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Three-component Reactions of Tetranitromethane with Olefins

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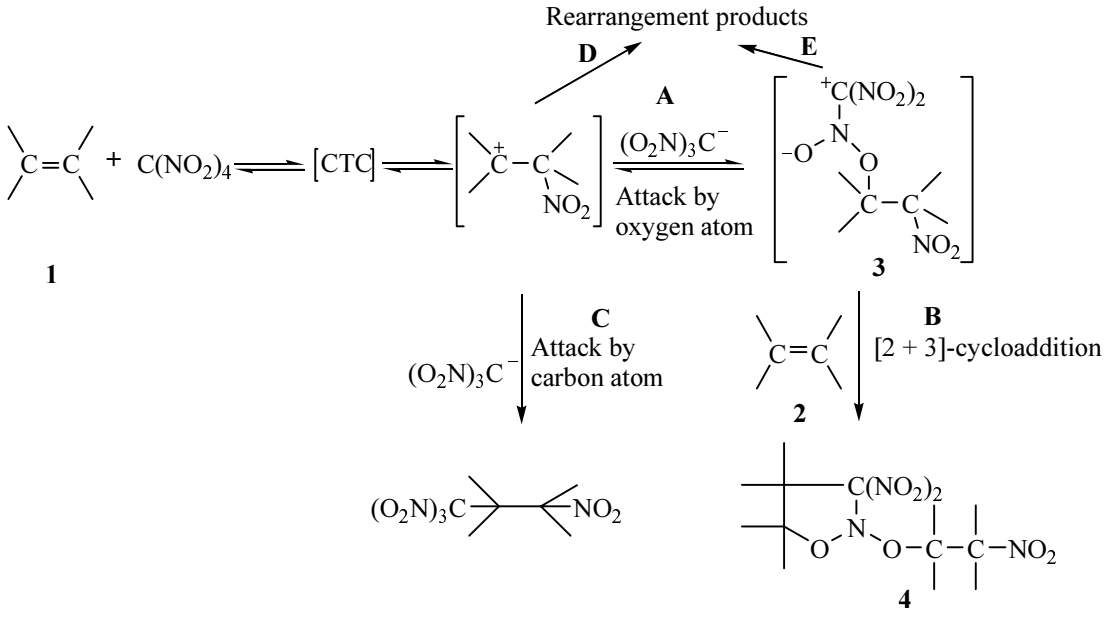
Abstract—Three-component reactions of tetranitromethane with two different olefins taken in equimolar amounts are procedures fit for preparation of 3,3-dinitroisoxalidines of a mixed composition.

A significant position among diverse transformations of nitro compounds hold reactions resulting in formation of heterocyclic structures. From versatile heterocyclizations involving nitro compounds of the most interest are reactions of tetranitromethane (TNM) and its derivatives with alkenes that underlie procedures for syntheses of heterocyclic compounds containing nitrogen and oxygen [1].

The principal rules governing the reactions of TNM with alkenes were established in nineteen seventies by the research of K.V.Altukhov, V.V.Perekalin, V.A.Tartakovskii, and their collaborators [2–10]. It was demonstrated that depending on the reaction conditions and the structure of the initial olefin formed various classes of organic compounds among which were mentioned arylnitroalkenes [3, 11], α-nitroketones [3–5, 12, 13], tetranitroalkanes [4, 6–9, 11] etc. However the high and specific TNM reactivity toward alkenes makes these reactions first and foremost a convenient synthetic procedure for substituted dinitroisoxazolidines [2–4, 5, 7, 14–17].

We showed formerly investigating the reactions between tetranitromethane and olefins containing small rings that the main direction of the process was formation of 3,3-dinitroisoxazolidines of cyclobutane and cyclopropane series [18, 19]. However sometimes, mainly with olefin containing three-membered rings a formation of

Scheme 1.



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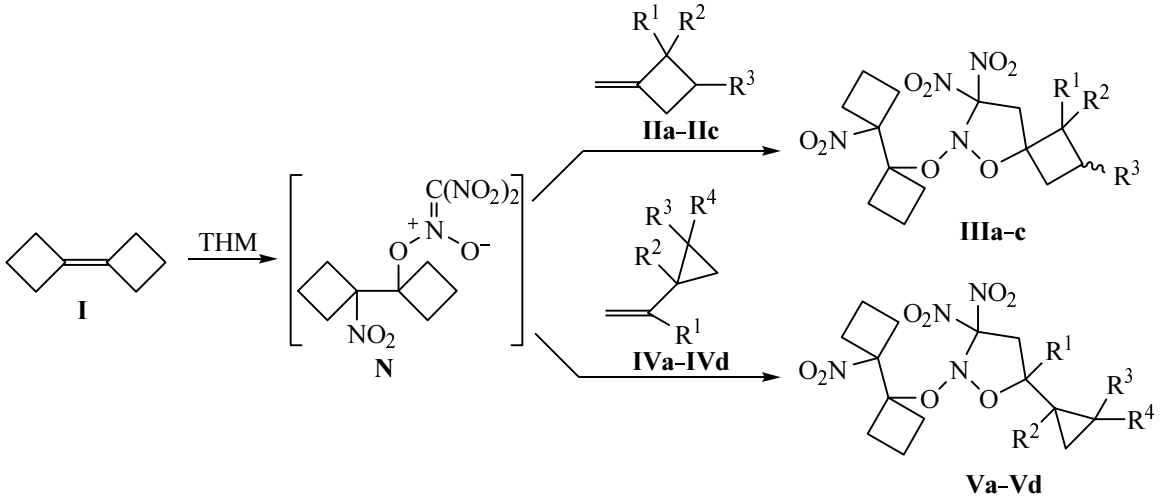
Scheme 2.



II, III: $R^1 = R^2 = R^3 = H$ (**a**) [18]; $R^1 = R^2 = CH_2CH_2$, $R^3 = H$ (**b**); $R^1 = R^2 = H$, $R^3 = CN$ (**c**) [18]. **IV, V**: $R^1 = R^2 = R^3 = R^4 = H$ (**a**); R^1 = cyclopropyl, $R^2 = R^3 = R^4 = H$ (**b**); $R^1 = R^2 = H$, $R^3 = R^4 = CO_2Et$ (**c**); R^1 = Me, R^2 = isopropenyl, $R^3 = R^4 = H$ (**d**).

tetranitropropanes or rearrangement products was observed [19].

Taking into account the published data and also our own results we can present the general pattern of the TNM reaction with olefins as follows.

According to Scheme 1 the reaction of alkenes with TNM proceeds via nitro carbocation formation. The latter depending on the degree of positive charge delocalization reacts further with trinitromethyl anion either at the oxygen atom (O-alkylation, **A**), or at the carbon site (C-alkylation, **C**), or undergoes rearrangements (**D**, **A**). Depending on the structure of the olefin substrate or, to lesser extent, on the reaction conditions any of the processes designated on the scheme can come true.

The synthetic prospects of TNM reaction with olefins where two molecules of the same alkene build up with TNM a molecule of 3,3-dinitroisoxazolidine are limited by a condition that it can be successfully carried out only with sterically unhindered alkenes with a sufficiently nucleophilic double bond [7, 19]. The general scheme suggests that isoxazolidines formation occurs in a tandem process which can be represented as a sequence of two stages. The first stage involves a generation of nitronic ester of type **3**, that is a 1,3-dipole. The second stage consist in [2+3]-cycloaddition of nitronic ester of type **3** to the olefin giving a product of type **4**. Since the sterical and electronic requirements with respect to alkene are different in the first and second stages of heterocyclization it is possible to extend the opportunities of reaction between TNM and olefins applying different alkenes at the stage of nitronic ester formation (alkene **1**, **A**, Scheme 1) and at the stage of cyclization (alkene **2**, **B**, Scheme 1).

The fundamental possibility to synthesize isoxazolidines of mixed composition was demonstrated formerly by an example or reaction between 1-phenylcyclohexene TNM in solution of another sterically unhindered and alkene taken in a 10-fold excess [10]. However this procedure is not promising for preparative methods.

In this study we investigated heterocyclization of a wide range of alkenes effected by TNM. The reaction was carried out at equimolar quantities of the reagents. As a result of studies a method was developed for the synthesis of 3,3-dinitroisoxazolidines of a mixed composition. We believed that for the generation of nitronic ester tri- and tetrasubstituted olefins with a nucleophilic double bond should be used for they actively reacted with TNM but were poor 1,3-dipolarophiles due to steric factors. Three-component reactions of TNM with polysubstituted alkenes were studied by examples of tetramethylethylene, bicyclobutylidene, 1-phenyl-substituted cyclopentene and cyclohexene, and also 1-methylcyclobutene. The structure of compounds obtained was established with the use of unidimensional and two-dimensional ^1H and ^{13}C NMR spectroscopy and of mass spectrometry. The spectral parameters of compounds synthesized are compiled in Tables 1–3 and in EXPERIMENTAL.

