SYNTHESIS OF ISOXAZOLINES FROM NITRILE N-OXIDES GENERATED FROM NITROALKENES

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In this review, information on the production of isoxazolines and condensed isoxazoline systems by the intramolecular 1,3-bipolar cycloaddition of unsaturated nitrile N-oxides generated in situ from nonconjugated nitroalkenes is generalized and systematized. The isoxazoline derivatives formed as the result of these reactions are promising synthons in the synthesis of various natural compounds and their analogues.

Among the various chemical transformations of unsaturated nitro compounds, reactions leading to the formation of heterocyclic systems have come into wide use [1-3]. In recent years, a special place among these reactions has been taken by 1,3-dipolar cycloaddition using nitroalkenes as dipolarophiles, which enables various types of five-membered nitrogen-containing heterocycles to be obtained [4].

At the same time, definite interest from the point of view of the methodology of directed organic synthesis may be presented by the 1,3-dipolar cycloaddition reaction using as the dipoles the N-oxides of nitriles of unsaturated acids generated in situ from nonconjugated nitroalkenes. Reactions of this type can be carried out both intermolecularly (the heterocycle is formed from two different molecules – a dipole and a dipolarophile) and intramolecularly (the dipole – the nitrile oxide – and the dipolarophile – an unsaturated C–C bond – being fragments of the same molecule), and they take place with definite regio- and stereoselectivity and lead to isoxazole or isoxazoline derivatives.

It is known [5, 6] that isoxazoles and isoxazolines are convenient synthons for the construction of the carbon skeletons of organic compounds of various classes – β-diketones, β-hydroxy ketones, enoximes, γ-amino alcohols, enones, enamino ketones, etc. At the present time, isoxazole derivates are being widely used in the total chemical synthesis of natural compounds and their analogues – prostanoids, antibiotics, vitamins, nucleosides, alkaloids, antitumoral agent, etc. [6-9].

It must also be mentioned that information on the intramolecular reactions of only such unsaturated dipoles as nitrones, nitrile imines, nitrile ylides, azides, zwitterions, and diazocompounds has been generalized in monographs devoted to 1,3-dipolar cycloaddition reactions [10, 11], while there is only isolated information on similar reactions of nitrile oxides generated from hydroxamic acid chlorides.

In the present review we have attempted to systematize information on the synthesis of isoxazolines from N-oxides of nitriles of unsaturated acids generated from nonconjugated nitroalkenes and to consider the most important, from our point of view, aspects of 1,3-dipolar cycloaddition reactions of dipoles of this type (regio- and stereochemistry of the reactions, reactivities of the dipoles, etc.) and also to give an idea of the synthetic possibilities of the cycloadducts in the production of natural compounds and their analogues.

SYNTHESIS OF ISOXAZOLINES FROM NONCONJUGATED NITROALKENES OF THE ALIPHATIC SERIES

At the present time, various methods of converting primary nitro compounds into nitrile N-oxides are known [3, 12-14], but for similar transformations of nonconjugated nitroalkenes use is generally made of Mukaiyama and Hoshino's method [15], which consists in the low-temperature dehydration of primary nitro compounds under the action of aryl isocyanates in

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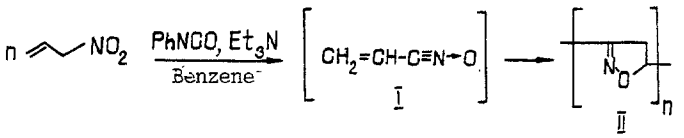
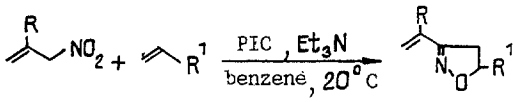
the presence of catalytic amounts of tertiary amines. It must be mentioned that in this reaction N,N'-diarylureas are formed as by-products.

When a solution of 3-nitroprop-1-ene in benzene was treated with a twofold excess of phenylisocyanate (PIC) in the presence of triethylamine, the unstable acrylonitrile N-oxide (I) was obtained, and, under the conditions of the reaction, this was converted by a scheme of poly-[2+3]-cycloaddition into the poly-Δ^2-isoxazoline (II) (yield 44%, molecular mass 850) [16, 17].

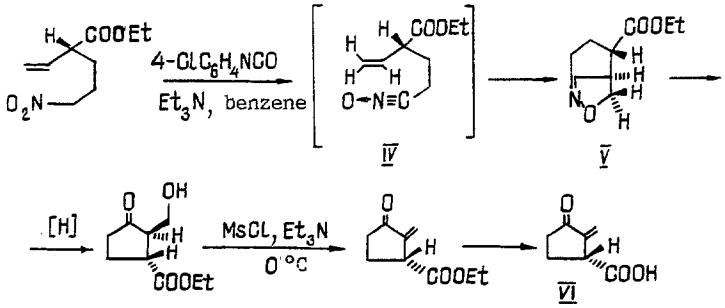


When this reaction was performed in the presence of an excess of the alkene (molar ratio nitroalkene:PIC:alkene = 1:2:4-5), 3-alkenyl-5-substituted Δ^2-isoxazolines (III) were synthesized with yields of 60-84% [17], and some of these have exhibited a considerable antituberculosis activity in vitro [18].



