ISSN 0027-1314, Moscow University Chemistry Bulletin, 2008, Vol. 63, No. 3, pp. 131–149. © Allerton Press, Inc., 2008.
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Acyclic Nitronic Esters: Generation and Utilization in the Synthesis of *N*- and *O*-Heterocycles

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Received September 20, 2007

Abstract—The literature concerning the chemistry of acyclic nitronic esters is surveyed and analyzed with special reference to tandem heterocyclization of unsaturated compounds with acyclic nitronic esters as 1,3-dipoles.

DOI: 10.3103/S0027131408030012

Nitronic esters (nitronates) are esters of unstable nitronic acids or aci forms of nitro compounds. The great variety and relative accessibility of nitro compounds makes it possible to prepare a wide range of nitronates for synthetic use. Due to the high and specific reactivity of nitronates, they are very important reagents for organic synthesis; they are successfully used as 1,3-dipoles in heterocyclic synthesis. This primarily refers to rather stable five- and six-membered cyclic nitronic esters, as well as to silyl nitronates, whose chemistry is comprehensively surveyed in [1–4].

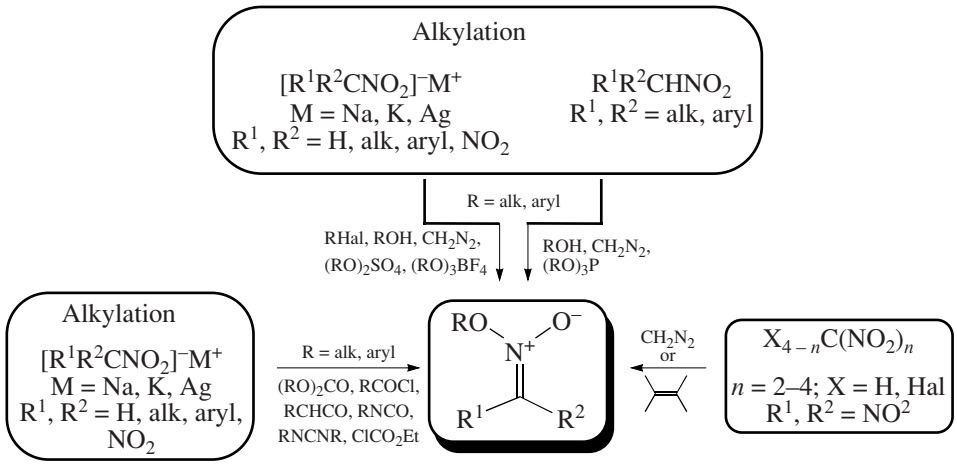
Acyclic nitronates have been known for more than one hundred years; before the 1960s, however, their reactivity was poorly studied, primarily because of their low stability. The feasibility of generation of nitronic O-esters in situ and their subsequent participation in [3 + 2] cycloaddition with alkenes was first demonstrated in 1964 [5]; this enhanced the development of the chemistry of acyclic nitronic esters.

An important stage of these investigations concerned reactions of polynitromethanes with unsaturated compounds. These reactions involve the in situ generation of unstable acyclic alkyl nitronates, which then add to alkenes as 1,3-dipoles. Investigations of this type of reaction resulted in the development of general and efficient syntheses of five-membered *N*- and *O*-heterocycles [5, 6].

Here, we review the literature on the chemistry of acyclic nitronic esters, including [3 + 2] cycloaddition reactions with unsaturated compounds published during the last decade with reference to a number of works that have not been cited in earlier reviews and monographs [1–4].

GENERATION OF ACYCLIC NITRONIC ESTERS

Acyclic nitronic esters are less studied than cyclic and silyl nitronates. Their synthesis methods can be represented by the following reactions (shown by scheme 1): alkylation of nitronate salts and nitroalkanes, acylation of nitronate salts, and polynitromethane-based syntheses.



Scheme 1.

None of the aforementioned methods is universal; each has some weaknesses, which will be discussed below. Synthetic approaches to alkyl and acyl nitronates based on nitroalkanes and their salts are covered by monographs and reviews [1–4] and works cited therein. Therefore, here we will mainly focus on the last studies in this field.

Alkylation of Nitronate Salts and Nitro Compounds

Alkylation of sodium, potassium, and silver nitronates, including polynitroalkane salts, is the best studied approach to the synthesis of nitronic esters [6–9]. The alkylating agents described include alkyl halides [10–15], trialkyl oxonium borofluorides [16, 17], alcohols [18, 19], dialkyl sulfates, and diazoalkanes [1, 2].

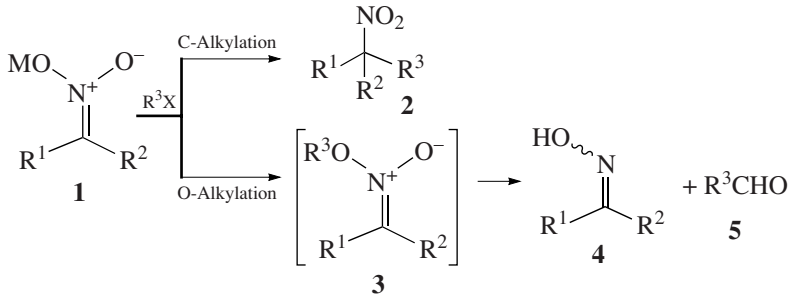
The synthetic weaknesses of this method are due to the possibility of both C- and O-alkylation of ambident nitronate anion **1** [3] (scheme 2). The ratio between the C- and O-alkylation products is determined by the following factors: the nature of the leaving group of the alkylating agent, the structures of the nitronate salt and alkylating agent, and the reaction parameters [1, 13–15, 20, 21]. Most O-alkylation products (nitronic esters **3**) are metastable and convert under the reaction conditions into a mixture of oximes **4** and carbonyl compounds **5** [1–3] (scheme 2).

Recent works [22, 23] are of interest in this context; they describe the synthesis of a set of stable enantiomerically pure alkyl nitronates **7–15** from sodium or potassium salts of chiral nitro ester **6** and alkyl halides (Table 1). The reaction is enantioselective and generates Z-isomers exclusively. The authors explain this fact by the considerable difference in the chemical surrounding of the two delocalized N–O bonds of the nitro groups.

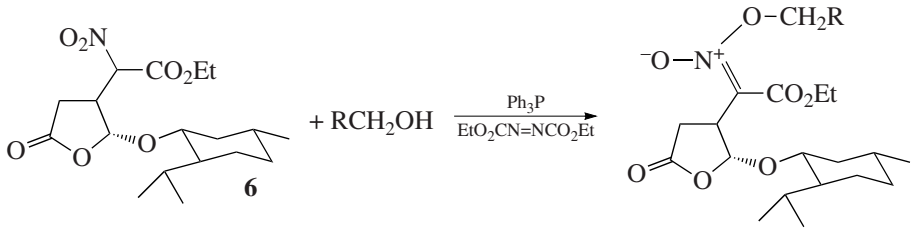
A later work [24] performed conformational analysis of compound **15** and its analogue with a *tert*-butyl substituent in the position 4 of cyclohexane fragment **16**. An alternative approach used in this work for their synthesis was based on the Mitsunobu reaction, in which nitro compound **6** is alkylated by an alcohol in the presence of triphenylphosphine and diethylazodicarboxylate (scheme 3).

This method had earlier been employed to synthesize nitronates of simpler structure [25–27]. Under the conditions of the Mitsunobu reaction, the hydroxy fragment of an alcohol molecule becomes a good leaving group, and nitronate yields are 30–85%. The limitation of the Mitsunobu reaction in nitronate synthesis is the need for a nitro compound to contain an α-proton with increased acidity.

Direct preparation of nitronic esters from nitroalkanes is also described. The most frequently used alkylating agents are diazomethane and diazoethane [1, 2, 10, 15, 28, 29], alkyl phosphites [30], and alcohols under the Mitsunobu reaction conditions [24]. The best known method for the generation of methyl and ethyl nitronates from nitroalkanes involves alkylation with diazomethane and diazoethane [31–36] (scheme 1).



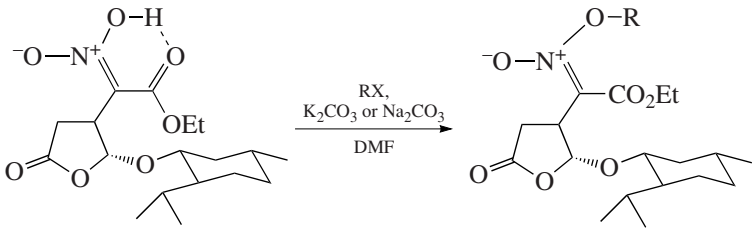
Scheme 2.