We established that the universal olefin for nitronic ester generation was bicyclobutylidene **I** for this olefin reacted with TNM even at 0°C forming first apparently a charge-transfer complex and then the nitronic ester of

Table 1. ^{1}H NMR spectra of isoxazolidines (**IIIb, Va–Vd, VIIIc, VIIIe, VIIIi,VIII j**), δ, ppm. (*J,* Hz) in $CDCl_3$

Compd. no.	Diastereomer[a]	$CH_2C(NO_2)_3$[b]	Other groups of atoms
IIIb	**A**	3.17 d, 3.73 d (^2J 15.3)	CH_2: 0.09–0.91 m (4H + 4H, cyclo-Pr), 1.55–2.88 m (16H + 16H, cyclo -Bu)
	B	3.31 d, 3.43 d (^2J 15.2)	
Va	**A**	2.89 d.d (^2J 15.3, ^3J 6.7), 3.70 d.d (^2J 15.3, ^3J 8.0)	0.30–0.84 m (5H + 5H, cyclo-Pr); CH_2: 1.60–3.00 m (16H + 16H, cyclo-Bu); CH: 3.99 d.d (^3J 6.7, 8.0)
	B	3.41 d.d (^2J 15.2, ^3J 6.8), 3.53 d.d (^2J 15.2, ^3J 8.0)	CH: 3.67 d.d.d (^3J 6.8, 8.0)
Vb		3.02 d, 3.53 d (^2J 15.6)	0.06–0.58 m (10H, cyclo-Pr); 1.68–2.80 m (12H, cyclo-Bu)
Vc[c] 1 fr.	**A**	3.01 d.d (^2J 15.6, ^3J 6.6), 3.91 d.d (^2J 15.6, ^3J 7.9)	CH_3: 1.27 t (3H, ^3J 7.1), 1.34 t (3H, ^3J 7.1), 1.40–2.90 m (15H + 15H, cyclo-Bu, cyclo-Pr), 4.19 q (2H, $CH_3\underline{CH_2}O$, ^3J 7.1), 4.29 q (2H, $CH_3\underline{CH_2}O$, ^3J 7.0);
	B	3.47 d.d (^2J 15.2, ^3J 7.7), 3.65 d.d (^2J 15.2, ^3J 7.2)	CH: 4.18 m CH_3: 1.30 t (3H, ^3J 7.1), 1.34 t (3H, ^3J 7.1), 4.00–4.35 m [5H, 2×CH_3CH_2O, $CHCH_2C(NO_2)_3$]
2 fr.	**A'B'**	3.10 d.d (^2J 15.4, ^3J 6.6), 3.90 d.d (^2J 15.4, ^3J 6.0)	CH_3: 1.27 t (3H), 1.30 t (3H), 1.40–2.90 m (15H + 15H, cyclo -Bu, cyclo -Pr),
		3.51 d.d (^2J 14.9, ^3J 7.6), 3.90 d.d (^2J 14.9, ^2J 7.8)	4.08–4.48 m [5H + 5H, 2×CH_3CH_2O, $CHCH_2C(NO_2)_3$] CH_3: 1.28 t (3H), 1.29 t (3H)
Vd	**A**	3.35 d, 3.60 d (^2J 15.6)	0.43 m (1H, cyclo-Pr), 0.60 m (2H, cyclo-Pr), 0.69 m (1H, cyclo -Pr); CH_3: 1.48 s (3H), 1.74 s (3H), 1.60–2.80 m (12H + 12H, cyclo-Bu); CH_2=: 4.89 br.s (1H), 4.97 br.s (1H)
	B	3.42 d, 3.60 d (^2J 15.8)	0.60 m (2H, cyclo-Pr), 0.69 m (1H, cyclo-Pr), 0.85 m (1H, cyclo-Pr); CH_3: 1.26 s (3H), 1.78 s (3H); CH_2=: 4.90 br.s (1H), 4.96 br.s (1H)
VIIIe[d]	**A**	3.19 d.d (^2J 15.5, ^3J 6.1), 3.85 d.d (^2J 15.5, ^3J 9.2)	CH_2: 1.61–2.98 m (12H); CH_2Cl: 3.68 m (2H, ^2J 12.1); CH: 4.95 m (1H) CH_2: 1.61–2.98 m (12H), 3.47 d.d (1H, ^2J 11.1, ^3J 9.2), 3.54 d (2H, ^2J 7.2),
	B[d]	3.65–3.70 m	3.68 m (1H); CHO: 4.63 m (1H)
VIIIf	**A**	3.09 d.d (^2J 15.6, ^3J 6.2), 3.83 d.d (^2J 15.6, ^3J 8.3)	CH_2: 1.60–3.00 m (12H + 12H, cyclo-Bu), 3.49 m [2H + 4H, CH_2Br, **A, B,** $CHCH_2C(NO_2)_3$, **B,** ^2J 12.1]; CHO: 4.88 m (1H) CHO: 4.73 m (1H)
	B	3.48–3.53 m	
VIIIi		3.37 d.d (^2J 15.8, ^3J 7.2), 4.25 d.d (^2J 15.8, ^3J 8.8)	CH_2: 1.70–2.93 m (12H, cyclo-Bu); CH: 5.97 d.d (1H, ^3J 7.2, 8.8)
VIIIj		3.05 d.d (^2J 15.6, ^3J 7.4), 4.20 d.d (^2J 15.6, ^3J 8.3)	CH_2: 1.50–3.00 m (12H, cyclo-Bu); CH: 5.59 d.d (1H, ^3J 7.4, 8.3), 7.09 d (2H, Ph, ^3J 6.6), 7.48 d (2H, Ph, ^3J 6.6)

[a] Diastereomers **A–D** ratio is given in EXPERIMENTAL.

[b] Here and hereinafter the fragment of isoxazolidine ring $(ONO)C(NO_2)_2$ is designated as $C(NO_2)_3$.

[c] The product was separated in two fractions each containing two diastereomers.

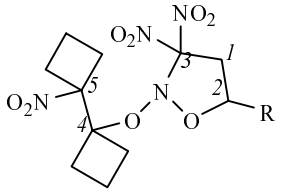
[d] The signals of diastereomer **B** of compound (**VIIIe**) were not assigned due to overlapping with the signals of the major diastereomer.

type 3 (Scheme 1) that at cooling (0–5°C) was not further involved into the 1,3-dipolar cycloaddition with the second molecule of the initial olefin **I**. A subsequent addition to the mixture of TNM and olefin **I** of 1 equiv of some other alkene resulted in formation of mixed isoxazolidines.

We found that the reaction of TNM and bicyclobutylidene **I** with methylenecyclobutanes **IIa–c** and vinylcyclopropanes **IVa–d** occurred regioselectively and furnished the corresponding isoxazolidines of mixed composition **IIIa–c, Va–d** in high yields (Scheme 2).

It is known that in 1,3-dipolar cycloaddition of N-oxides to 1,1-disubstituted olefins the oxygen atom is bound to the more substituted carbon of the double bond [20]. A similar regioselectivity was also observed in the reactions under study, It is in particular confirmed by NMR data (Tables 1 and 2). The isoxazolidine ring of compounds **III, V** appears as characteristic NMR signals. The methylene groups protons have signals in the range δ 2.9–3.5 and 3.4–3.9 ppm. [*AB*-systems for compounds **IIIa–c, Vb, d** or *AB*-part of *ABX*-systems for compounds **Va, b,** ^2J 15–16 Hz]. In the ^{13}C NMR spectrum

Table 2. ^{13}C NMR spectra of isoxazolidines **IIIb, Va–d, VIIIc, f, i, j** of general formula shown below (δ, ppm [^1J(CH), Hz] in $CDCl_3$)