R=H, Me; R^1=Ph, EtO, NC, $ClCH_2$, MeOOC

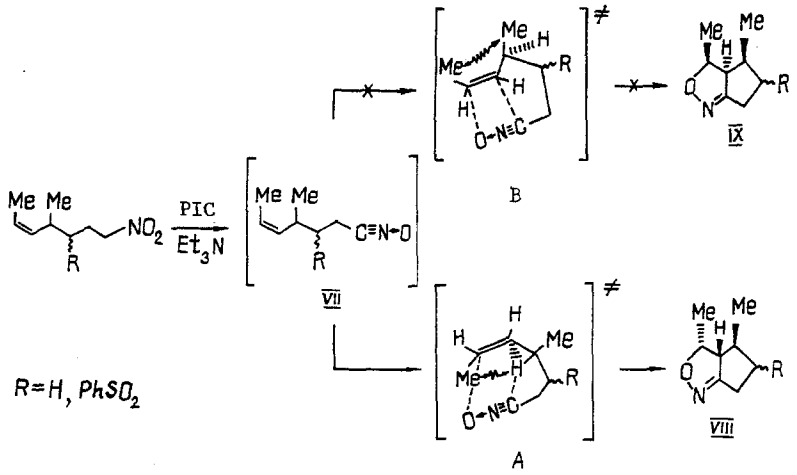
The removal of the primary nitro away group from the multiple bond in ω-nitroalkenes leads to the nitrile N-oxides formed from them in the absence of an "external" dipolarophile giving products of intramolecular [2+3]-cycloaddition by the "head-to-head" or "head-to-tail" principle. For example, the nitrile oxide (IV) generated from 3-ethoxycarbonyl-6-nitrohex-1-ene under the action of 4-chlorophenyl isocyanate (CPIC) in benzene forms in situ, by the "head-to-head" principle, with a yield of 55%, 3,4-(3-ethoxycarbonyltrimethylene)-Δ^2-isoxazoline (V), which is a convenient intermediate in the synthesis of the antitumoral drug sarkomycin (VI) [19].



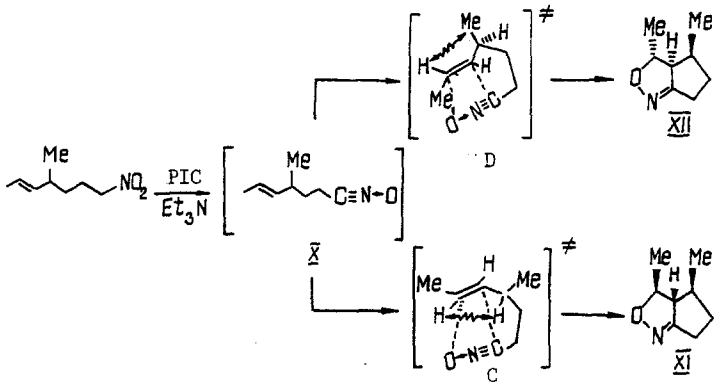
We may note that the cyclization of the N-oxide (IV) takes stereospecifically as a cis-addition, and, of the two theoretically possible stereoisomeric cycloadducts, that for which there is less axial 1,3-strain ($A^{1,3}$-strain) in the transition state [20] is formed.

In the case of the intramolecular cyclization of the nitrile oxides (VII) generated from 4-methyl-7-nitro-5-R-hept-2Z-enes the only reaction products obtained were the cycloadducts (VIII) [21] (see top of following page).

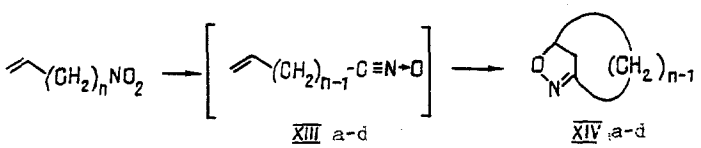
In the opinion of the authors concerned, the high stereospecificity of the reaction is explained by the considerable $A^{1,3}$-strains in the transition state B, leading to the cycloadduct (IX), which was caused by the strong repulsion of the methyl groups. In the transition state A, leading to the cycloadduct (VIII), there is a strong interaction between the hydrogen atom and a methyl group.



In the case of the cyclization of the nitrile oxide (X) obtained from 4-methyl-7-nitrohept-2E-ene, the $A^{1,3}$-strains in the transition states C and D, leading to the cycloadducts (XI) and (XII), are comparable, and therefore a mixture of the stereoisomeric 3,4-trimethyleneisoxazolines (XI) and (XII) in a ratio of 3:1 was formed [21].