15: R = *c*-C_6H_{11}, 28%;
16: R = 4–*t*-Bu–*c*-C_6H_{10}, 10%

Scheme 3.

Table 1.



6 **7–15**

Nitronic ester	RX	Yield, %	Nitronic ester	RX	Yield, %
7	CH_3I	96	**12**	*n*-$C_9H_{19}Br$	72
8	C_2H_5I	96	**13**	*n*-$C_{12}H_{25}Br$	70
9	*n*-C_3H_7Br	85	**14**	*c*-C_5H_9Br	66
10	*n*-C_4H_9Br	74	**15**	*c*-C_6H_{11}	30
11	$C_6H_5CH_2Br$	86			

This reaction, as a rule, has high nitronate yields. This method has been widely used for nitroalkanes containing electron-acceptor groups. The limitations of this method, as for the Mitsunobu reaction, are due to the requirement of high acidity of the α proton in precursor nitro compounds.

Acylation of Nitronate Salts and Nitro Compounds

Various classical acylating agents, such as anhydrides, acid chlorides, and other, have been used to generate acyl nitronates from nitro compounds [37–45]. Nitroalkanes in these reactions are first converted into nitronate salts directly in the reaction mixture. Acylation of nitronates, unlike alkylation, occurs mainly at the oxygen atom. Acyl nitronates based on primary nitro compounds are labile and are detected either by their rearrangement products **19** and **20** (scheme 4, path **a**) or by isoxazolines or isoxazolidines generated in the presence of dipolarophiles (scheme 5) [3, 4]. Secondary nitro compounds yield more stable acyl derivatives, which can be isolated. Isomerization of acylated secondary nitro compounds **18** generates nitrosoacyloxy compounds **21** (scheme 4, path **b**).

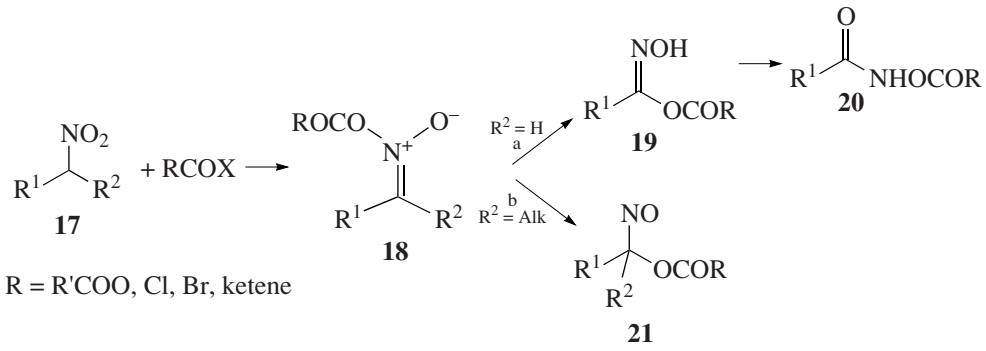
The only exception is the acylation product of secondary nitronate salt **22**: unstable nitronic ester **23** is cyclized into stable cyclic nitronate **24** due to the free hydroxy group in molecule **22** [46] (scheme 6).

In the presence of alkenes or alkynes, acyl nitronate **18** enters the [3 + 2] cycloaddition reaction to yield unstable N-acyl heterocycles like **25** and **28**, which convert to isoxazoline **26** or isoxazol **29**, respectively, under the reaction conditions [44] (scheme 5).

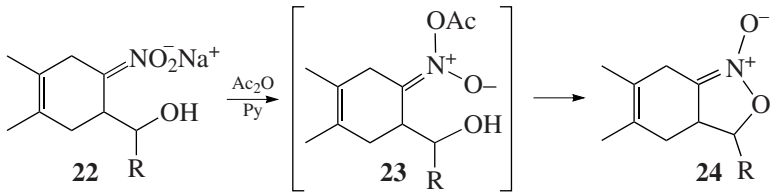
Other researchers [4, 38] believe that nitronate **18** is first rearranged into nitrile oxide **27**, which then reacts, as a 1,3-dipole, with unsaturated compounds.

Given that there is a double bond in a nitro compound molecule, nitronate acylation can be followed by intramolecular [3 + 2] cycloaddition, as demonstrated for nitronate **30** [47]. Analogous cyclization occurs during treatment of nitronate **30** first with HBr and then with triethylamine; in both cases, isoxazol **31** is generated in 80% yield (scheme 7).

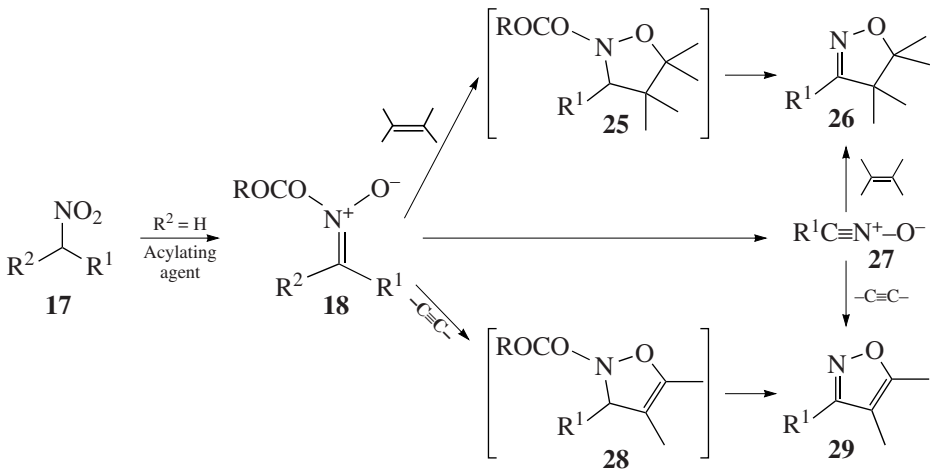
Examples of syntheses of nitronic esters from nitroalkenes and ketones are also described [48, 49]. Acyl nitronates **32** were generated by treatment of a mixture of nitroalkene and lithium enolate ketone with



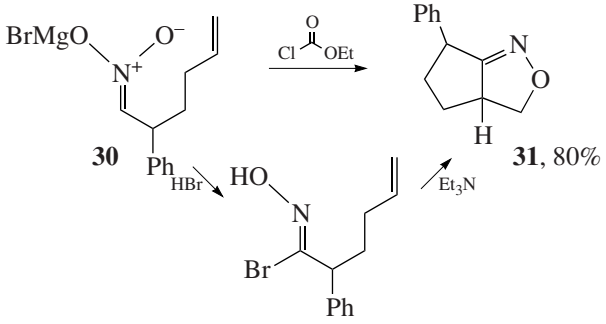
Scheme 4.



Scheme 5.



Scheme 6.



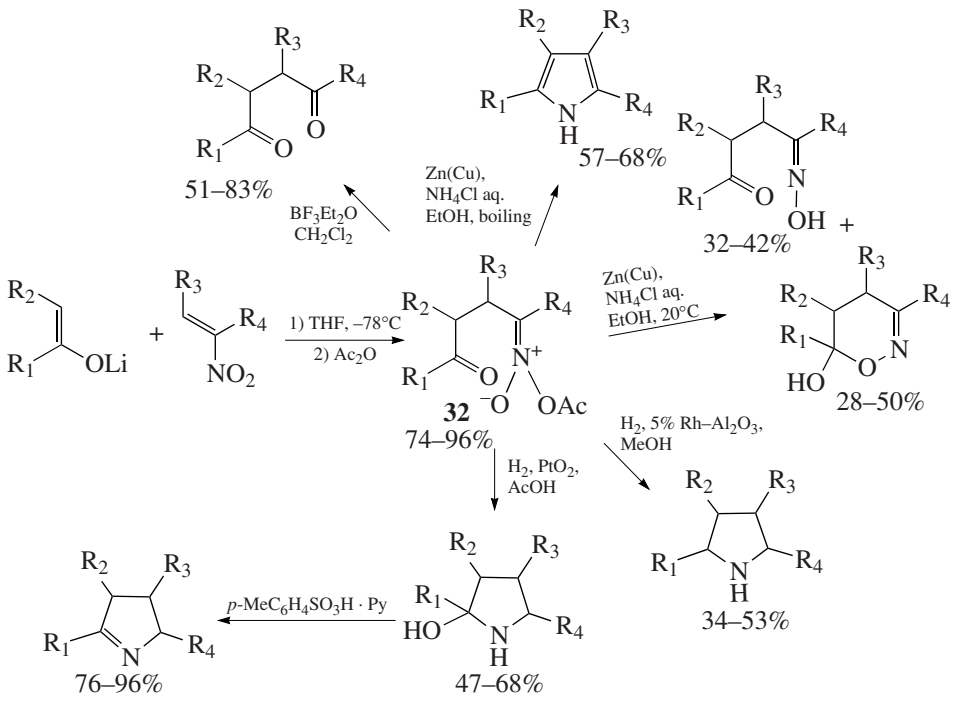
Scheme 7.