Compd. no.	Diastereomer	C^1	C^3	C^2	C^4, C^5	Other carbon atoms
IIIb	**A**, **B**	40.34, 42.66	128.25, 129.47	90.93, 90.94, 92.16, 92.19, 93.63, 94.48		CH_2, cyclo-Bu: 12.48, 12.96, 13.23, 14.14, 24.10, 25.39, 28.84, 29.03, 29.09, 29.14, 29.42, 29.69, 30.23, 30.34, 30.45, 31.01; CH_2, cyclo-Pr: 7.86 (162), 9.35 (162), 10.32 (×2, 163); C_{spiro}: 33.00, 35.79
Va	**A**	39.16	128.78	87.24 89.64	89.72, 91.2789.82,	CH_2, cyclo-Bu: 13.75, 14.19, 26.85, 28.00, 28.29, 30.06; cyclo-Pr, CH_2: 2.44, 3.90; CH: 12.38
	B	37.78	[a]		91.01	CH_2, cyclo-Bu: 13.59, 14.18, 27.85, 27.99, 28.66, 28.87; cyclo-Pr, CH_2: 3.31, 4.38; CH: 16.11
Vb		42.44	129.01	93.74	89.87, 90.69	CH_2, cyclo-Bu: 13.42, 14.12, 27.67, 27.85, 28.52, 28.82; cyclo-Pr, CH_2: 0.11, 1.31, 3.01, 3.14; CH: 16.23, 20.00
Vc 1 fr.	**A**	39.3538.23	128.43 128.42	82.68 84.20	90.02, 91.21 90.21, 90.96	CH_2, cyclo-Bu: 13.75, 26.80, 28.29, 28.69, 30.06; cyclo-Pr, CH_2: 19.37, CH: 27.30, C: 33.44; COOEt, CH_3: 14.01 (×2); CH_2: 62.31 (×2); C: 166.88, 168.92
	B					CH_2, cyclo-Bu: 13.54, 14.32, 27.91, 27.97, 28.68, 28.74; cyclo-Pr, CH_2: 19.68; CH: 19.68; C: 34.00; COOEt, CH_3: 14.08 (×2); CH_2: 62.18 (×2); C: 166.88, 168.92
2 fr.	**A'**	39.30 (140) 37.80 (142)	128.19 127.51	80.94 (157) 82.46 (157)	89.88, 90.99 90.32, 91.05	CH_2, cyclo-Bu: 13.49 (144), 14.36 (139), 27.87, 28.05, 28.83, 29.06; cyclo-Pr, CH_2: 17.61 (166); CH: 27.60 (162); C 32.58; COOEt, CH_3: 14.18 (×2, 127); CH_2: 62.28 (148), 62.41 (148); C: 166.84, 168.85
	B'					CH_2, cyclo-Bu: 13.59, 14.37 (139), 28.19, 28.84, 28.99, 31.90; cyclo-Pr, CH_2: 18.59; CH: 27.79; C 34.10; COOEt, CH_3: 14.18 (×2, 127); CH_2: 62.08, 62.50; C: 167.82, 168.27
Vd	**A**	44.07 (139)	129.84 127.79	93.89	90.14, 90.89	CH_2, cyclo-Bu: 13.53, 14.27, 27.68, 27.94, 28.47, 28.97; cyclo-Pr, CH_2: 9.84 (160), 9.95 (160); C: 33.58; CH_3: 22.71 (126), 27.11; CH_2=: 118.46 (156); C=: 145.27
	B	41.16 (141)		91.87	89.95, 90.78	CH_2, cyclo-Bu: 13.46, 14.23, 28.29, 28.43, 28.52, 29.15; cyclo-Pr, CH_2: 10.40, 11.43; C: 33.42; CH_3: 22.80, 25.99; CH_2=: 117.22 (150); C=: 144.98
VIIIc	**A B**	35.02 32.38	127.37 127.51	84.55 85.47	90.40, 91.14 90.36, 90.72	CH_2, cyclo-Bu: 13.60, 14.17, 26.69, 27.82, 28.10, 30.00; CH_3: 26.76; CO: 200.88
						CH_2, cyclo-Bu: 13.16, 14.50, 27.67, 27.73, 28.18, 29.20; CH_3: 25.67; CO: 201.77
VIIIe	**A B**	42.32 44.88	127.82 127.12	80.39 82.89	90.09, 91.19 90.60, 91.99	CH_2, cyclo-Bu: 13.12, 14.20, 26.87, 28.10, 28.18, 29.61; CH_2Cl: 35.72 CH_2, cyclo-Bu: 13.01, 14.31, 27.72, 27.87, 28.59, 28.78; CH_2Cl: 37.44

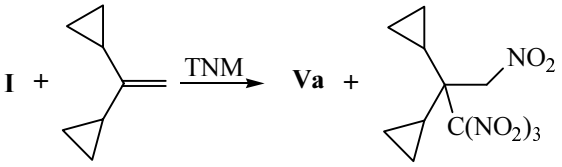
Table 2. (Contd.)

Compd. no.	Diastereomer	C^1	C^3	C^2	C^4, C^5	Other carbon atoms
VIIIf	**A**	37.36 38.15	127.50	79.98	90.16, 90.19	CH_2: 13.59, 14.11, 26.91, 28.11, 28.21, 29.61, 30.09
	B		127.40	82.94	90.56, 90.95	CH_2: 13.47, 14.23, 27.71, 27.95, 28.63, 28.67, 32.24
VIIIi		37.99	128.13	72.46	90.69, 91.12	CH_2, cyclo-Bu: 13.66, 14.10, 26.84, 28.16 (×2), 29.88; C: 107.59; CF: 137.81 d [^1J (C, F) 251, ×2], 142.68 d [^1J (C, F) 262], 145.96 d [^1J (C, F) 251, ×2]
VIIIj		41.32	[a]	82.57	90.24, 91.26	CH_2, cyclo-Bu: 13.66, 14.15, 26.92, 28.20, 28.23, 29.75; CH, Ph: 128.58 (×2), 132.22 (×2); C, Ph: 128.99, 133.31

[a] No signals observed.

(Table 2) the carbon signal of the same CH_2 group is observed in the region δ 38–44 ppm. Spiro carbons in heterocycles **IIIa–c** and the corresponding methine or quaternary carbons of compounds **Va–d** appear as downfield signals at δ 81–93 ppm. The carbons of $C(NO_2)_2$ groups are strongly deshielded (δ 127–129 ppm), and their resonance lines are broadened.

Since in the isoxazolidine molecule alongside an asymmetric nitrogen atom arises a new asymmetric carbon center compounds **IIIc, Va–d** form as mixture of stereoisomers present in various ratios (Tables 1 and 2). It is known [21–23] that N-alkoxysubstituted isoxazolidines possessing bulky substituents are characterized by relatively high barriers to inversion of the nitrogen in the five-membered heterocycle with the values in the range from 60 to 120 kJ mol^{-1}. The presence of an asymmetric carbon center in the isoxazolidines molecules alongside the hindered inversion of nitrogen atom results in conformational diastereomerism.

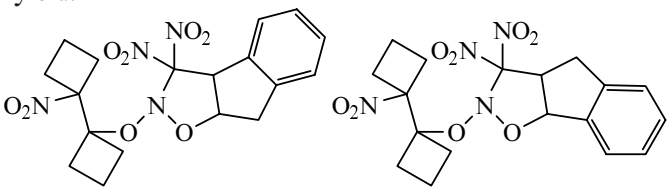


IVb **VI**

It turned out that reaction of 1,1-dicyclo-propylethylene **IVb** with TNM and olefin **I** alongside 3,3-dinitroisoxazolidine **Vb** afforded tetranitropropane **VI** in 1:1 ratio.

Here presumably nitrocarbocations from olefins **I** and **IVb** at treatment with TNM form with comparable rate, and the subsequent C-addition of trinitromethylanion to dicyclopropylcation (**C**, Scheme 1) results in adduct **VI**. We formerly obtained tetranitropropane **VI** as individual product in the two-component reaction of TNM with dicyclopropylethylene [19].

We demonstrated that the synthetic prospects of the three-component reactions between TNM and alkenes can be considerably extended by using as alkene 2 (Scheme 1) a series of olefins with electron-acceptor, aromatic, and heterocyclic substituents **VIIa–j**. Inasmuch the olefins with electron-withdrawing substituents do not directly react with TNM but being dipolarophiles they react with nitronic esters of type 3 (**B**, Scheme 1), the general procedure of mixed heterocyclization consists in a simple mixing of all the three components in 1:1:1 ratio in petroleum ether at 0→20°C. Mixed 3,3-dinitroisoxazolidines **VIIIa–j** were in all cases isolated in good yield.



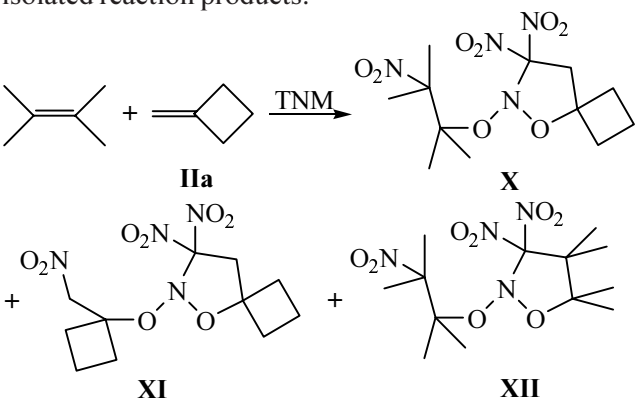
IXa, b

VII, VIII: R = Me, R' = CO_2Me (a); R = H, R' = CN (**b**); R = H, R' = COMe (**c**); R = H, R' = $CH(OEt)_2$ (**d**); R = H, R' = CH_2Cl (**e**); R = H, R' = CH_2Br (**f**) R = H, R' = Ph (**g**); R = H, R' = Py (**h**); R = H, R' = C_6F_5 (**i**); R = H, R' = *p*-Br-C_6H_4 (**j**).

As demonstrated by ^1H and ^{13}C NMR spectra the reaction of TNM with olefins **I** and **VII** occurred like in the above cited case in highly regioselective fashion providing single regioisomers of isoxazolidines **VIIIa–j** (Tables 1 and 2). The formation of two regioisomers **IXa, b** in equal amount as a result of reaction of indene with TNM and bicyclobutylidene is an exception.