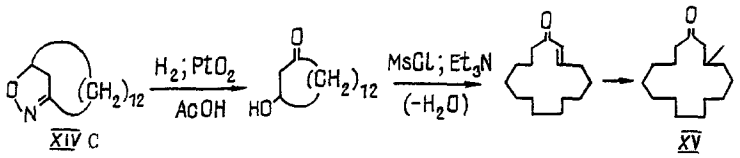
The nitrile N-oxides (XIIIa-d) generated from the corresponding ω-nitroalkenes by the action of CPIC in the presence of triethylamine (molar ratio 1:10:10) in the absence of an "external" dipolarophile undergo intramolecular cyclization to the polymethylene-Δ^2-isoxazolines (XIVa-d) by the "head-to-tail" principle [22]. The reactions were performed by the prolonged boiling of the reactants in benzene, toluene, or xylene, and the yields of the cycloadducts (XIVa-d) amounted to 21-63%



a) n=10, b) n=12, c) n=13, d) n=14

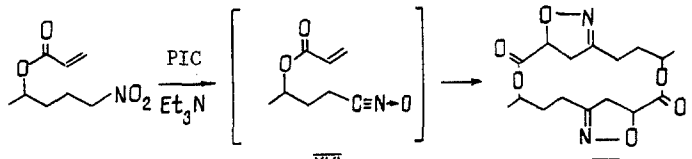
The 3,5-dodecamethylene-Δ^2-isoxazoline (XIVc) obtained in this way has been used as the starting compound in the synthesis of (±)-muscone (XV) [22] (see top of following page).

The cyclization of the nitrile N-oxides obtained from ω-nitroalkyl acrylates takes place in a peculiar fashion. Japanese scientists [23, 24] have shown that, depending on the length of the chain of the nitroalkyl radical and the conditions of performing the reaction, different types of macrocyclic lactones containing Δ^2-isoxazoline fragments are formed. For



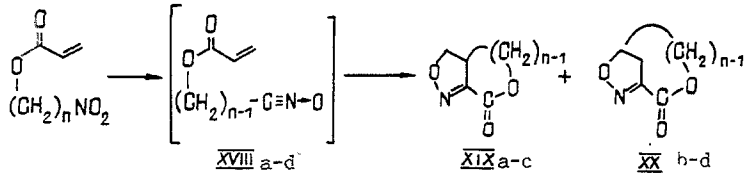
XIV c XV

example, the N-oxide (XVI), generated under the action of PIC and triethylamine on a dilute (c = 0.003 M) solution of 1-methyl-4-nitrobutyl acrylate (30-35°C, 7 days), formed with a yield of 34% the 16-membered dilactone (XVII) as a result of dimerization by the "head-to-tail" principle [23].



XVI XVII

The authors observed that the dilactone (XVII) is a convenient intermediate in the total synthesis of (±)-pyrenophorin. At the same time, the nitrile oxides (XVIIa-d) obtained by the dehydration of 6-nitrohexyl, 9-nitrononyl, 11-nitroundecyl, and 12-nitrododecyl acrylates by the action of CPIC in boiling benzene (12-30 h) gave the monolactones (XIXa-c) and (XXb-d) as the result of intramolecular [2+3]-cycloaddition [24]

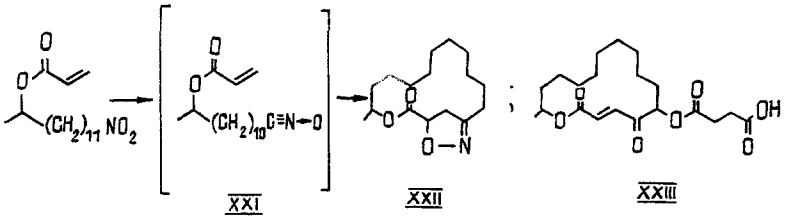


XVIII a-d XIX a-c XX b-d

a) n=6, b) n=9, c) n=11, d) n=12

It must be mentioned that the cyclization of the N-oxide (XVIIIa) takes place only by the "head-to-head" principle with the formation, as the sole reaction product, of the lactone (XIXa) (yield 44%), while the N-oxides (XVIIIb and c) each give a mixture of regioisomeric lactones (yields 74 and 82%, respectively) in which the isomer of the "head-to-tail" type predominates [ratios (XXb):(XIXb) = 5:1, and (XXc):(XIXc) = 6.5:1]. Cyclization of the nitrile N-oxide (XVIIId) (n = 12) takes place exclusively by the "head-to-tail" principle with the formation of the adduct (XXd) (yield 67%).

The nitrile oxide (XXI) reacts analogously, and its cyclization product (XXII) [24] has been used in the synthesis of the macrolactone (XXIII) – the antibiotic A26771 [25, 26].