aceticanhydride (scheme 8). A large set of nitronates that contained a ketone functionality in the γ position of nitronate **32** were generated from various combinations of ketones and nitroalkenes. These γ-ketonitronic anhydrides are relatively stable: their solutions in hexane or ethyl acetate can be stored at reduced temperatures for a long time; many of them are isolated by preparative column chromatography. The spectrum of possible conversions of nitronates **32** is very wide; they can be used to prepare 1,4-diketones, monooximes, N- and O-heterocycles (alkylpyrrols, dihydro-1,2-oxazines, 2,5-dialkylpyrrolidines, and 2-hydroxypyrrolidines) [48, 49] (scheme 8). A possibility of acyl nitronate generation as a result of the intramolecular rearrangement of 2-nitroindenone ester **33** was discovered in an attempt to acylate it [50]. Treatment of nitro compound **33** with a base (triethyl-amine or pyridine) at room temperature generates acetyl nitronate **34** in quantitative yield (scheme 9).

We should note that an attempt to carry out similar intramolecular alkylation on other substrates failed. For example, when methyl derivative **33** was treated with a base, the double bond migrated without generating nitronic ester (scheme 9).

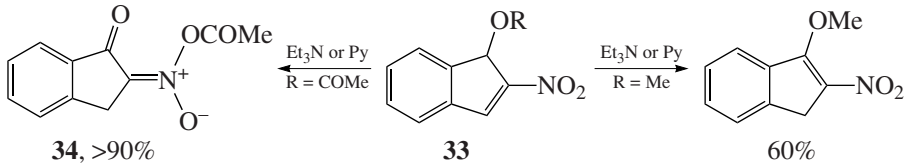
REACTIVITY OF NITRONIC ESTERS

Recall that acyclic nitronic esters are unstable compounds and decompose in a period of several minutes to



R_1 = Me, Pr, Bu, Hex; R_2 = Me, Et; $R_1 = R_2 = -(CH_2)_3-$; R_3 = H, Me; R_4 = Me, Et, Bu

Scheme 8.



Scheme 9.

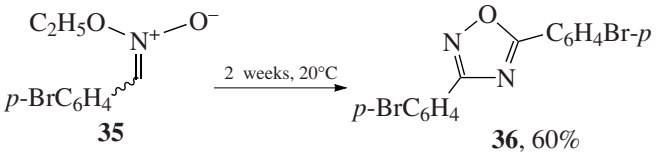
several days at room temperature [2]. The major decomposition products of alkyl and acyl nitronates **3** are oximes **4** and carbonyl compounds **5**; this makes it possible to employ this reaction to prepare oximes, aldehydes, and ketones [1–3, 54–56] (scheme 2).

In some cases, more complex products can form; for example, *p*-bromophenylnitromethane ethyl nitronate **35** generates oxadiazol **36** during storage [15] (scheme 10).

In general, alkyl nitronates synthesized on the base of primary nitroalkanes have higher stability than those based on secondary nitro compounds. For example, 1-nitrobutane ethyl ester completely decomposes in 3 days at room temperature, whereas 2-nitropropane ethyl ester cannot be isolated in an individual state [15]. For acyl nitronates, the opposite tendency is observed: more substituted nitronates are more stable than acyl nitronates prepared from primary nitro compounds [1, 3].

We can find only a few examples of relatively stable alkyl nitronates that can be stored for one or several weeks (Table 2). Chemical transformations of alkyl nitronates induced by various reagents are considered in detail in monographs [1–4]. In particular, heating nitronates in the presence of reducing agents generates aldehydes of ketones. Hydrolysis to the precursor nitroalkanes is not characteristic of alkyl nitronates, unlike silyl nitronates. Concentrated sulfuric acid converts alkyl nitronates into hydroxamic acids; hydrochloric acid treatment gives rise to hydroxamic acid chlorides. Nitronic esters based on primary α-nitroketones, ethyl nitroacetates, and phenylsulfonylnitromethane enter the alkoxy group elimination reaction and generate nitrile oxides in the presence of TsOH. Hydrogen iodide converts alkyl nitronates into oximes; catalytic reduction over platinum yields amines [1–4].

The ability of nitronic esters to participate in [3 + 2] cycloaddition with unsaturated compounds is of the greatest interest; these reactions will be considered in the following section.



Scheme 10.

Reactions of Acyclic Nitronates with Alkenes

The first report on the feasibility of using nitronic esters as 1,3-dipoles in [3 + 2] cycloaddition reactions with alkenes dates to 1964 [5]. In that work and [28, 34, 57], it was demonstrated that reactions between alkyl nitronates and alkenes yield N-alkoxyisoxazolidines. More recently [29, 35], various alkyl nitronates and a large set of unsaturated compounds were studied in these reactions. The reactions occur under mild conditions and generate 5-substituted isoxazolidines in good yield (Table 3).

It was shown for O-methyl α-nitroacetate esters [28] that 1,3-dipolar cycloaddition to activated alkenes, i.e., alkenes containing electron-acceptor substituents (R' = COOMe, CN, or COMe), occurs at higher rates than to other olefins (R' = Ph or CH_2Cl). Nitronates of arylnitromethanes (R = Ar) are less reactive in 1,3-dipolar cycloaddition than α-nitroacetate ester based nitronates (R = COOAlk). The only dipolarophiles for them are activated alkenes with electron-acceptor substituents [5, 36].

Inasmuch as the rate of nitronic ester cycloaddition to alkenes is virtually independent of the solvent, a medium suitable for alkylation of nitro compounds can be used (the alkylation stage is most sensitive to the nature of the solvent). Benzene, ethyl acetate, tetrahydrofuran, diethyl ether, methylene chloride, and chloroform are the most frequently used solvents [36].

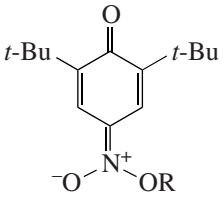
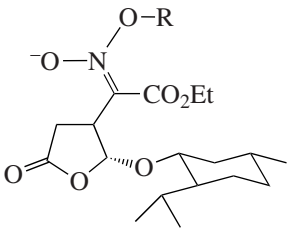
Reactions of Alkyl Nitronates with Dienes

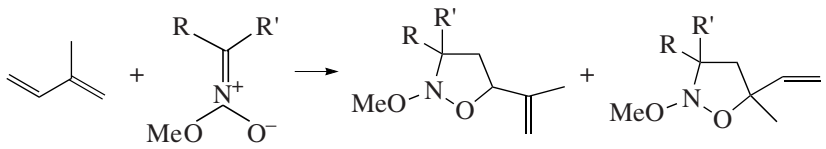
In reactions of nitronic esters with conjugate dienes, cycloaddition occurs at one of the multiple bonds of the unsaturated compound. Nonsymmetrical dienes, for example, usually generate two isomeric isoxazolidines **59a**, **59b** and **60a**, **60b** [58] (scheme 11).

If one multiple bond in diene is not terminal, however, its reaction with a 1,3-dipole occurs selectively and generates adduct **61** exclusively at the terminal double bond [58] (scheme 12).

In the course of this reaction, partial degradation of isoxazolidine **61** was observed with elimination of methanol, and by-product isoxazoline **62** was formed. Isoxazolidine **61** can be completely converted into isoxazoline **62** with the use of boron trifluoride etherate [58].