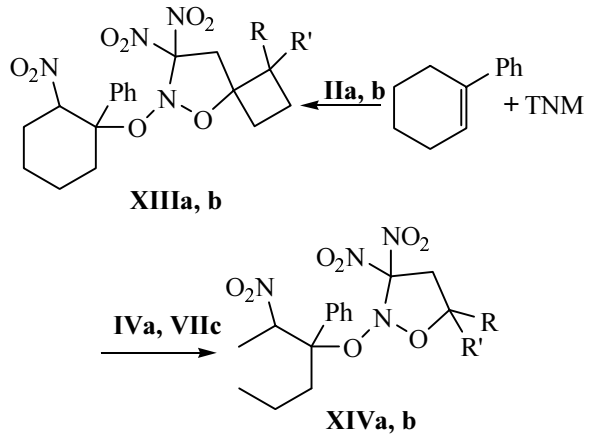
We found that olefins with two electron-withdrawing substituents attached to the double bond did not react with nitronic ester of type 3, and the mixed isoxazolidines do not form. Thus in reactions of TNM and bicyclobutylidene **I** with dimethyl maleate, 4-cyclo-hexene-1,2-dicarbonitrile, coumarin, β-nitrostyrene, and 3,5-dimethylphenylmaleimide we isolated the initial alkenes and

homoisoxazolidine formed from olefin **I** and TNM that we had described before [18]. Interestingly the small amoumts of the same homoisoxazolidine arose also in the three-component reaction between bicyclobutylidene, acrylonitrile, and TNM from olefin (**I**) and TNM. All the other reagents afforded mixed isoxazolidines as the only isolated reaction products.



We investigated the possibility of application in the three-component reactions of TNM with alkenes of the other polysubstituted olefins beside the bicyclobutylidene that could be involved in formation of nitronic ester of type 3 (**A**, Scheme 1).

We found that an equimolar mixture of tetramethylethylene and methylenecyclobutane **IIa** reacted with TNM giving mainly the expected mixed isoxazolidine **X** alongside two homoisoxazolidines **XI** [18] and **XII** [5] in a ratio 3:1:1.



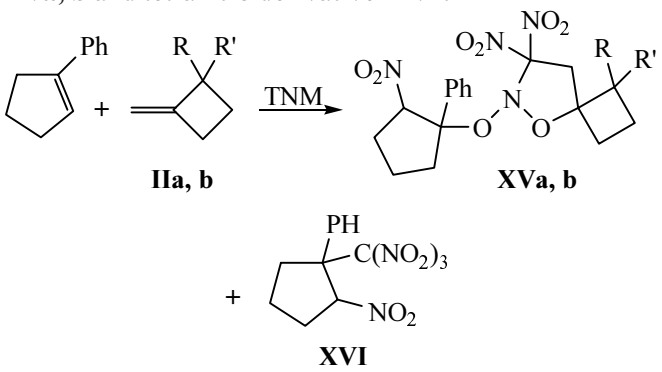
II, XII: R = R' = H (**a**); R, R' = CH_2CH_2 (**b**). **IV, XIV**: R = Me, R' = cyclopropyl (**a**). **VIIc, XIVb**: R = H, R' = Ac.

The low selectivity of the heterocyclization here may be due to poor reactivity toward TNM of the double bond in the tetramethylethylene caused by domination of the steric factors over electronic ones. As a result the rates of nitronic ester formation from tetramethylethylene and methylenecyclobutane become comparable.

The application of three-substituted olefins proved to be more feasible. Phenylcyclohexene was involved into mixed heterocyclization with TNM and olefins containing both electron-donor and electron-acceptor substituents using the ratio of initial reagent 1 : 1 : 1 . The corresponding isoxazolidines of mixed composition **XIIIa, XIIIb** and **XIVa, XIVb** were thus obtained.

The characteristic features of NMR parameters mentioned above provided a possibility of unambiguous structural assignment of compounds **XIII** and **XIV**. NMR spectra of compounds **XIIIa, XIIIb, XIVa, XIVb** evidence that heterocyclization with participation of phenylcyclo-hexene like that with bicyclobutylidene occurred regioselectively furnishing diastereomers in different ratios (Table 3) because of the presence in the structures under discussion of asymmetric carbon atoms and asymmetric nitrogen whose inversion is hampered. Inasmuch as the number of diastereomers is less than possible we believe that in the course of the reaction certain stereocenters arise in a definite relative configuration, and thus the process is diastereoselective.

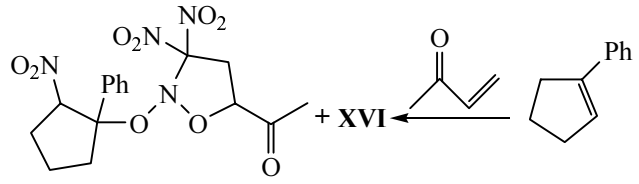
The more strained homolog of 1-phenylcyclohexene, 1-phenylcyclopentene, reacted with TNM and olefins **IIa, b** to furnish a mixture of adducts of the mixed composition **XVa, b** and tetranitro derivative **XVI.**



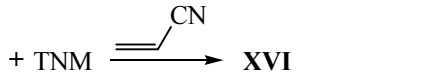
II, XV: R = R' = H (**a**); R, R' = CH_2CH_2 (**b**).

As show NMR data isoxazolidines **XV** were obtained as a mixture of two **XVa** and four **XVb** diastereomers in the ratios 6:5 and 10:8:5:4 respectively. Similar chemical shifts of protons and carbons in the same fragments of isomers **XVa, b** evidence that a single regioisomer is produced by heterocyclization.

As already mentioned, in the three-component reaction with phenylcyclopentene in contrast to the process with phenylcyclohexene beside the principal products **XVa, b** formed tetranitro derivative **XVI**. This version of reaction proved to be the dominant when with TNM and



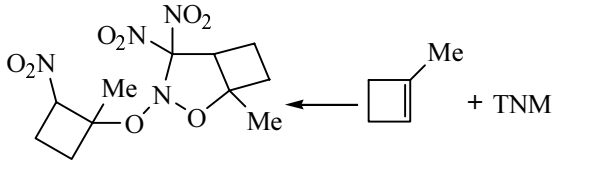
XVII



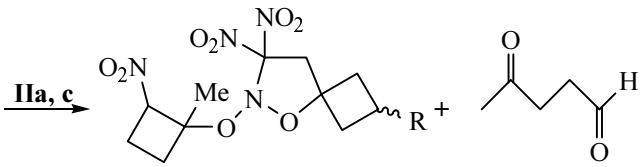
phenylcyclopentene were used olefins containing electron-withdrawing substituents. For instance, bringing into the reaction methyl vinyl ketone resulted in a mixture of products where according to spectral data only 30% consisted of mixed isoxazolidine **XVII** and the main component was tetranitro derivative **XVI.** The latter compound was the only product of the reaction with acrylonitrile

We failed to isolate individual isoxazolidine **XVII**, and therefore it was characterized only by spectral methods. In the ^{1}H NMR spectrum of compound **XVII** appeared a double set of signals in the ratio 5:4, the protons of the CH_2 group in the isoxazolidine ring were observed as two doublets of doublets at δ 3.58 and 3.92 ppm (^2J 15.3 Hz) and δ 3.51 and 3.97 ppm (^2J 15.4 Hz), and the proton signals of the CH fragment gave resonances as doublets of doublets at δ 4.38 ppm (^3J 5.9 Hz, ^3J 9.0 Hz) and δ 4.68 ppm (^3J 5.9 Hz, ^3J 9.0 Hz) respectively.

Note that the reaction of phenylcycloalkenes proper with TNM in the ratio 2:1 furnished the corresponding tetranitro derivatives [2]. This fact and the analysis of our results shows that in the reaction of TNM with these olefins compete two processes: kinetically controlled fast formation of nitronic ester and thermodynamically controlled formation of tetranitro derivative. When the nitronic ester is rapidly removed from the reaction mixture through the cycloaddition to an olefin, the product is



XIX **XVIII**



XXa, c

II, XX: R = H (**a**); **IIc, XXb**: R = CN

isoxazolidine. Otherwise the process is directed to the tetranitro derivative formation [24].

We investigated as olefin 1 (Scheme 1) in reactions with TNM a cyclic alkene with a strained double bond, namely 1-methylcyclobutene **XVIII**. The reaction of TNM with olefin **XVIII** at the initial reagents ratio 1:2 provided homoisoxazolidine **XIX** as a mixture of six isomers in a ratio 10:9:2:1:1:1. Note that the two main isomers are 5,5-disubstituted isoxazolidines: thus the reaction of TNM with methylcyclobutene as in all the other instances proceeded with a high regioselectivity. The number of isomers is apparently due to the presence of several asymmetric centers in the molecule of isoxazolidine **XIX**. Only signals of major isomers in the NMR spectra were attributed for those of the minor isomers were weak and partially overlapped with the stronger signals of the main components (Table 3).

Under conditions of three-component reaction olefin **XVIII** reacted with TNM and olefins **IIa, c** in an expected manner affording mixed isoxazolidines **XXa, b**. A specific feature of these reactions is the formation of a little (8%) levulinaldehyde, a product of oxidative cleavage of methylcyclobutene **XVIII** under the action of TNM.