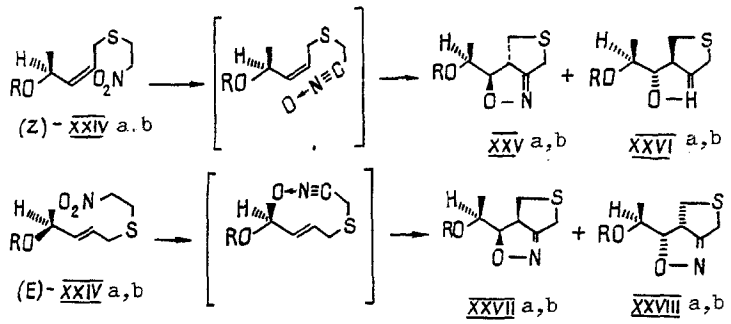


XXI XXII XXIII

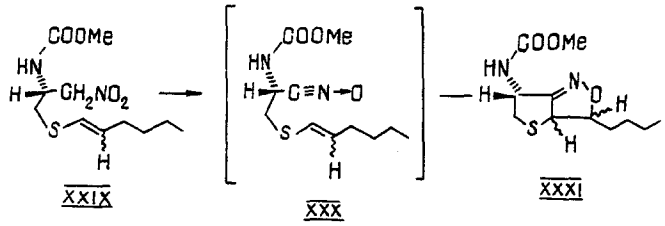
Annunziata and colleagues [27] have reported the intramolecular cycloaddition of nitrile N-oxides generated from the optically pure (Z)- and (E)- isomers of (S)-4-R-oxy-1-(2-nitroethylthio)pent-2-enes (XXIVa, b) under the action of CPIC in the presence of triethylamine (benzene, boiling, 12 h). These authors reported that the cycloaddition of both the (Z)- and (E)-isomers took place by the "head-to-head" principle with the formation of mixtures of diastereoisomeric cycloadducts in which the isoxazolines (XXVa, b) and (XXVIIa, b), respectively, predominated (see Table 1).

TABLE 1. Intramolecular [3+2]-Cycloaddition of the (Z)- and (E)- Isomers of (4S)-4-R-Hydroxy-1-(2-nitroethylthio)pent-2-enes (XXIVa, b) (CPIC, Et_3N, benzene, 80°C, 12 h) [27]

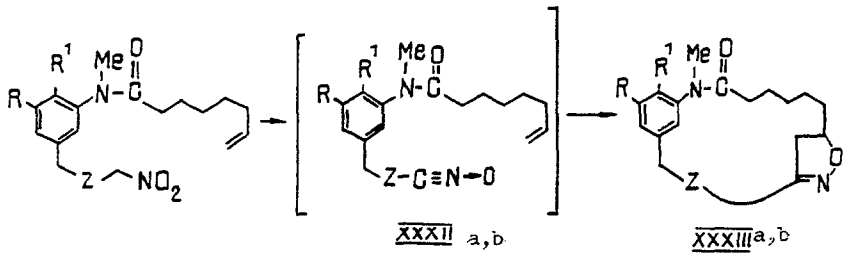
R	Substrate	Reaction products	Yield, %	Ratio of the diastereomers
$PhCH_2$	(Z)-XXIVa	XXVa+XXVIa	91	66:34
$PhCH_2$	(E)-XXIVa	XXVI[a]+XXVIIIa	65	66:34
tert-$BuMe_2Si$	(Z)-XXIV[b]	XXV[b]+XXVIb	80	67:33
tert-$BuMe_2Si$	(E)-XXIV[b]	XXVII[b]+XXVIIIb	70	64:36



The treatment of a mixture (1:1) of the (E)- and (Z)- isomers of the nitroalkene (XXIX) (obtained by a five-stage synthesis from N-methoxycarbonyl-L-cysteine) with an excess of PIC in boiling benzene led to the corresponding nitrile N-oxides (XXX), which, on being boiled in benzene, were converted with a yield of 92% into a mixture of stereoisomeric isoxazolines (XXXI) [28]. The latter are convenient synthons in the synthesis of deoxybiotin and D-biotin [28].

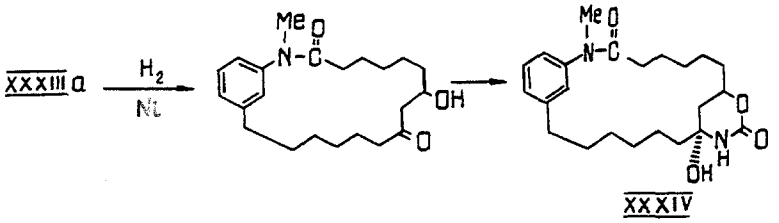


The nitrile oxides (XXXII) obtained from the corresponding ω-nitroalkyl- or ω-nitroalkadienyl-substituted anilides of oct-7-enoic acid react by the "head-to-tail" principle with the formation of the cycloadducts (XXXIIIa, b) [29].

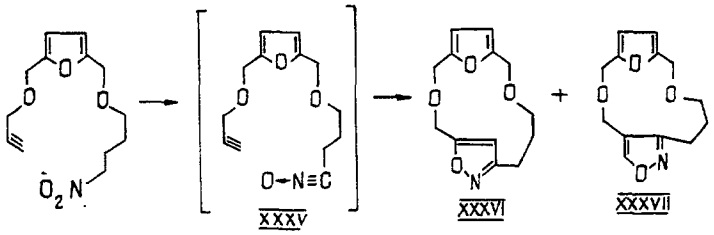


a) $Z=(CH_2)_5$, $R=R^1=H$; b) $Z=C(Me)=CH-CH=CHCH_2-$, $R=MeO$, $R^1=Cl$

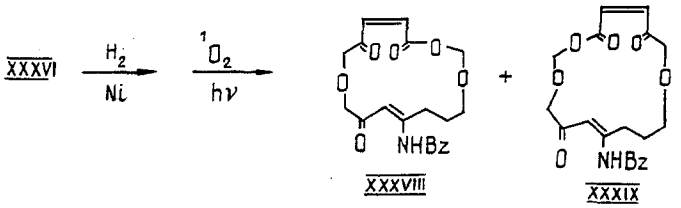
The cycloadduct (XXXIIIa), obtained with a yield of 82%, has been transformed through several stages into the macrocycle (XXXIV), which is an analogue of mitatsin (maytansine) and has shown a high antitumoral activity in in vitro experiments [29].