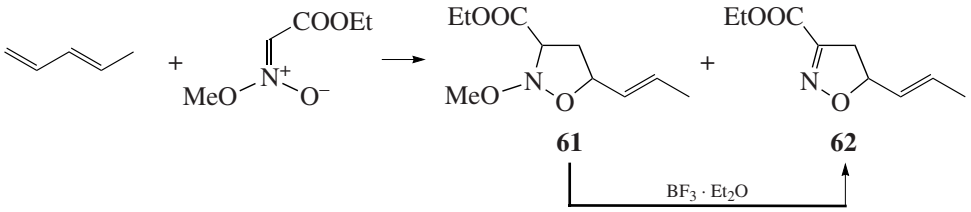
Table 2

Compound no.	Nitronic ester	Half-life period	Source
37	4-$BrC_6H_4CH{=}NO_2CH_3$ (*trans*)	2 weeks	[2]
38	4-$O_2NC_6H_4CH{=}NO_2CH_3$ (*cis*, *trans*)	Several weeks	[2]
39	$C_6H_5N_2CH{=}NO_2CH_3$	1 week	[2]
40	4-$O_2NC_6H_4CH{=}NO_2C_2H_5$ (*trans*)	2 weeks	[2]
41–46	 R = Me, Et, *i*-Pr, $CH_3CH(OH)(CH_2)_2$, $HO(CH_2)_5CH_2$, $PhCH_2$	Several months	[24, 27, 29, 30]
7–16	 R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, $C_6H_5CH_2$, *n*-C_9H_{19}, *n*-$C_{12}H_{25}$, *c*-C_5H_9, *c*-C_6H_{11}	Several months	[22, 23]



59: R = COOMe, R' = COOMe: **59a, 60a** **59b, 60b**
60: R = COOEt, R' = H
a:**b** = 2 : 1

Scheme 11.



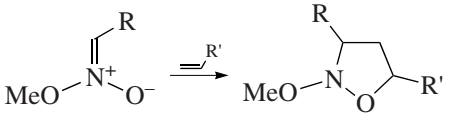
Scheme 12.

Reactions of Alkyl Nitronates with Alkynes

The reaction of nitronic ester **63** with vinylacetylene (the simplest conjugate enyne) was studied for comparing the reactivities of double and triple bonds with respect to alkyl nitronates. Cycloaddition occurs at the enyne double bond exclusively and generates N-methoxy-3-carbethoxy-5-ethynylisoxazolidine **64**; this signifies the lower reactivity of triple bonds compared to double bonds in [3 + 2] cycloaddition with nitronates [58] (scheme 13). Several examples of reactions of acyclic nitronic esters with acetylenes generating N-alkoxyaziridines **66–78** are described in the literature. Presumably, these compounds are generated as a result of the isomerization of the initially formed isoxazolines **65** (Table 4).

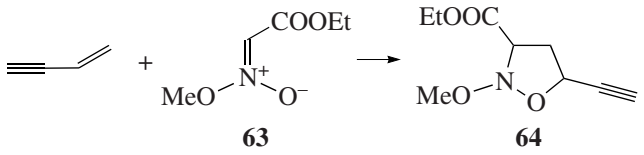
Several alternative mechanisms have been proposed to explain aziridine generation in these reactions: ionic [62], radical, and sigmatropic [63] mechanisms, each suggesting the rearrangement of 4-isoxazoline **65** generated at the first stage (scheme 14). The ionic or radical

Table 3.



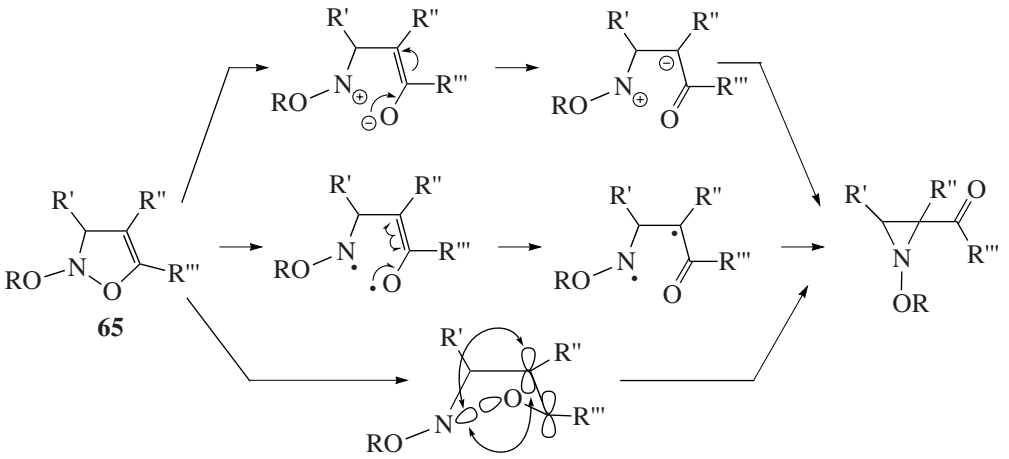
47–58

Isoxazolidine	R	R'	Reaction time, days	Yield, %	Source
47	COOEt	Ph	3	65	[28]
48	COOEt	CH_2Cl	3	76	[28]
49	COOEt	COOMe	1	90	[28]
50	COOEt	COMe	1	78	[28]
51	COOEt	CN	1	76	[28]
52	COOMe	COOMe	1.5	74	[28]
53	Ph	COOMe	4	34	[57]
54	Ph	CN	–	–	[5]
55	4-$NO_2C_4H_6$	COOMe	7	53	[35]
56	4-$NO_2C_4H_6$	COMe	1	24	[35]
57	4-$NO_2C_4H_6$	CN	5	34	[35]
58	4-$OMeC_4H_6$	COOMe	7	38	[35]



63 **64**

Scheme 13.

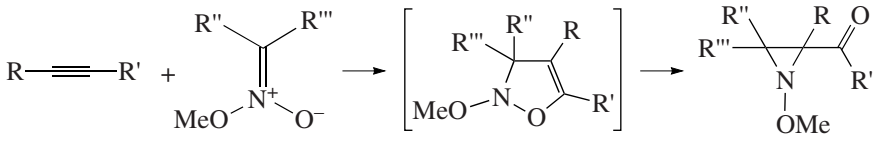


65

Scheme 14.

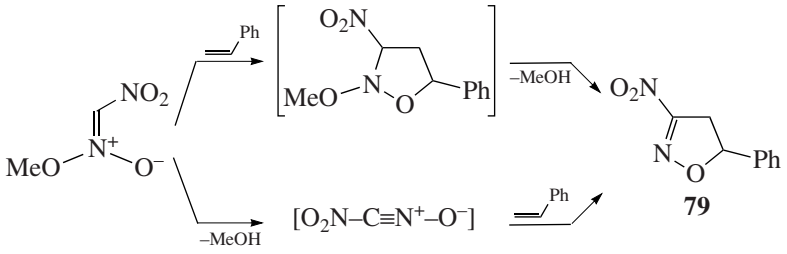
mechanism of aziridine generation was suggested because the N–O bond in the heterocycle can readily open under the reaction conditions, generating rearrangement products [63, 65]. However, the high stereoselectivity of the reaction excludes an acyclic transition state, which would have generated a great number of isomers because of the possibility of free rotation around the C–N bond. Therefore, the mechanism including 1,3-sigmatropic shift better matches the observations.

Table 4.

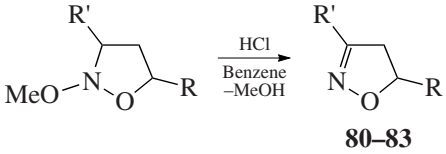


65 **66–78**

Aziridine	R	R'	R"	R"'	Yield, %	Source
66	H	COMe	COOEt	H	82	[59, 60]
67	H	COOMe	COOEt	H	74	[59, 60]
68	H	COOMe	COOMe	H	79	[64]
69	H	Ph	COOEt	H	46	[59, 60]
70	H	CH_2Cl	COOEt	H	55	[59, 60]
71	H	CH_2OH	COOEt	H	52	[59, 60]
72	H	COOMe	COOMe	COOMe	39	[59, 60]
73	Me	COOMe	COOEt	H	15	[60]
74	H	COPh	CN	H	62	[63, 64]
75	H	COPh	COOMe	H	100	[63, 64]
76	H	COMe	CN	H	76	[63, 64]
77	H	COMe	COOMe	H	100	[63, 64]
78	H	COOMe	CN	H	–	[63, 64]

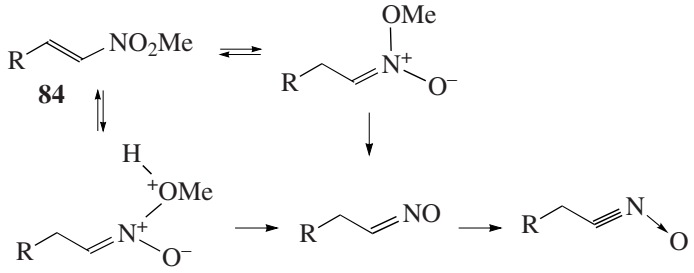


Scheme 15.