According to NMR data (Table 3) mixed isoxazolidines **XXa, b** form regioselectively and contain two stereoisomers each. The stereoisomerism is caused by formation during the heterocyclization of three asymmetric centers (taking into account the asymmetric nitrogen atom characterized by the hampered inversion). The reciprocal *cis*-position of the methyl group and the proton from the $CHNO_2$ was proved by Overhauser effect. Thus TNM adds stereoselectively across the double bond of the methylcyclobutene, and the asymmetric centers arising in the course of reaction acquire a definite relative configuration.

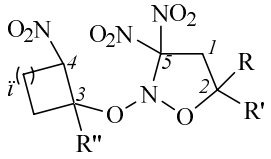
Alkenes possessing strong electron-withdrawing substituents (acrylonitrile, methyl methacrylate) were not involved into heterocyclization with TNM and olefin **XVIII**, and these reactions yielded as the main product homoisoxazolidine **XIX**.

Thus in this study we developed a convenient preparative procedure for alkoxy-substituted 3,3-dinitroisoxazolidines of a mixed composition based on a three-component reaction of TNM with two different olefins.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered from solutions of compounds in $CDCl_3$ on spectrometers

Table 3. ^{13}C NMR spectra of isoxazolidines **XIII–XV, XIX**, and **XX**



Compd. no.	Diastereomer	C^1	C^2	C^3	C^4	C^5	R^1, R^2	Other groups of atoms	R^3			
									R^3 = Ph			
									ortho	*meta*	*para*	*ipso*
XIIIa	**A**	44.02	88.12	82.92	85.22	127.32	CH_2, cyclo-Bu: 12.96, 34.59,	CH_2, cyclo-Hex: 18.88,	126.80	128.24	129.27	137.07
	B	44.21	87.92	83.99	85.33	[a]	37.64	20.35, 27.71, 28.42	126.54	128.36	129.11	137.34
XIIIb	**A**	43.69	91.86	84.26	85.57	127.84	CH_2, cyclo-Pr: 9.32, 10.36; CH_2, cyclo-Bu, cyclo-Hex, C_{spiro}: 19.63, 20.88, 24.07, 28.28, 28.56, 29.33, 33.53		126.65	128.54	129.26	137.53
	B	41.59	89.41	83.57	85.76	[a]	CH_2, cyclo-Pr: 8.49, 11.28; CH_2, cyclo-Bu, cyclo-Hex, C_{spiro}: 19.06, 20.61, 23.53, 27.81, 28.83, 29.03, 33.81		126.99	128.44	129.50	137.15
	C	43.69	91.92	83.09	85.22	[a]	CH_2, cyclo-Pr: 9.27, 10.48; CH_2, cyclo-Bu, cyclo-Hex, C_{spiro}: 19.06, 20.61, 23.95, 27.94, 28.73, 28.83, 35.81		126.90	128.40	129.50	136.98
	D	41.59	[a]	83.25	85.65	[a]	CH_2, cyclo-Pr: 7.99, 11.45; CH_2, cyclo-Bu, cyclo-Hex, C_{spiro}: 19.22, 20.65, 23.12, 29.33, 33.82		127.29	[a]	[a]	136.80
XIVa	**A, B**	44.07, 45.44	88.80, 90.00	83.26, 84.27	85.10, 85.33	127.84 [a]	cyclo-Pr, CH_2: 1.60, 1.82, 2.68, 3.61;	18.94, 19.59, 20.10, 21.13, 27.45, 28.25, 28.88, 29.65	126.68, 127.05	128.19, 128.34	129.10, 129.38	136.48, 137.40
XIVb	**A**	35.52	83.55	83.85	85.84	127.10	CH_3: 26.17; CO: 200.75	18.65, 20.37, 26.63, 27.50	126.46	128.37	129.31	138.57
	B	35.62	83.61	85.78	85.26	[a]	CH_3: 26.52; CO: 201.00	19.83, 21.13, 28.43, 31.17	126.66	128.44	129.40	137.00
XVa	**A**	44.06	88.85	98.12	92.13	127.67	13.21, 22.13, 31.12, 33.84, 34.52, 37.96		127.81	128.40	129.31	134.89
	B	44.14	88.79	97.95	91.84	[a]	13.35, 22.28, 31.03, 33.61, 34.36, 38.07		128.36	128.46	130.32	135.25
XVb	**A, B,**	40.77,	91.02,	97.47,	92.32,	126.73	CH_2, cyclo-Pr: 10.17, 9.21, 9.13, 10.15, 7.55, 8.02, 11.41,		127.54	128.17	129.42	134.49,
	C, D	42.91,	91.38,	97.80,	91.82,	[a]	11.58; CH_2, cyclo-Pen, cyclo-Bu, C_{spiro}: 21.96, 22.11, 22.48,		127.54	128.17	129.08	134.59,
		43.03,	91.80,	97.94,	91.73,	[a]	22.54, 22.60, 23.01, 23.47, 23.74, 23.85, 28.00, 28.17, 29.42,		127.60	128.17	129.24	135.07,
		42.88	91.70	97.80	92.58	[a]	29.72, 30.78, 30.96, 31.10, 31.19, 31.91, 32.83, 33.00, 33.28,		127.60	128.17	129.50	135.14
XIX	**A**	50.01	86.60,	86.49,	81.66	128.86	CH_2: 16.04, 17.92, 25.75, 31.18; CH_3: 22.25		CH_3: 18.21			
	B	50.69	86.66,	89.63	81.46	130.26	CH_2: 16.60, 17.87, 26.62, 31.70; CH_3: 22.94		CH_3: 18.36			
XXa	**A**	43.95	90.80	85.84	81.56	128.30	CH_2: 13.61, 17.95, 25.38, 34.12, 38.93		CH_3: 18.39			
	B	43.87	89.86	83.98	81.30	128.25	CH_2: 13.52, 18.09, 26.40, 34.24, 39.09		CH_3: 18.72			
XXb	**A, B,**	43.33	88.95	85.96	81.06	127.49	CHCN: 16.14; CH_2: 17.99, 24.92, 37.73, 42.07; CN: 121.20		CH_3: 17.64.			
	C, D	43.45,	87.98,	86.00,	81.00	127.17	CHCN: 16.14, 14.64, 14.62; CH_2: 17.77, 18.00, 19.05, 24.95,		CH_3: 17.77, 18.26, 18.28.			
		43.71,	88.18[a]	86.05,	81.06		26.08, 26.04; 37.75, 38.07, 37.45, 42.98, 42.07, 42.78; CN:					
		43.20		86.15	81.10		121.00, 120.25, 120.14					

[a] No signals observed.

Varian VXR-400 at operating frequencies 400 and 100 MHz respectively and Bruker DPX-300 at operating frequencies 300 and 75 MHz respectively. The chloroform signals were used as internal standards (δ_H 7.24, δ_C 77.10 ppm). Mass spectra on Varian MAT-311A instrument at ionizing electrons energy 70 eV were measured.

TNM was prepared from acetic anhydride and concentrated HNO_3 (d_4^{20} 1.5) by procedure [25]. Initial olefins were synthesized by the following known methods: vinylcyclopropane, [26]; 1,1-dicyclopropyl-ethylene, [27]; 1,1-diisopropenylcyclopropane, [28]; diethyl-2-vinylcyclopropane-1,1-dicarboxylate, [29]; tetramethyl-ethylene, [30]; 1-methylcyclobut-1-ene, [31]. Besides the commercial samples of bicyclo-butylidene, methylenecyclobutane, 4-methylenespiro-[2.3]hexane, 1-phenyl-1-cyclopentene, and 1-phenyl-1-cyclohexene were applied.

General procedure for preparation of isoxazolidines of a mixed composition. (a) With a preliminary nitronic ester generation. To a solution of TNM (2.5 mmol) in 5 ml of hexane cooled to 0°C was added within 30 min at stirring a solution of olefin 1 (2.5 mmol) in 5 ml of hexane. The mixture was stirred for 30 min more at 0°C, and a solution was added within 30 min of olefin 2 (2.5 mmol) in 5 ml of hexane. The reaction mixture was stored at room temperature for 24–48 h. Then the solvent was evaporated, the residue was dissolved in 1 ml $CHCl_3$. The products were isolated by column chromatography (eluent chloroform).

(b) One-pot synthesis. To a solution of olefin 2 (2.5 mmol) and TNM (2.5 mmol) in 7 ml of hexane cooled to 0°C was added within 1.5 h at stirring a solution of olefin 1 (2.5 mmol) in 7 ml of hexane. The reaction mixture was stored at room temperature for 24–48 h and then worked up as in procedure (a).

7,7-Dinitro-6-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-oxa-6-aza-spiro-[3.4]-octane (IIIa). (a) Yield 0.43 g (46%), mp 41–42°C, R_f 0.43 ($CHCl_3$). Found, %: C 45.07; H 5.07. $C_{14}H_{20}N_4O_8$. Calculated, %: C 45.16; H 5.38.