The nitrile N-oxide (XXXV), generated from the corresponding 2,5-disubstituted furan, was converted by treatment with PIC in boiling benzene (48 h) with a yield of 40% into a mixture of two regioisomeric furoisoxazolophanes (XXXVI) and (XXXVII) in a ratio of 9:1 [30].

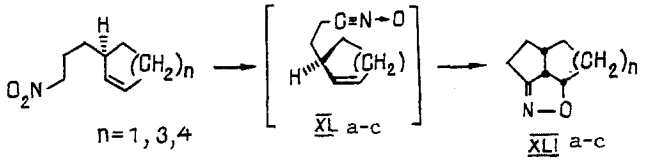


The cycloadduct (XXXVI) yielded a mixture (1:1) of regioisomeric 16-membered macrolides (XXXVIII) and (XXXIX) [3], which are of interest as biologically active substances [31].



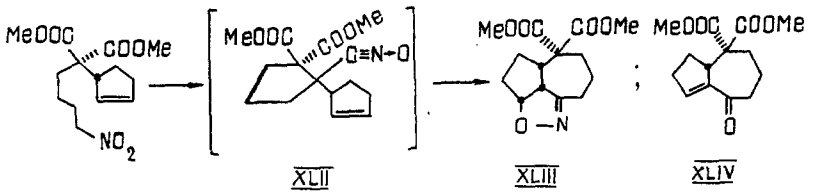
SYNTHESIS OF ISOXAZOLINES FROM NONCONJUGATED NITROALKENES OF THE ALICYCLIC AND HETEROCYCLIC SERIES

Wollenberg and Goldstein [32] have studied the intramolecular cyclization of the nitrile N-oxides (XLa-c) obtained from 3-(3-nitropropyl)cycloalkenes under the action of an excess of PIC in benzene. It was found that, regardless of the size of the ring, the attack of the nitrile oxide grouping on the endocyclic double bond took place from the same side of the nominal plane of the ring as that upon which the 3-nitropropyl radical was located. As a result, the tricyclic Δ^2-isoxazo nes (XLIa-c) were formed with yields of 82-96%.



Other alicyclic nitrile N-oxides with endocyclic double C=C bonds react similarly. For example, under the action of PIC in boiling benzene the N-oxide (XLII), generated from 3-(2,2-dimethoxycarbonyl-5-nitropentyl)cyclopentene formed the cycloadduct (XLIII) (yield 83%),

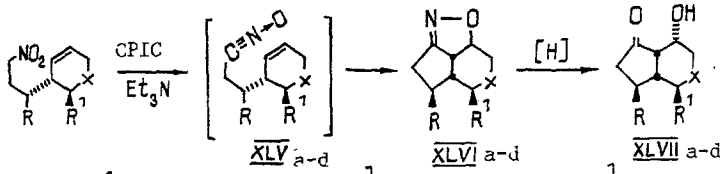
which, by simple trivial reactions, was converted into the hydroazulone dimethoxycarbonyl derivative (XLIV) (yield 80%) [33].



XLII XLIII XLIV

The authors observe that this method is of considerable interest for obtaining compounds with guaiane and pseudoguaiane structures [34].

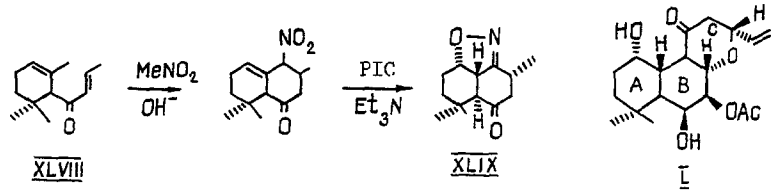
Similarly, the tricyclic Δ^2-isoxazolines (XLVIa-d) were synthesized with yields of 70-90% from the N-oxides (XLVa-d), and their reduction led to the bicyclic β-hydroxy ketones (XLVII) with the cis- configuration [35, 36].