80: R = Ph, R' = COOEt, 98%;
81: R = CH_2Cl, R' = COOEt, 100%;
82: R = COOMe, R' = Ph, 39%;
83: R = COOMe, R' = NO_2, 48%.

Scheme 16.



Scheme 17.

Nitronates as Synthetic Equivalents of Nitrile Oxides

The β-elimination of alcohol is characteristic of *N*-alkoxyisoxazolidines, resulting in 2-isoxazolines [28, 34, 35, 66, 67]. This reaction occurs due to the dissociation of a relatively weak exocyclic N–O bond (53 kcal/mol [3]) in heterocycles; it can occur spontaneously, under heating, or be induced by electrophilic agents. Dilute mineral acids also facilitate the generation of 2-isoxazolines **79**–**83** from *N*-alkoxyisoxazolidines (schemes 15, 16). The alternative route to isoxazoline **79** involves the generation of nitrile oxide from nitronate and its addition to an alkene molecule [66]. The scheme proposed in [39] for nitrile oxide generation from nitronic esters involves the protonation of nitronate **84** with subsequent elimination of methanol (scheme 17).

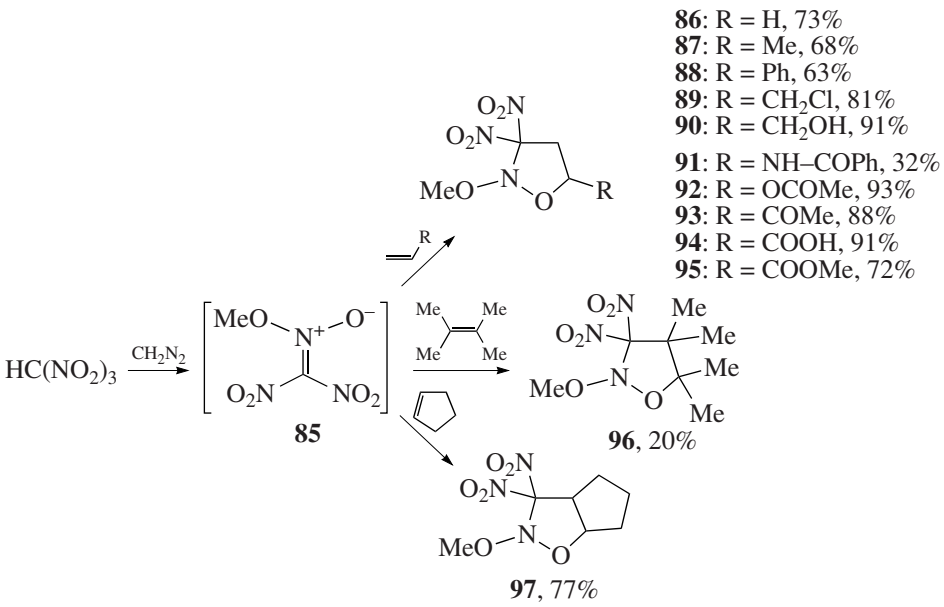
Thus, 2-isoxazolines **79**–**83** can be generated by either the [3 + 2] cycloaddition of nitronates to alkenes followed by the β-elimination of an alcohol molecule or the reaction of alkenes with nitrile oxides. In this case, nitronates can be regarded as synthetic equivalents of nitrile oxides.

ALKYL NITRONATES GENERATED FROM POLYNITROMETHANES

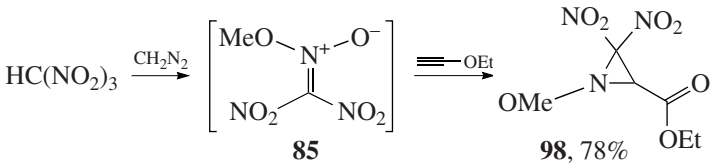
Nitronic esters generated from polynitromethanes in their reactions with diazoalkanes or alkenes are unstable and cannot be isolated from the reaction mixture. The existence of dinitronitronates can only be judged from the products of their reaction with olefins; therefore, 1,3-cycloaddition offers a reliable way to fix unstable polynitromethane nitronic O-esters [1–4].

Alkyl Nitronates Based on Polynitromethanes and Diazoalkanes

Data on the generation of nitronic esters based on polynitro compounds appeared in the middle 1960s. It was demonstrated [5, 16] that the reaction of diazomethane with nitroform generates O-methyl trinitromethane ester **85**, which cannot be isolated in an



Scheme 18.



Scheme 19.

individual form because it vigorously decomposes in attempts to remove the solvent. Inasmuch as nitronate **85** is stable only in solutions at temperatures below 10°C, it was generated in situ with subsequent olefin addition. *N*-methoxy-3,3-dinitroisoxazolidines **86–97** were obtained in all cases. For monosubstituted alkenes, the reaction with nitronate **85** has high regioselectivity and produces only one of the two possible regioisomers, namely, 5-substituted isoxazolidines (scheme 18).

The low yield of isoxazolidine **96** was explained in [16] by steric hindrances created by the four methyl groups of the dipolarophile. Steric factors can also explain the fact that nitronic ester **85** does not react with stilbene, methyl cinnamate, dimethyl fumarate, and dimethyl maleate [16].

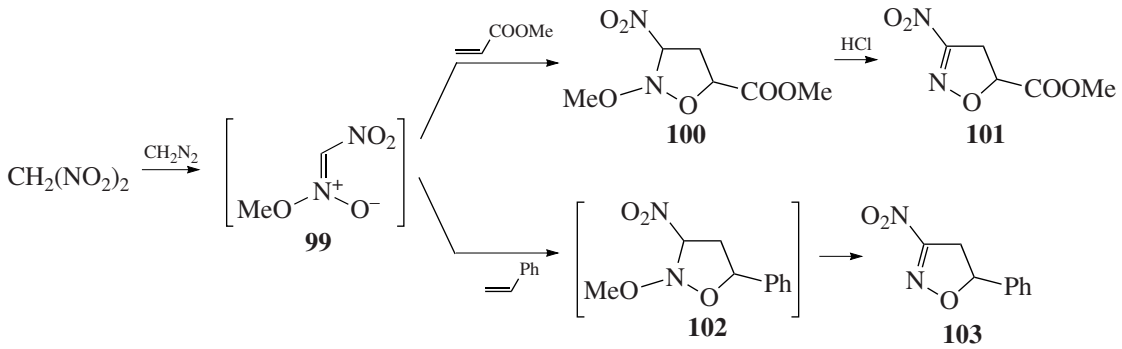
It was demonstrated recently that the reaction in the presence of ethoxyacetylene produces *N*-methoxy-2,2-dinitroaziridine **98** in high yield instead of isoxazolidine [68] (scheme 19). The mechanism of the reaction between O-methyl trinitromethane ester and acetylenes is an analogue of that described above for alkyl nitronates [63].

The reaction of dinitromethane with diazomethane also generates unstable nitronic ester **99**; then, the latter reacts with methyl acrylate to generate *N*-methoxy-3-nitroisoxazolidine **100** [66] (scheme 20).

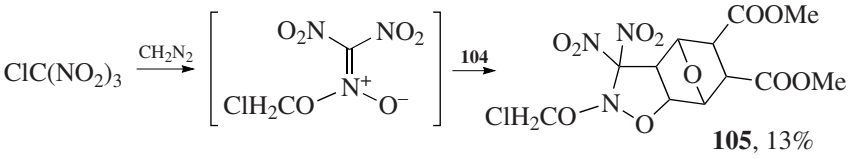
In the reaction of nitronate **99** with styrene, isoxazoline **103** was isolated instead of expected isoxazolidine **102**; its generation can result from the spontaneous β-elimination of methanol under the reaction conditions. Isoxazolidine **100** can be converted into isoxazoline **101** only by gaseous HCl [66].