9,9-Dinitro-8-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-7-oxa-8-azadispiro-[2.2.4.0]decane (IIIb). (a) Yield 0.66 g (67%) (mixture of two diastereomers, **A**/**B**[*] = 6:5), R_f 0.71 ($CHCl_3$). Mass spectrum, *m/z* (I_{rel} %): 352 (1) $[M - NO_2]^+$, 228 (5), 182 (16), 170 (31), 154 (30), 140 (37), 124 (73), 107 (55), 96 (69), 81 (70), 68 (100), 55 (87).

7,7-Dinitro-6-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-2-cyano-5-oxa-6-aza-spiro-[3.4]octane (IIIc). (b)Yield 0.65 g (66%) (mixture of two diastereomers, **A**/**B** = 4:1), mp 86–90°C, R_f 0.20 ($CHCl_3$). Found, %: C 45.49; H 4.85; N 17.38. $C_{15}H_{19}N_5O_8$. Calculated, %: C 45.34; H 4.79; N 17.63.

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-cyclopropylisoxazolidine (Va). (a) Yield 0.87 g (68%) (mixture of two diastereomers, **A**/**B** = 5:1), mp 62–69°C, R_f 0.60 ($CHCl_3$). Found, %: C 45.46; H 5.52; N 15.45. $C_{14}H_{20}N_4O_8$. Calculated, %: C 45.16; H 5.38; N 15.05.

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5,5-dicyclopropylisoxazolidine (Vb). (a) Yield 0.26 g (25%), R_f 0.77 ($CHCl_3$). Found, %: C 49.41; H 6.28; N 13.59. $C_{17}H_{24}N_4O_8$. Calculated, %: C 49.51; H 5.83; N 13.59.

Diethyl 2-{3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]isoxazolidine-5-yl}-cyclopropane-1,1-dicarboxylate (Vc). (b) Yield 0.52 g (43%) (mixture of four diastereomers). After chromatographic separation two fractions were obtained containing two diastereomers each: oily substance with R_f 0.57 ($CHCl_3$), and crystalline compound with R_f 0.36 ($CHCl_3$), mp 94–98°C. Found, %: C 46.30; H 5.41. $C_{20}H_{28}N_4O_{12}$. Calculated, %: C 46.51; H 5.43.

5-(1-Isopropenylcyclopropyl)-5-methyl-3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yl-oxy]isoxazolidine (Vd). (a) Yield 0.35 g (33%) (mixture of two diastereomers, **A**/**B** = 3:1), R_f 0.66 ($CHCl_3$). Found, %: C 50.73; H 6.13. $C_{18}H_{26}N_4O_8$. Calculated, %: C 50.70; H 6.10.

Methyl 5-methyl-3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]isoxazolidine-5-carboxylate (VIIIa). (b) Yield 0.60 g (59%) (mixture of two diastereomers, **A**/**B** = 2:1), R_f 0.65 ($CHCl_3$). Found, %: C 41.92; H 4.92. $C_{14}H_{20}N_4O_{10}$. Calculated, %: C 41.58; H 4.95.

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-cyanoisoxazolidine (VIIIb). (b) Yield 0.32 g (56%) (mixture of two diastereomers, **A**/**B** = 3:1), mp 116–117°C, R_f 0.17 ($CHCl_3$). ^1H and ^{13}C NMR spectra were registered from solution of compound **VIIIb** in $CDCl_3$–DMSO-d_6. Found, %: C 40.01; H 3.76; N 20.07. $C_{12}H_{15}N_5O_8$. Calculated, %: C 40.34; H 4.20; N 19.61.

5-Acetyl-3,3-dinitro-2-[1'-nitro-1,1'- bi(cyclobutyl)-1-yloxy]isoxazolidine (VIIIc). (a) Yield 0.61 g (65%) (mixture of two diastereomers, **A**/**B** = 3:2), mp 83–85°C (EtOH). Found, %: C 42.22; H 4.58; N 14.67.

[*] Isomers ratio here and hereinafter was determined by ^1H NMR spectroscopy.

$C_{13}H_{18}N_4O_9$. Calculated, %: C 41.71; H 4.81; N 14.97.

5-Diethoxymethyl-3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]isoxazolidine (VIIId). (a) Yield 0.56 g (52%) (mixture of two diastereomers, **A**/**B** = 15:1), mp 47–48°C, R_f 0.63 ($CHCl_3$). Found, %: C 44.46; H 6.09. $C_{16}H_{26}N_4O_{10}$. Calculated, %: C 44.24; H 5.99.

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-chloromethylisoxazolidine (VIIIe). (a) Yield 0.37 g (39%) (mixture of two diastereomers, **A**/**B** = 3:1); R_f 0.33 ($CHCl_3$). Mass spectrum, *m/z* ($I_{rel.}$, %): 306, 304 (5) $[M - NO_2–NO]^+$, 226 (7), 210 (16), 180 (30), 164 (28), 140 (22), 124 (68), 115 (58), 95 (62), 81 (74), 70 (69), 55 (100). Found, %: C 37.32; H 4.55. $C_{12}H_{17}ClN_4O_8$. Calculated, %: C 37.82; H 4.47.

5-Bromomethyl-3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]isoxazolidine (VIIIf). (a) Yield 0.53 g (50%) (mixture of two diastereomers, **A**/**B** = 4:1), R_f 0.31 ($CHCl_3$). Mass spectrum, *m/z* (I_{rel}, %): 348, 350 (5) $[M - NO_2–NO]^+$, 205, 207 (11), 192, 194 (22), 147, 149 (31), 147, 149 (78), 123 (100), 102 (41).

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-phenyl-isoxazolidine (VIIIg). (a) Yield 0.51 g (50%) (mixture of two diastereomers, **A**/**B** = 6:1), R_f 0.68 ($CHCl_3$). Found, %: C 49.95; H 4.90. $C_{17}H_{20}N_4O_8$. Calculated, %: C 50.00; H 4.90. 3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-(4-pyridyl)isoxazolidine (**VIIIh**).

(b) Yield 0.25 g (24%) (mixture of two diastereomers, **A**/**B** = 8:1), R_f 0.68 ($CHCl_3$). Mass spectrum, *m/z* ($I_{rel.}$, %): 362 (1) $[M - HNO_2]^+$, 348 (1) $[M - HNO_2–CH_2]^+$, 333 (4), 288 (4), 193 (7), 170 (13), 146 (24), 123 (92), 106 (100), 96 (68), 78 (86), 55 (98).

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-5-pentafluorophenylisoxazolidine (VIIIi). (a) Yield 0.43 g (35%), mp 95–96°C, R_f 0.30 ($CHCl_3$). МаСС-Спектр, *m/z* ($I_{rel.}$, %): 405 (2) $[M - 2NO_2–H]^+$, 328 (6), 299 (31), 239 (34), 195 (60), 181 (42), 168 (43), 143 (49), 123 (72), 88 (100), 69 (87), 55 (94), 46 (77). Found, %: C 43.47; H 3.80; N 10.87. $C_{17}H_{15}F_5N_4O_8$. Calculated, %: C 40.96; H 3.01; N 11.24.

5-(4-Bromophenyl)-3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-isoxazolidine (VIIIj). (a) Yield 0.8 g (66%), R_f 0.30 ($CHCl_3$). Found, %: C 41.13; H 3.67. $C_{17}H_{19}BrN_4O_8$. Calculated, %: C 41.89; H 3.90.

3,3-Dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-3,3a,4,8b-tetrahydro-2H-indeno[2,1-d]-isoxazole (IXa) and 3,3-dinitro-2-[1'-nitro-1,1'-bi(cyclobutyl)-1-yloxy]-3,3a,8,8a-tetrahydrO-2H-indeno[1,2-d]isoxazole (IXb). (a) Yield 0.53 g (50%) (mixture of two regioisomers in a ratio 1:1), R_f 0.90 ($CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz), of the mixture of two isomers: 1.30–3.40 m (13H + 14H), 3.39 d.d [1H, $C\underline{H}_2CHC(NO_2)_3$, ^2J 17.5, ^3J 9.7, 14a], 4.72 m [H, $CHC(NO_2)_3$, 14a], 5.44 d [1H, $CHC(NO_2)_3$, ^{3}J 6.9, 14b], 5.56 m (1H, CHO, 14b), 6.08 d (1H, CHO, ^{3}J 6.9, 14a), 7.20–7.44 m (4H + 4H, Ph). ^{13}C NMR spectrum, δ, ppm, of the mixture of two isomers: 14.82, 14.97, 15.52 (2×), 28.37, 28.53, 29.30, 29.50 (2×), 29.89, 30.52, 31.11 (CH_2, cyclo-Bu), 34.21 ($\underline{C}H_2Ph$), 36.90 ($\underline{C}H_2Ph$), 50.73 [$\underline{C}HC(NO_2)_3$], 58.75 [$\underline{C}HC(NO_2)_3$], 89.16 (CHO), 91.14, 91.30 (C, cyclo-Bu), 92.61 (2×C, cyclo-Bu), 93.45 (CHO), 126.40 (CH, Ph), 126.81 (CH, Ph), 127.21 (2× CH, Ph), 129.20 (CH, Ph), 129.31 (CH, Ph), 131.46 (CH, Ph), 132.20 (CH, Ph), 133.08 [$C(NO_2)_3$], 133.63 [$C(NO_2)_3$], 134.28 (C, Ph), 136.81 (C, Ph), 142.65 (C, Ph), 143.37 (C, Ph). Mass spectrum, m/z ($I_{rel.}$, %): 374 (2) $[M - NO_2]^+$, 344 (14) $[M - NO_2–NO]^+$, 250 (13), 204 (61), 158 (70), 143 (84), 128 (82), 116 (74), 103 (76), 96 (70), 77 (61), 55 (100). Found, %: C 51.34; H 4.96; N 12.98. $C_{18}H_{20}N_4O_8$. Calculated, %: C 51.43; H 4.76; N 13.33.