XLV a-d XLVI a-d XLVII a-d

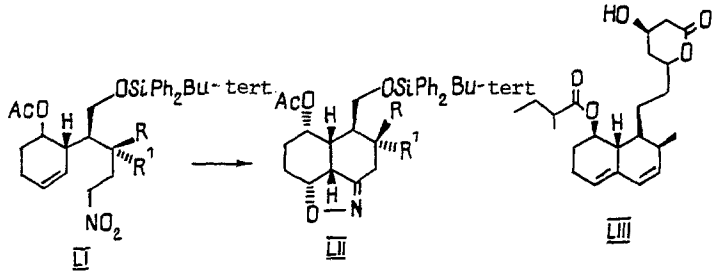
a) $R=R^1=H$, $X=CH_2$; b) $R=CH_3$, $R^1=H$, $X=CH_2$; c) $R=H$, $R^1=EtO$, $X=O$; d) $R=CH_3$, $R^1=EtO$, $X=O$

The high stereospecificity of intramolecular cycloaddition enabled Italian chemists to convert α-damascone (XLVIII) into the bicyclic system (XLIX) (yield 20%) [37], which is characteristic for the AB rings of forskolin (L) – a diterpenoid isolated from the plant Coleus forskohlii [38].



XLVIII XLIX L

Kozikowski and Li [39] have reported the intramolecular cycloaddition of nitrile oxides generated from the nitroalkenes (LI) under the action of PIC, leading to the condensed isoxazolines (LII) – intermediates in the total synthesis of compactin (LIII), which is a coenzyme (HMG–CoA) controlling the biosynthesis of cholesterol.

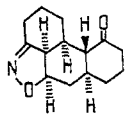
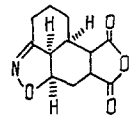
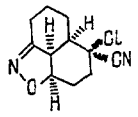
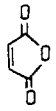
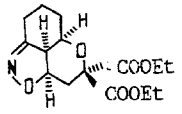


LI LII LIII

a) $R=H$, $R^1=Me$; b) $R=Me$, $R^1=H$

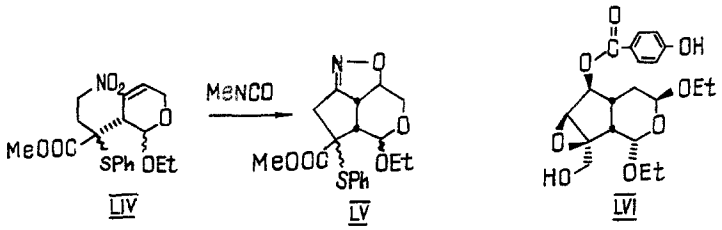
Kim et al. [36] have shown that γ-nitroalkyl derivatives of 5,6-dihydro-2H-pyran (LIV) are converted on treatment with methyl isocyanate and triethylamine (molar ratio 1:4:1.7) in

TABLE 2. Tandem [4+2]-Cycloaddition and [3+2]-Intramolecular Cycloaddition Reactions Based on 8-Nitroocta-1,3-diene [40]

Dienophile	Conditions for performing [4+2]-cycloaddition	Yield of adduct, %	Product of [3+2]-cycloaddition	Yield, %
1. $(EtOOC)_2C=O$	Toluene 110°C 15h	60		88
2. 	Toluene 110°C, 15h	73		71
3. 	Toluene 70°C, $AlCl_3$, 19 h	52		67
4. 	Toluene 110°C, 15h	91		85

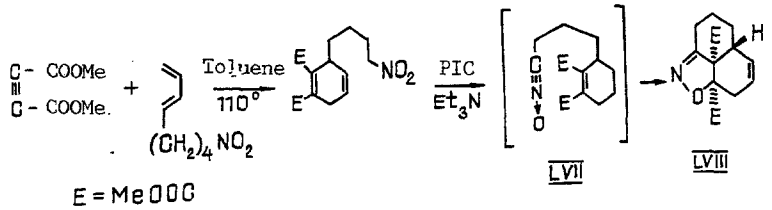
*PIC, Et_3N, benzene, 80°C, 15 h.

benzene (25°C, 14 h; 80°C, 1 h) into the isoxazolines (XLV), which are convenient synthons in the total stereoselective synthesis of the optically active natural aglycon of (−)-specionin (LVI) [39].



LIV LV LVI

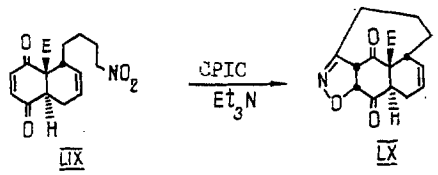
Tandem [4+2]- and intramolecular [3+2]-cycloaddition reactions with the participation of 8-nitroocta-1,3-diene have been used for the synthesis of condensed tri- and tetracyclic steroid-like systems [40].