Nitromethane O-esters can also be generated from halotrinitromethanes by alkylation with diazomethane. The resulting nitronates are unstable and have not been isolated in an individual form; however, when generated in situ, they enter 1,3-dipolar cycloaddition reactions with dipolarophiles, e.g., with dimethyl 7-oxabicyclo[2.2.1]heptenedicarboxylate **104** [69]. The reaction with chlorotrinitromethane produces *N*-chloromethoxyisoxazolidine **105** in 13% yield (scheme 21).

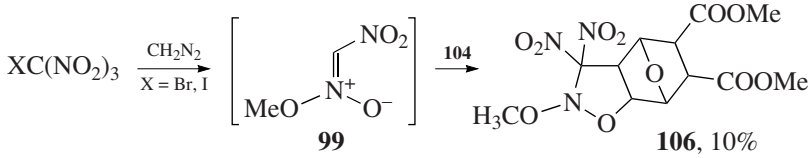
In the reactions of bromo- and iodotrinitromethanes, isoxazolidine **106** (the product of cycloaddition of nitronic ester **99** to unsaturated diether **104**) was isolated in 10% yield instead of halomethoxy derivatives [69] (scheme 22).



Scheme 20.



Scheme 21.



Scheme 22.

Apparently, the halogen atom of bromo- and iodotrinitromethanes is readily exchanged for the diazomethane hydrogen atom. This generates nitroform, which reacts with a second diazomethane molecule to generate nitronate **99**, and the latter enters the [3 + 2] cycloaddition reaction with diester **104**.

Alkyl Nitronates Based on the Reaction of Tetranitromethane or Halotrinitromethanes with Alkenes

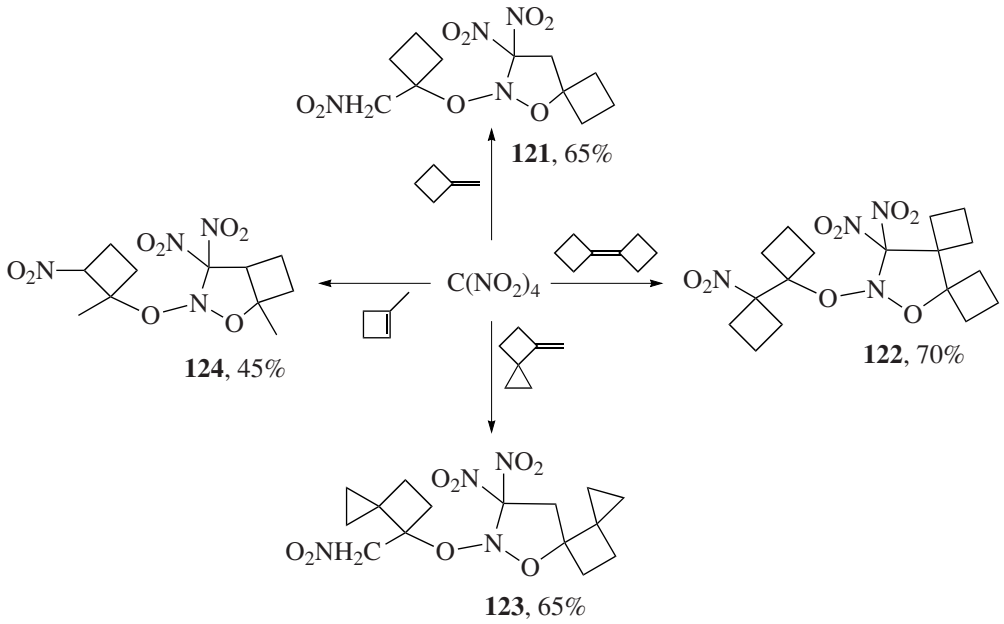
The main rules governing the reactions of tetranitromethane or halotrinitromethanes with alkenes were established in the 1970s [70–80]. These studies postulate nitronic ester generation as the key stage in alkene heterocyclization by tetranitromethane or halotrinitromethanes. The reaction of polynitromethanes with the first alkene molecule generates nitronic ester **N**, which then enters the [3 + 2] cycloaddition reaction with a second alkene molecule, producing isoxazolidine. Alkenes with electron-donor substituents mostly enter such reactions. The results are compiled in Table 5.

This specific reactivity of tetranitromethane and halotrinitromethanes with alkenes makes these reactions convenient for the synthesis of a number of *N*- and *O*-heterocyclic compounds. Frequently, this is the only possible approach to target heterocyclic compounds (see reviews [1–4] and the references cited therein).

A cycle of studies of the tandem heterocyclization of unsaturated compounds caused by polynitromethane reagents [68, 81–88] was a new stage in the development of the chemistry of acyclic nitronates. Unusual alkenes—strained polycyclic olefins with small cycles having unusual reactivity—were studied in reactions with tetranitromethane and its derivatives [85]. For example, alkenecyclobutanes containing an exo- or endocyclic double bond of various degrees of substitution under the action of tetranitromethane generate 3,3-dinitroisoxazolidines **121**–**124** of the cyclobutane series with sufficient yields (scheme 23).

Methylenecyclobutanes and cyclobutene react with tetranitromethane regioselectively to yield 5-substituted isoxazolidines **121**–**124** exclusively.

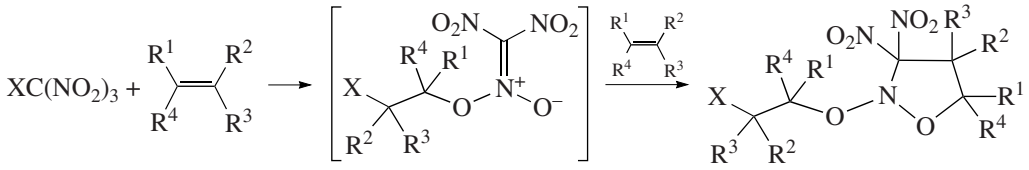
Methylenecyclopropanes, unlike methylenecyclobutanes, do not yield identifiable products with tetranitromethane because of their tendency to polymerize under the reaction conditions.



Scheme 23.

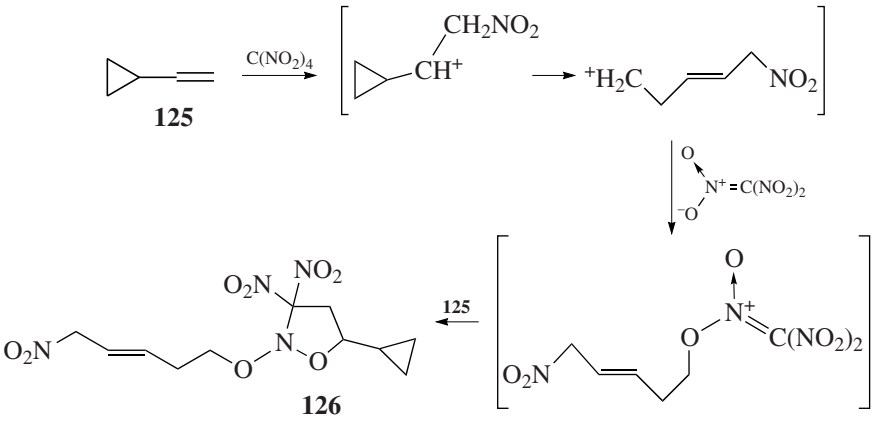
The reactions of tetranitromethane with vinylcyclopropanes of various degrees of substitution at the double bond were studied in [84]. Tetranitromethane was shown to react with two equivalents of vinylcyclopropane **125** through a nitronic ester intermediate and subsequent 1,3-dipolar addition of a second olefin molecule. The specific feature of this reaction is the homoallyl-type opening of the three-member ring in the process of nitronic ester generation, which leads to unsaturated cyclopropane isoxazolidine **126** (scheme 24).

Table 5.