7,7-Dinitro-6-(2-nitro-1-phenylcyclo-hexyloxy)-5-oxa-6-azaspiro[3.4]octane (XIIIa). (a) Yield 0.47 g (45%) (mixture of two diastereomers, **A**/**B** = 7:5), mp 113–114°C (EtOH). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 1.50–2.82 m (14H + 14H, cyclo-Bu, cyclo-Hex), 3.28 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **B**], 3.29 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **A**), 3.82 br.d [1H + 1H, $CH_2C(NO_2)_3$, ^2J 14.9), 5.38 m (1H, $CHNO_2$, **B**), 5.68 m (1H, $CHNO_2$, **A**), 7.32–7.37, 7.39–7.43, 7.48–7.75 m (5H + 5H, Ph). Found, %: C 51.30; H 5.45. $C_{18}H_{22}N_4O_8$. Calculated, %: C 51.18; H 5.21.

9,9-Dinitro-8-(2-nitro-1-phenylcyclohexyloxy)-7-oxa-8-azadispiro[2.2.4.0]decane (XIIIb). (a) Yield 0.23 g (21%) (mixture of four diastereomers, **A**/**B**/**C**/**D** = 16:9:6:2); mp 143–144°C (EtOH). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 0.08–0.92 m (4H + 4H + 4H + 4H, cyclo-Pr), 1.50–2.75 m (12H + 12H + 12H + 12H, cyclo-Bu, cyclo-Hex), 3.21 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **B**], 3.23 d [1H, $CH_2C(NO_2)_3$, ^2J 15.2 **A**], 3.25 [*AB*-system, 1H, $CH_2C(NO_2)_3$, ^2J 15.3 **C**], 3.26 [*AB*-system, 1H, $CH_2C(NO_2)_3$, ^2J 15.1, **D**], 3.45 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **B**), 3.54 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **D**], 3.83 d [1H, $CH_2C(NO_2)_3$, ^2J 15.2, **A**], 3.84 d [1H, $CH_2C(NO_2)_3$, ^2J 15.3, **C**], 5.33 m (1H, $CHNO_2$, **A**), 5.43 m (1H, $CHNO_2$, **D**), 5.58 m (1H, $CHNO_2$, **B**), 5.74 m (1H, $CHNO_2$, **C**), 7.27–7.52 m (5H + 5H + 5H + 5H, Ph).

Found, %: C 53.57; H 5.40; N 12.31. $C_{20}H_{24}N_4O_8$. Calculated, %: C 53.57; H 5.36; N 12.50.

5-Methyl-3,3-dinitro-2-(2-nitro-1-phenylcyclohexyloxy)-5-cyclopropyl-cycloxazolidine (XIVa). (a) Yield 0.49 g (45%) (mixture of two diastereomers, **A**/**B** = 1:1), mp 129–130°C (EtOH). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 0.30–0.95 m (5H + 5H, cyclo-Pr), 0.98 C (3H, CH_3), 1.20–1.48 m (1H + 1H), 1.50 c (3H, CH_3), 1.54–1.90 m (3H + 3H), 2.10–2.80 m (4H + 4H), 2.94 d [1H, $CH_2C(NO_2)_3$, ^2J 15.3, **A**], 3.12 d [1H, $CH_2C(NO_2)_3$, ^2J 15.3, **B**], 3.63 d [1H, $CH_2C(NO_2)_3$, ^2J 15.3, **B**], 3.65 d [1H, $CH_2C(NO_2)_3$, ^2J 15.3, **A**], 5.44 m (1H, $CHNO_2$, **A**), 5.83 m (1H, $CHNO_2$, **B**), 7.35, 7.41, 7.52 m (5H + 5H, Ph). Found, %: C 52.54; H 5.44; N 12.80. $C_{19}H_{24}N_4O_8$. Calculated, %: C 52.41; H 5.29; N 12.87.

5-Acetyl-3,3-dinitro-2-(2-nitro-1-phenylcyclohexyloxy)isoxazolidine (XIVb). (a) Yield 0.40 g (38%) (mixture of four diastereomers, **A**/**B**/**C**/**D** = 10:9:2:1), R_f 0.70 ($CHCl_3$). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 1.50–3.05 m (8H + 8H + 8H + 8H, iso-Hex), 1.75 C (3H, CH_3, **A**), 1.96 C (3H, CH_3, **D**), 2.01 C (3H, CH_3, **C**), 2.06 C (3H, CH_3, **B**), 3.23 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.2, ^3J 7.9, **C**], 3.30 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.4, ^3J 8.4, **D**], 3.33 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.5, ^3J 5.8, **A**)], 3.38 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.5, ^3J 5.9, **B**], 3.82 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.5, ^3J 8.9, **A**], 3.85 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.5, ^3J 9.0, **B**], 4.18 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.4, ^3J 7.1, **D**], 4.20 d.d [1H, $CHCH_2C(NO_2)_3$, ^2J 15.2, ^3J 8.0, **C**], 4.49 d.d [1H, $CHCH_2C(NO_2)_3$, ^3J 8.4, ^3J 7.1, **D**], 4.52 d.d [1H, $CHCH_2C(NO_2)_3$, ^3J 7.9, ^3J 8.0, **C**], 4.73 d.d [1H, $CHCH_2C(NO_2)_3$, ^3J 5.8, ^3J 8.9, **A**], 5.09 d.d [1H, $CHCH_2C(NO_2)_3$, ^3J 5.9, 9.0, **B**], 5.30 m (1H, $CHNO_2$, **B**), 5.39 m (1H, $CHNO_2$, **C**), 5.49 m (1H, $CHNO_2$, **A**), 5.52 m (1H, $CHNO_2$, **D**), 7.30–7.60 m (5H+ 5H + 5H + 5H, Ph).

7,7-Dinitro-6-(2-nitro-1-phenylcyclo-pentyloxy)-5-oxa-6-azaspiro[3.4]octane (XVa). (a) Yield 0.45 g (45%) (mixture of two diastereomers, **A**/**B** = 6:5), mp 146–147°C (EtOH). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 1.55–3.05 m (12H + 12H), 3.27 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **A**], 3.28 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **B**], 3.78 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **B**], 3.79 d [1H, $CH_2C(NO_2)_3$, ^2J 15.1, **A**], 5.55 d.d [1H, $CHNO_2$, ^2J 3.1, ^3J 7.6, **B**], 5.68 br.d [1H, $CHNO_2$, ^3J 7.1, **A**], 7.20–7.50 m (5H + 5H, Ph). Found, %: C 50.12; H 4.85; N 13.48. $C_{17}H_{20}N_4O_8$. Calculated, %: C 50.00; H 4.90; N 13.73.

9,9-Dinitro-8-(2-nitro-1-phenylcyclopentyloxy)-7-oxa-8-azadispiro[2.2.4.0]decane (XVb). (a) Yield 0.44 g (41%) (mixture of four diastereomers, **A**/**B**/**C**/**D** = 10:8:5:4), R_f 0.64 ($CHCl_3$). ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 0.05–0.90 m (4H + 4H + 4H + 4H, cyclo-Pr), 1.50–3.20 m (10H + 10H + 10H + 10H), 3.24 d [1H, $CH_2C(NO_2)_3$, ^2J 15.4, **A**], 3.26 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **D**], 3.33 d [1H, $CH_2C(NO_2)_3$, ^2J 15.5, **B**], 3.33 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **C**], 3.55 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **C**], 3.57 d [1H, $CH_2C(NO_2)_3$, ^2J 14.9, **D**], 3.82 d [1H, $CH_2C(NO_2)_3$, ^2J 15.5, **B**], 3.84 d [1H, $CH_2C(NO_2)_3$, ^2J 15.4, **A**], 5.50 m (1H, $CHNO_2$, **A**), 5.55 m (1H, $CHNO_2$, **B**), 5.98 m (1H, $CHNO_2$, **C**), 6.24 m (1H, $CHNO_2$, **D**), 7.25–7.50 m (5H + 5H +5H + 5H, Ph). Mass spectrum, *m/z* (I_{rel}, %): 387 (1) [M – NO_2–H]$^+$, 341 (2) [M – 2NO_2–H]$^+$, 340 (15) [M – 2NO_2–2H]$^+$, 293 (1) [M – 3NO_2–3H]$^+$, 264 (8), 189 (42), 170 (52), 157 (62), 143 (81), 128 (78), 105 (100), 68 (100), 55 (87).

