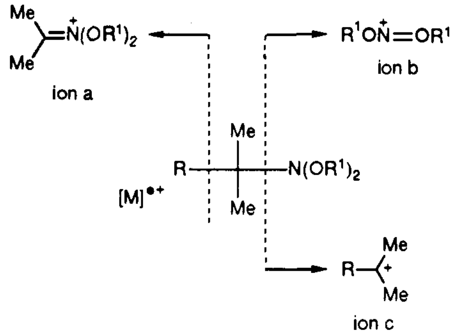
Conformation of ONO systems is greatly affected by steric effects. Thus, by NMR[217,218] and X-ray analysis[219] it has been shown that bicycles **15** have cis-fused rings with the R group equatorial to the 6-membered ring and pseudoaxial to the 5-membered ring. Such a geometry is favorable for effective $n_{\pi(O)}$–$\sigma^*_{N\text{-}O}$ interaction where the oxygen atom of the 5-membered ring acts as an n donor (the average value of dihedral angles CONO equals to 75.9°).[157] At the same time almost orthogonal orientation of $n_{\pi(O)}$ orbital of 6-membered ring and $\sigma^*_{N\text{-}O}$ orbital of the 5-membered ring (the average value of the angles between them equals to 88.6°)[157] actually excludes their overlapping. The consequences of that are the shortening of the N–O bond of the 5-membered ring in comparison with that one of the 6-membered ring and the selective cleavage of the latter bond in reactions (see section III.C.1) of bicycles **15** (kinetic anomeric effect).[156,157]

The structure of such bicycles containing isoxazolidine cycle as **9a**,[220] **12a**,[113] **16a**,[24] **17a**,[119] **18a**,[120] and **18b**[120] has been examined by X-ray analysis.

The conformational peculiarities of heterocycles with endocyclic ONO fragment have been studied in detail. It was established[198] that 1,3,2-dioxazine **67b**, both in the crystalline state and in solution, exists in a chair conformation and its N-substituent has equatorial orientation. Geometry is the same for the unsubstituted at nitrogen 1,3,2-dioxazine **59b** as well.[164] 1,3,2-Dioxazolidine ring of **59a**[164] adopts a curved envelope conformation. N–H proton is pseudoaxial oriented. The structure of bicyclic 1,3,2-dioxazolidines **20a**[221] and **24**[124] has been determined by X-ray analysis.

Tetramethoxyhydrazine **61a** in the crystalline state[206] has an unusual, for hydrazines, geometry with antiperiplanar orientation of nitrogen lone electron pairs. The orientation of the methoxy groups is characterized by the dihedral angles CONO equal to 108.1° and −131.7°, i.e. the conformation of CONOC fragments is close to (+ac, −ac). It is assumed that such a geometry is the most favorable for simultaneous realization of two stabilizing $n_{\pi(O)}$–$\sigma^*_{N\text{-}O}$ and $n_{\pi(O)}$–$\sigma^*_{N\text{-}N}$ interactions. The latter is thought to be responsible for the lengthening of the N–N bond in **61a** (1.484 Å) compared to that in $N_2H_4$ (1.446 Å).

**Scheme 27**



Cyclic hydrazine **63** exists in solution as a mixture of ee and ae isomers. Parameters ($k$ = 188.7 s$^{-1}$, $\Delta G^{\ddagger}$ = 11.3 kcal/mol) for interconversion of the latter (ae $\rightleftarrows$ ea) were determined by $^{13}$C NMR.[172]

## B. Spectral Properties

The decrease the p character of nitrogen lone electron pair in compounds with the ONO fragment (see sections III.B and IV.A) is reflected in their spectral properties as well. Thus, the first ionization potential of *O*-methyl-*N*-methoxyhydroxylamine **58a** (9.49 eV)[222] is much higher than that of, for instance, dimethylamine (8.93 eV).[223] In accordance with that, either the decrease of contribution or absence of amine-type fragmentation (Scheme 27, ion a) under the electron impact of acyclic **28**[224] and cyclic **67**[158,224] dialkoxyamines has been observed and attributed to a weak delocalizing ability of the dialkoxyamine nitrogen atom. In the mass spectra of these compounds ions b or c (depending on the type of R substituent) predominate. The amine-type fragmentation is not the main decomposition route under the electron impact of isoxazolidines **1a**[156] and **66**[158] as well. However, the heaviest ion in the mass spectra of bicycles **9** (R = $NO_2$) appears correct on $\alpha$-cleavage with nitro group elimination.[225,226]

The intensive absorption band at 1010–1060 cm$^{-1}$ in the IR spectra of **1** and **9** was attributed to the ONO fragment.[227]

## V. Optically Active Derivatives

ONO systems present one of those few types of compounds[228] which pyramidal stability (section III.A) is sufficient for their resolution into geometrical and optical isomers with an asymmetric nitrogen atom. It was experimentally proved for the first time in 1969 by Muller and Eschenmoser, who managed[43] to separate the diastereomers of isoxazolidine **1f**. The first optically active compounds of this type were also obtained from isoxazolidines **1**,[195] for which many of those classical methods of antipode resolution, which are developed for the compounds with a chiral carbon atom, can be applied. Thus, the enantiomer-differentiating amidation of isoxazolidines **1a**[74] and **1g**[195] by 1-ephydrine leads to unreacted **1a** and **1g** enriched by one of the antipodes. The crystallization of isoxazolidine **1g** tetraamide either from 1-methyl lactate or from a mixture 1-methyl lactate–$H_2O$ (3:5) gives either right- or left-rotating amides.[195] Heating of isoxazolidine **1a** diamide in 1-methyl lactate (100 °C, 6.5 h) followed by chiral solvent removal produces left-rotating diamide (the asymmetric reaction of nitrogen inversion).[229] Methanolysis of 2-chloroisoxazolidine (+)-**30** occurs with the retention of optical activity and leads to isoxazolidine (−)-(2*R*)-**1a**.[131,132] All these methods give the products only partially enriched by one of enantiomers. The complete separation of isoxazolidine **1a** bis(methylamide) into antipodes was accomplished via diastereomeric salts of (*S*)- and (*R*)-phenylethylamine with monoacids obtained from **1a**.[196,197] The optical purity of antipodes (100 and 93%) was determined by NMR using Eu(tfc)$_3$ as a chiral shift reagent, and the absolute configuration, by X-ray analysis of one of the diastereomeric salts.[197]

The possibility of the existence of optical isomers with asymmetric nitrogen atom in the open chain was first demonstrated[27] for resolution of dialkoxyamines **28d**[27,28] and **28e**[28,29] into antipodes. It has been carried out via diastereomeric salts of (*S*)- and (*R*)-phenylethylamine with corresponding acids obtained from **28d** and **28e**. However, these isomers undergo rapid racemization at room temperature ($t_{1/2}$ = 5.18 h, 20 °C, MeOH).[28]

Sufficiently high pyramidal stability ($\Delta G^{\ddagger}$ 18.9 kcal/mol) and considerably hindered exchange of NH proton provided the partial separation of diastereomers of compound **58b** by its single crystallization at normal conditions.[140] It is the first example of the separation of optical isomers with an asymmetric nitrogen atom in NH group. The complete resolution of diastereomers of this compound is possible, probably, only at low temperature, since its half-epimerization time equals to 8.5 s at 20 °C.

## VI. Application

Mutagenic activity has been found for some isoxazolidines **1**[230] and benzamides **37**.[142,143] Compounds **57**, **59**, and **67** can be used for prevention of photofading in colored materials.[231] **56** acts as an effective chemiluminescence energy transducing agent.[155]

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## VIII. References

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