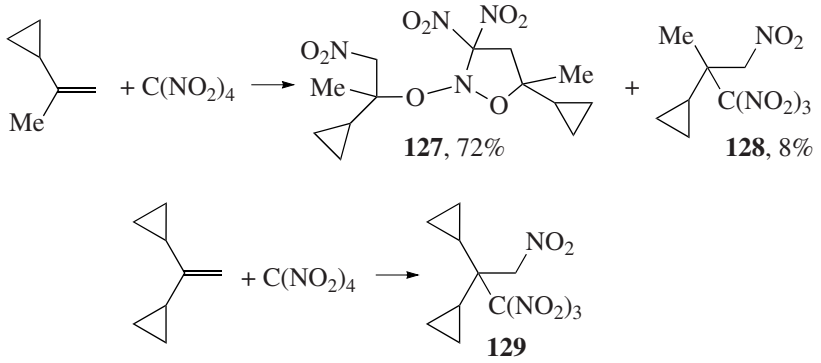


N **107–120**

Isoxazolidine	X	R^1	R^2	R^3	R^4	Yield, %	Source
107	I	H	H	H	H	71	[72]
108		Me	Me	H	H	82	[72]
109		$SiMe_3$	H	H	H	92	[73]
110		$-(CH_2)_4-$		H	H	–	[71, 74]
111	Br	H	Me	Me	H	61	[75]
112		$-(CH_2)_4-$		Me	H	45	[75]
113	NO_2	Ph	H	H	H	60	[76]
114		OEt	H	H	H	55	[77]
115		OCOMe	H	H	H	65	[77]
116		CH_2OPh	H	H	H	17	[77]
117		CH_2OCOMe	H	H	H	15	[77]
118		$CH{=}CH_2$	H	H	H	74	[78]
119		$CH{=}CH_2$	H	Me	H	66	[79]
120		Ph	H	Me	H	83	[80]



Scheme 24.



Scheme 25.

Substitution at the double bond in a vinylcyclopropane molecule gives rise to competition between the C- and O-alkylation of the nitrocarbocation generated at the first stage: in the case of methylcyclopropylethylene, isoxazolidine **127** is the major product, whereas the reaction of 1,1-dicyclopropylethylene with tetranitromethane exclusively produces 2,2-dicyclopropyl-1,1,1-trinitro-3-nitropropane **129** in 80% yield [84] (scheme 25).

Thus, the study of tetranitromethane in reactions with small-ring alkenes showed that cyclobutane olefins, regardless of their structure, generate spirocyclobutanedinitroisoxazolidines. Cyclopropane-substituted olefins in their reactions with tetranitromethane yield isoxazolidines, tetranitroalkanes, or rearrangement products, depending on their structure [84, 85]. We should mention that introduction of certain substituents makes it possible to intentionally perform either heterocyclization (O-alkylation) or tetranitromethane addition at a multiple bond (C-alkylation).

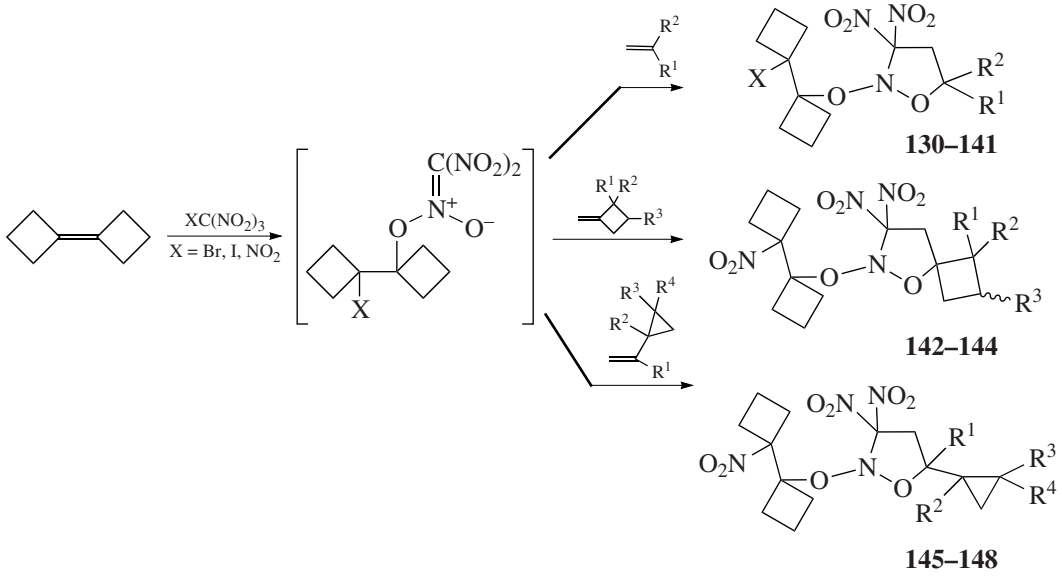
Three-Component Reactions of Tetranitromethane and Halotrinitromethanes with Unsaturated Compounds

Isoxazolidine generation is a tandem reaction and can be represented as a sequence of two stages. The first stage is the generation of nitronic ester, which is a 1,3-dipole. The second stage is [3 + 2] cycloaddition of nitronic ester to olefin with heterocycle formation. Because alkene should satisfy different steric and electronic requirements at the first and second heterocyclization stages, it is possible to make the reaction of tetranitromethane with olefins more universal by using different alkenes at the nitronic ester generation and cycloaddition stages [76–80, 82, 83, 89–95].

A fundamental possibility of generating mixed-structure isoxazolidines was demonstrated for the reaction of 1-phenylcyclohexene with tetranitromethane in another sterically unhindered alkene taken in a tenfold excess [96]. For preparative practice, however, this approach is unpromising.

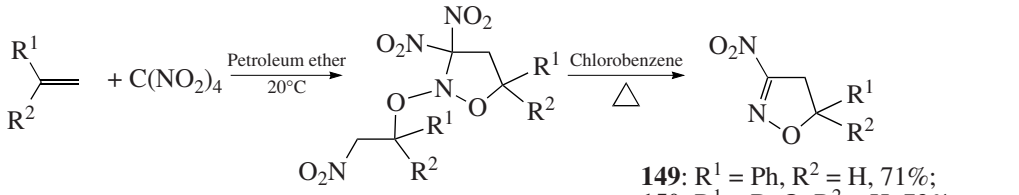
Three-component heterocyclization reactions induced by tetranitromethane or halotrinitromethanes

Table 6.



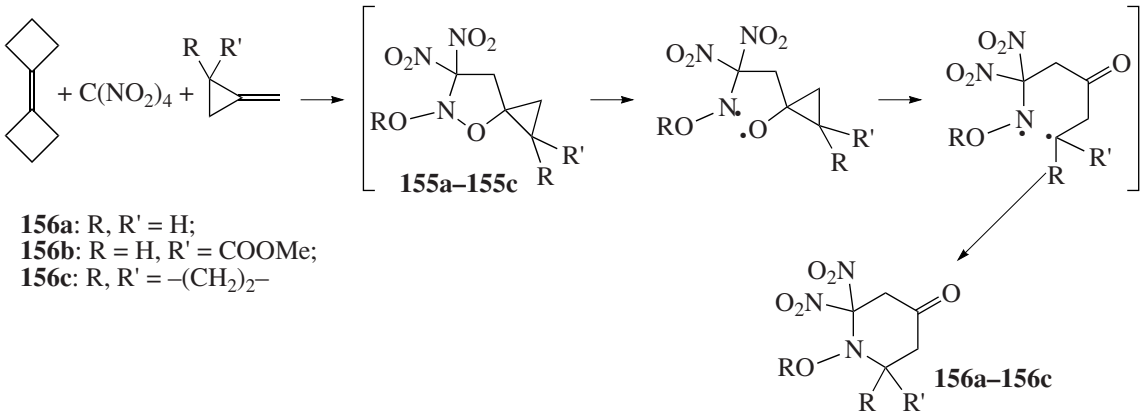
Isoxazolidine	X	R^1	R^2	R^3	R^4	Yield, %	Source
130	Br	$-(CH_2)_3-$		–	–	46	[81, 82]
131		$-CH_2CH(CN)CH_2-$		–	–	75	[81, 82]
132		H	COMe	–	–	40	[81, 82]
133		H	CN	–	–	47	[81, 82]
134		H	$CH(OEt)_2$	–	–	56	[81, 82]
135	I	$-(CH_2)_3-$		–	–	67	[82]
136		$-CH_2CH(CN)CH_2-$		–	–	–	[82]
137	NO_2	CN	H	–	–	56	[83, 88]
138		Me	COOMe	–	–	59	[83, 88]
139		$(EtO)_2CH$	H	–	–	52	[83, 88]
140		Ph	H	–	–	50	[83, 88]
141		Py	H	–	–	24	[83, 88]
142		H	H	H	–	46	[83, 88]
143		H	H	CN	–	66	[88]
144		$-(CH_2)_2-$		H	–	67	[88]
145		H	H	H	H	65	[88]
146		▷	H	H	H	25	[88]
147		H	H	COOEt	COOEt	43	[88]
148		Me	$CH_2{=}CH{-}CH_2-$	H	H	33	[88]

were studied for a wide range of alkenes in the mixed interaction version with the equimolar reagent ratio [81–83, 88]; as a result, a general one-pot preparative synthesis was developed for highly functionalized mixed-structure 3,3-dinitroisoxazolidines **130–148**. Tri- and tetrasubstituted alkenes with a nucleophilic double bond were used for generating nitronic esters: they readily react with polynitro compounds, but are poor 1,3-dipolarophiles; a wide range of alkenes containing electron-acceptor, donor, aromatic, and heterocyclic substituents were used as the second component at the [3 + 2] cycloaddition stage (Table 6). In [81–83, 88], the main laws and applicability of three-component heterocyclization reactions were determined with all three reagents being varied. Isoxazolidine generation occurs with high regioselectivity and, in some cases, diastereoselectivity [97, 98].