1-Methyl-3-(1-methyl-2-nitrocyclobutoxy)-4,4-dinitro-2-oxa-3-azabicyclo[3.2.0]heptane (XIX) (mixture of diastereomers 10:9:2:1:1:1). Yield 0.75 g (45%), mp 88–95°C, R_f 0.40. ^{1}H NMR spectrum of the mixture of two main isomers, δ, ppm: 1.44, 1.33, 1.59, 1.63 s (CH_3), 1.8–2.50 m (cyclo-Bu), 3.83, 3.92 m [1H + 1H, $CHC(NO_2)_3$], 5.45 m (1H + 1H, $CHNO_2$). Found, %: C 39.90; H 4.83. $C_{11}H_{16}N_4O_8$. Calculated , %: C 39.76; H 4.82.

6-(1-Methyl-2-nitrocyclobutoxy)-7,7-dinitro-5-oxa-6-azaspiro[3.4]octane (XXa). (a) Yield 0.23 g (28%) (mixture of two diastereomers, **A**/**B** = 2/1), R_f 0.55. ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 1.55–2.61 m (10H + 10H, cyclo-Bu), 1.18 s (3H, CH_3, **A**), 1.29 s (3H, CH_3, **B**), 3.32 d [1H, $CH_2C(NO_2)_3$, ^2J 15.7, **B**], 3.36 d [1H, $CH_2C(NO_2)_3$, ^2J 15.7, **A**], 3.81 [*AB*-system, 1H, $CH_2C(NO_2)_3$, ^2J 15.7, **A**], 3.85 [*AB*-system, 1H, $CH_2C(NO_2)_3$, ^2J 15.7, **B**], 5.18 t (1H, $CHNO_2$, ^3J 9.3, **B**), 5.48 t (1H, $CHNO_2$, ^3J 9.3, **A**). Found, %: C 39.33; H 5.14. $C_{11}H_{16}N_4O_8$. Calculated, %: C 39.76; H 4.82.

6-(1-Methyl-2-nitrocyclobutoxy)-7,7-dinitro-2-cyano-5-oxa-6-azaspiro[3.4]octane (XXb). (a) Yield 0.30 g (34%) (mixture of four isomers, **A**/**B**/**C**/**D** = 14:6:5:3), mp 112–113°C (EtOH), R_f 0.16. ^{1}H NMR spectrum of isomer mixture, δ, ppm (*J*, Hz): 1.72–2.85 m (9H + 9H + 9H +9H, cyclo-Bu), 1.15 s (3H, CH_3, **A**), 1.17, 1.25, 1.28 s (3H, CH_3, **B**, **C**, **D**), 3.41 d [1H,

$CH_2C(NO_2)_3$, ^2J 15.8, **C**], 3.52 d [1H, $CH_2C(NO_2)_3$, ^2J 16.0, **A**], 3.54 d [1H, $CH_2C(NO_2)_3$, ^2J 15.7, **B**], 3.78 d [1H, $CH_2C(NO_2)_3$, ^2J 15.7, **B**], 3.84 d [1H, $CH_2C(NO_2)_3$, ^2J 15.8, **D**], 3.86 d [1H, $CH_2C(NO_2)_3$, ^2J 15.2, **C**], 3.87 d [1H, $CH_2C(NO_2)_3$, ^2J 15.7, **A**], 5.12 t (1H, $CHNO_2$, ^3J 9.0, **B**), 5.15 t (1H, $CHNO_2$, ^3J 9.0, **C**), 5.41 t (1H, $CHNO_2$, ^3J 9.0, **D**), 5.43 t (1H, $CHNO_2$, ^3J 9.0, **A**). Found, %: C 40.74; H 4.10; N 19.83. $C_{12}H_{15}N_5O_8$. Calculated, %: C 40.34; H 4.20; N 19.61.

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REFERENCES

1. Altukhov, K.V. and Perekalin, V.V., *Usp. khim*., 1976, vol. 45, p. 2050.
2. Altukhov, K.V., Tartakovskii, V.A., Perekalin, V.V., and Novikov, S.S., *Izv.* Akad. Nauk *SSSR. Ser. Khim.,* 1966, vol. 1, 197; Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1966, vol. 2, 1902; Andreeva, L.M., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1967, vol. 5, p. 220; Buevich, V.A., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1970, vol. 6, p. 187; Tartakovskii, V.A., Buevich, V.A., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1971, vol. 7, 1080; Buevich, V.A., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1971, vol. 7, p. 1380.
3. Buevich, V.A., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1970, vol. 6, p. 658.
4. Ratsino, E.V., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1972, vol. 8, p. 523.
5. Altukhov, K.V. and Perekalin, V.V., *Zh. Org. Khim.,* 1967, vol. 3, p. 2003.
6. Ratsino, E.V., Altukhov, K.V. and Pereklin, V.V., Zh. *Org. Khim.,* 1973, vol. 9, p. 58.
7. Ratsino, E.V. and Altukhov, K.V., Zh*., Org. Khim.,* 1972, vol. 8, p. 2281.
8. Altukhov, K.V., Ratsino, E.V. and Perekalin, V.V., *Zh. Org. Khim.,* 1969, vol. 5, p. 2246.
9. Andreeva, L.M., Altukhov, K.V. and Perekalin, V.V., *Zh. Org. Khim.,* 1969, vol. 5, p. 1313; Andreeva, L.M., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1972, vol. 8, p. 1419.
10. Buevich, V.A., Altukhov, K.V., and Perekalin, V.V., *Zh. Org. Khim.,* 1967, vol. 3, p. 2248.
11. Penzek, S., Jagur-Grodzinski, J., and Szware, M. , *J. Am. Chem. Soc.,* 1968, vol. 90, p. 2174.
12. Rathore, R., Lin, Z., and Kochi, J.K., *Tetrahedron Lett.,* 1993, vol. 34, p. 1859.
13. Rathore, R. and Kochi, J.K., *J. Org. Chem.,* 1996, vol. 61, p. 627.
14. Shveikhgeimer, G.A., Sobtsova, N.I., and Baran'ski, A., *Roczn. Chem.,* 1972, vol. 46, p. 1741.
15. Eberson, L., Hartshorn, M.P., and Persson, O., *Acta Chem. Scand.,* 1998, vol. 52, p. 745.
16. Eberson, L., Hartshorn, M.P., and Persson, O., *Acta Chem. Scand.,* 1998, vol. 52, p. 751.
17. Berg, U., Butts, C.P., Eberson, L., Hartshorn, M.P., and Persson, O., *Acta Chem. Scand.,* 1998, vol. 52, p. 761.
18. Averina, E.B., Ivanova, O.A., Grishin, Yu.K., Kuznetsova, T.S., and Zefirov, N.S., Zh. *Org. Khim.,* 2000, vol. 36, p. 1609.
19. Ivanova, O.A., Averina, E.B., Grishin, Yu.K., Kuznetsova, T.S., and Zefirov, N.S., *Dokl. Akad. Nauk*, 2002, vol. 382, p. 71.
20. Torsell, K.B.G., Nitrile, *Oxides, Nitrones, and Nitronates in Organic Synthesis,* New York: VCH, Publ., 1988, p. 332.
21. Isaacs, N.S. and Abed, O.H., *Tetrahedron Lett.,* 1982, vol. 23, p. 2799.
22. Lagodzinskaya, G.V., Zh. *S. Khim.*, 1970, vol. 11, p. 31.
23. Rudchenko, V.F., *Chem. Rev.,* 1993, vol. 93, p. 725.
24. Altukhov, K.V, Ratsino, E. V., and Perekalin, V.V., Zh. *Org. Khim.,* 1973, vol. 9, p. 269.
25. *Sint. Org. Prep.,* Moscow: Izd. Inostr. Lit., 1952, vol. 3, p. 411.
26. Crawford, R.J. and Cameron, D.M., *Canad. J. Chem.,* 1967, vol. 45, p. 691.
27. Zefirov, N.S., Kuznetsova, T.S., Budyka, M. I., and Koz'min, A.S., *Zh. Org. Khim.,* 1978, vol. 14, p. 2006.
28. Zefirov, N.S., Kuznetsova, T.S., Kozhushkov, S.I., Gleiter, R., and Ekkert-Makshich, M., Zh. *Org. Khim.,* 1986, vol. 22, p. 110.
29. Zefirov, N.S., Kozhushkov, S.I., Kuznetsova, T.S., Sosonkin, I.M., Domarev, A.M., Leibzon, V.N., and Egorova, T.I., *Zh. Org. Khim.,* 1987, vol. 23, p. 2109.
30. *Weygand-Hilgetag Organisch-chemische Experimentierkunst,* Hilgetag, G. and Martini, A., Eds., Leipzig: Johann Ambrosius Barth, 1964, 3rd ed. Translated under the title *Metody eksperimenta v organicheskoi khimii*, Moscow: Khimiya, 1968, p. 673.
31. Person, A.L. and Thamattoor, D.M., *Synth. Commun.,* 1999, vol. 29, p. 2973.