E = MeOOC

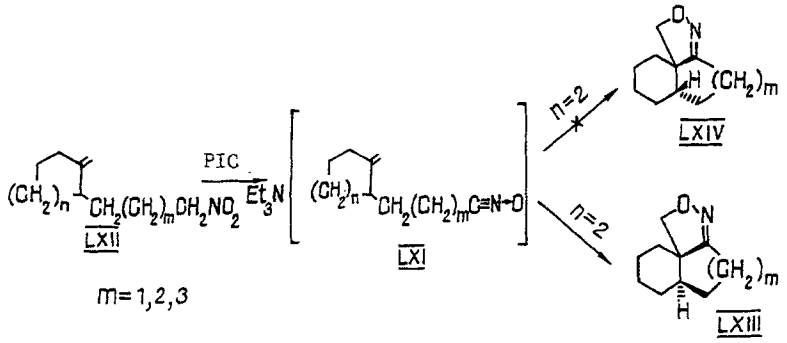
LVII LVIII

It must be mentioned that the intramolecular conversion of the nitrile oxide (LVII) into the tricyclic adduct (LVIII) takes place at the most substituted and, therefore, most activated double bond. Other nitroalkylcyclodienes react similarly; for example, from (LIX) the bridged structure (LX) is formed with a yield of 58% [40], and this can be used in the synthesis of several natural compounds [41]. Table 2 gives examples of the production of a number of polycyclic structures by this method.



LIX LX

Hassner et al. [42] have investigated the reactivity of the nitrile N-oxides (LXI) obtained by the action of PIC and triethylamine on nitroalkylcycloalkanes containing exocyclic methylene groupings (LXII). They established that the N-oxides (LXI) derived from cyclopentane (n = 1) do not give the products of [3+2]-intramolecular cycloaddition; in this case only the products of the polymerization of the N-oxides were isolated. At the same time, the N-oxides (LXI) derived from cyclohexane (n = 2) were readily converted into tricyclic adducts of the "head-to-tail" type, and of the possible two types of stereoisomers (LXIII) and (LXIV) only the stereoisomers (LXIII) were formed. The stereochemistry of cycloaddition was confirmed by quantum-chemical calculations by the MMX method.

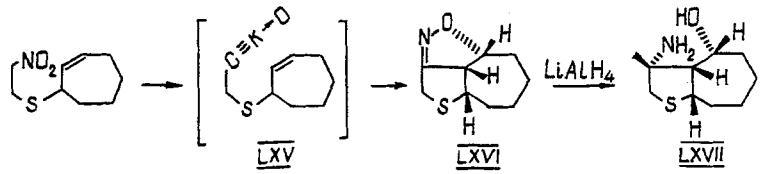


LXII LXI LXIV LXIII

m=1,2,3

Unsuccessful attempts at the cyclization of the N-oxide (LXI) generated from 1-methylene-2-(3-nitropropyl)cyclopentane [(LXII), m = n = 1] had been reported previously [43].

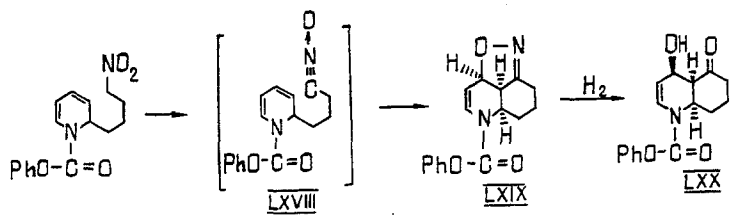
Confalone et al. [44, 45] have used the intramolecular [3+2]-cycloaddition of the nitrile N-oxide (LXV) generated from 3-nitroethylthiocycloheptene under the action of PIC and triethylamine in benzene (20°C, 24 h) in the stereospecific synthesis of 3,4aβ,5,6,7,8,9β,9aβ-octahydro[5,5a,6-f,g]thieno[3,4-c]isoxazole (LXVI) (yield 79%), the reduction of which formed with a yield of 92% 3-aminooctahydro-4H-cyclohepta[b]thiophene-4β-ol (LXVII) — a key compound in the total synthesis of (±)-biotin.



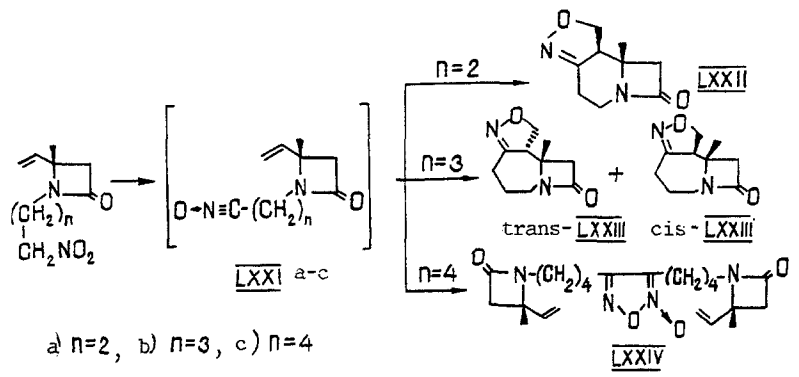
LXV LXVI LXVII

With the aim of developing a general method of synthesizing cis-decahydroquinoline alkaloids (gephyrotoxin, etc.) American scientists [46] have studied the intramolecular [3+2]-cycloaddition of the nitrile N-oxide (LXVIII), obtained from a 1-acyl-2-(4-nitrobutyl)-1,2-dihydropyridine (PIC, Et_3N, benzene, 20°C, 72 h). It was established that the reaction takes place stereospecifically as cis-addition with the formation of the tricyclic adduct (LXIX) (yield 68%). The catalytic hydrogenation of the latter led with a yield of 88% to the keto alcohol (LXX) (see top of following page).