149: R^1 = Ph, R^2 = H, 71%;
150: R^1 = BuO, R^2 = H, 73%;
151: R^1, R^2 = –$(CH_2)_5$–, 74%;
152: R^1 = $OCOCH_3$, R^2 = H, 72%.

Scheme 26.



156a: R, R' = H;
156b: R = H, R' = COOMe;
156c: R, R' = –$(CH_2)_2$–

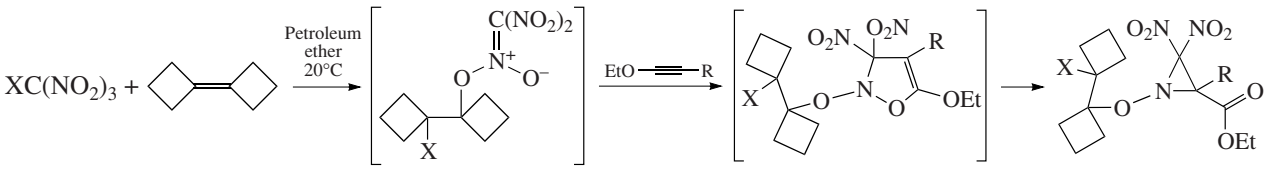
Scheme 27.

We should mention that iodoisoxazolidines **135** and **136**, which are generated in three-component one-pot reactions of iodotrinitromethane with bicyclobutylidene and methylenecyclobutanes, undergo spontaneous β-elimination to produce nitroisoxazolines [82]. A new approach to the synthesis of nitroisoxazolidines **149**–**152** was proposed on the basis of thermal β-elimination of *N*-alkoxy-3,3-dinitroisoxazolidines in chlorobenzene [86] (scheme 26).

The reaction of nitronic esters generated from bromotrinitromethane and alkynes, as for trinitromethane, does not generate halodinitroisoxazols; rather, it produces their rearrangement products, namely, *gem*-dinitroaziridines **153** and **154** [68] (Table 7).

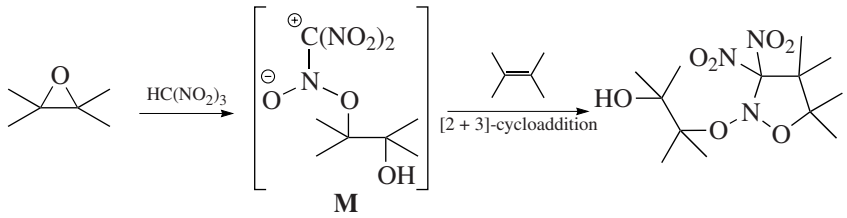
With the use of methylenecyclopropanes as dipolarophiles, three-component heterocyclization reactions produce, instead of expected spirocyclopropane-containing isoxazolidines, their rearrangement products (*gem*-dinitropiperidones **156a**–**156c**) [87] (scheme 27).

Table 7.

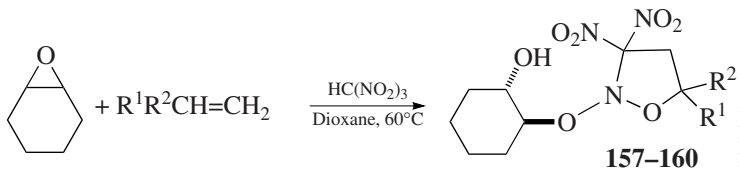


153a, 153b; 154a, 154b

Aziridine	X	R	Diastereomer excess	Yield, %
153a	NO_2	H	6 : 1	86
153b	NO_2	Et	3 : 1	18
154a	Br	H	7 : 3	25
154b	Br	Et	3 : 1	18

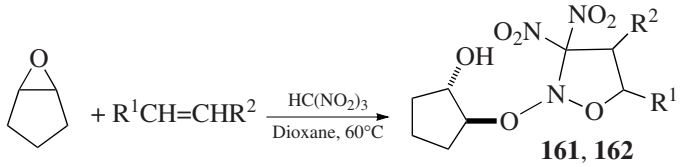


Scheme 28.

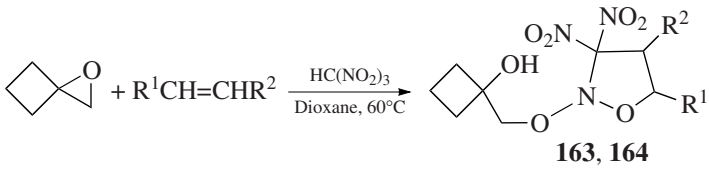


157: $R^1 = OCOCH_3$, $R^2 = H$, 62%;
158: $R^1 = Ph$, $R^2 = Ph$, 71%;
159: $R^1, R^2 = -(CH_2)_3-$, 79%;
160: $R^1 = OBu$, $R^2 = H$, 55%.

Scheme 29.



161: $R^1 = OCOCH_3$, $R^2 = H$, 45%;
162: $R^1, R^2 = -(CH_2)_4-$, 25%



163: $R^1 = OCOCH_3$, $R^2 = H$, 65%;
164: $R^1, R^2 = -(CH_2)_3-$, 42%

Scheme 30.

5-Spirocyclopropaneisoxazolidines **155a**–**155c** are first generated as one regioisomer; then, they are spontaneously and completely rearranged into piperidones **156a**–**156c** at room temperature. In the case of methylenespiropentane, two isomeric piperidones **156c** are generated in the ratio 1 : 1 with a total yield of 23%.

Thus, the three-component reactions of tetranitromethane and halotrinitromethanes with unsaturated compounds proceed as one-pot tandem heterocyclization reactions, including the in situ generation of acyclic nitronic esters followed by [3 + 2] cycloaddition and generation of various mixed-structure isoxazolidines.

Three-Component Reactions of Oxiranes and Alkenes with Trinitromethane

The possibility of generating nitronic esters in situ via the nucleophilic opening of oxiranes by trinitromethane in the presence of olefins was recently shown [99] (scheme 28).

A study of the reaction of cyclohexene oxide with trinitromethane and alkenes showed that this reaction generates nitronate **M**, which then enters [3 + 2] cycloaddition reaction to yield highly functionalized 3,3-dinitroisoxazolidines of mixed structure **157**–**160** (scheme 29).

The reactions of cyclohexene oxide and trinitromethane with various alkenes are regio- and diastereoselective and produce 3,3-dinitroisoxazolidines **157**–**160** in high yields.

Other alkene oxides react with trinitromethane in a similar way [100] (scheme 30).

It was shown for methylenecyclobutane oxide that a nuclephile attacks the unsubstituted carbon atom of oxirane.

Thus, reactions of oxiranes, trinitromethane, and alkenes are a simple and convenient route to functionally substituted 3,3-dinitroisoxazolidines of mixed composition.

The numerous reactions of acyclic nitronates described in this review demonstrate the wide synthetic opportunities for acyclic nitronic esters in preparative organic chemistry. As the main achievement in recent years, we consider the development of cascade multicomponent transformations, including the in situ generation of acyclic nitronic esters; these transformations under formal one-stage conditions generate various nitro-substituted *N*- and *O*-heterocycles of nontrivial structure, such as highly functionalized 3,3-dinitroisoxazolidines of mixed structure, nitroisoxazolines, and *gem*-dinitropiperidones, converting them into preparatively accessible compounds.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 07-03-00685-a), the Chemistry and Materials Science Department of the Russian Academy of Sciences (project no. 1.5), and the Presidential Program for Support of Leading Scientific Schools (grant no. 5538.2008.3 for Academician N.S. Zefirov).

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