The reactivity of the nitrile N-oxides (LXXI) generated from 4-methyl-1-nitroalkyl-4-vinylazetidin-2-ones has been investigated [47]. It was shown that the nature of the



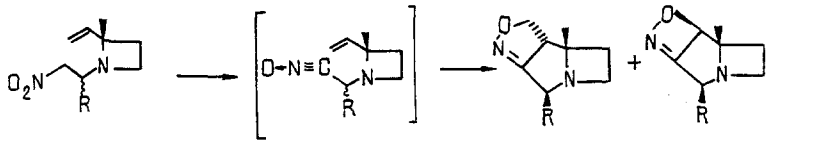
products formed from these N-oxides depends on the length of the chain of the nitroalkyl fragment.



a) n=2, b) n=3, c) n=4

For example, as the result of intramolecular cycloaddition of the "head-to-tail" type, the N-oxide (LXXIa) (n = 2) formed only one of the two possible stereoisomeric adducts (LXXII). At the same time, the N-oxide (LXXIb) (n = 3) gave a mixture of the two stereoisomers [trans-(LXXIII) and cis-(LXXIII)] in a ratio of 3:2. The N-oxide (LXXIc) (n = 4) did not react in the manner of an intramolecular cycloaddition but was converted into the furoxan (LXXIV).

The nitrile N-oxides (LXXVa, b) obtained from 1-(1R-2-nitroethyl)-4-methyl-4-vinylazetidines reacted similarly to the N-oxide (LXXIb) with the formation of the stereoisomeric [3+2]-cycloadducts [cis-(LXXVIa, b) and trans-(LXXVIa, b)] [for R = H, the ratio of cis-(LXXVIa) to trans-(LXXVIa) was 2:1, and the yield was 50%] [48].



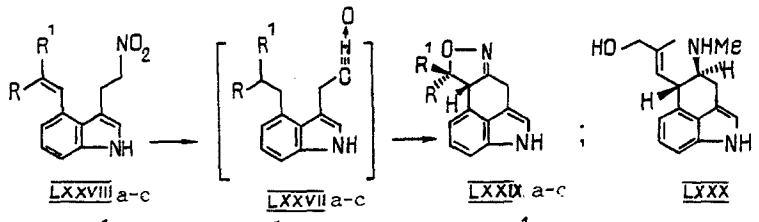
a) R=H, b) R=Ph

It is interesting to note that in the cycloadducts cis-(LXXVIb) and trans-(LXXVIb` R = Ph) the methyl and phenyl radicals had the cis-configuration, although the initial nit: -kene was a mixture (1:1) of diastereomers.

A. Kozikowski et al. [49-52] have used the intramolecular [3+2]-cycloaddition of the nitrile N-oxides (LXXVIIa-c) generated from the 3-(2-nitroethyl)indole derivatives (LXXVIIIa-c) in the total synthesis of a number of indole alkaloids (see top of following page).

For example, when the nitro derivatives XVIIIa-c) were treated with PIC in the presence of triethylamine in benzene, 20°C, 24 h) ne isoxazolines (LXXIXa-c) were formed with yields of 70-90%. The cycloadduct (LXXIXc) (R AcOCH$_2$, R^1 = H) was used as an intermediate in the synthesis of the alkaloid chanoclavine I (LXXX) [49].

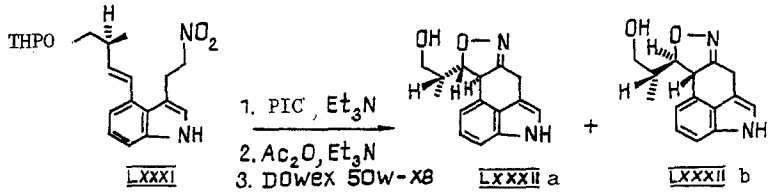
Under similar conditions, the nitro derivative (LXXXI) formed a mixture (1.1:1) of the diastereomeric cycloadducts (LXXXIIa and b), which are convenient starting compounds in the



LXXVIII a-c LXXVII a-c LXXIX a-c LXXX

a) R=R¹=H; b) R=MeO, R¹=H; c) R=AcOCH₂, R¹=H

production of ergot alkaloids: (+)-paliclavine [50, 51], 5-epipaliclavine [50], (+)-paspaliclavine [51], pyroclavine [51], agroclavine [51, 52], and fumigoclavine [51].



LXXXI LXXXII a LXXXII b

THP = tetrahydropyran-2-yl

Thus, the informagion given in this review indicates the great synthetic possibilities of the intramolecular [3+2]-cycloaddition reactions of the N-oxides of nitriles of unsaturated carboxylic acids generated from aliphatic, alicyclic, and tetracyclic nonconjugated nitroalkenes. We hope that the general laws of the occurrence of these reactions leading to condensed isoxazoline systems that have been described above will in the future assist in the generalization of new experimental results and serve as a basis for the directed synthesis of heterocyclic and polycyclic systems, including natural compounds and their analogues.

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