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3-Nitro- and 3-Bromo-3-nitroacrylates in Reactions with Phenyl Azide

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Abstract — 1,3-Dipolar cycloaddition of alkyl 3-nitro- and 3-bromo-3-nitroacrylates to phenyl azide gives regioisomeric alkyl 5(4)-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4(5)-carboxylates, the corresponding triazoles both with and without nitro group, and alkyl 3-nitro-1-phenylaziridine-2-carboxylates. Nitrotriazolecarboxylates were found to lose the ester moiety during chromatographic separation of the products on aluminum oxide. The structure of the products was determined on the basis of IR, ^{1}H NMR, and X-ray diffraction data.

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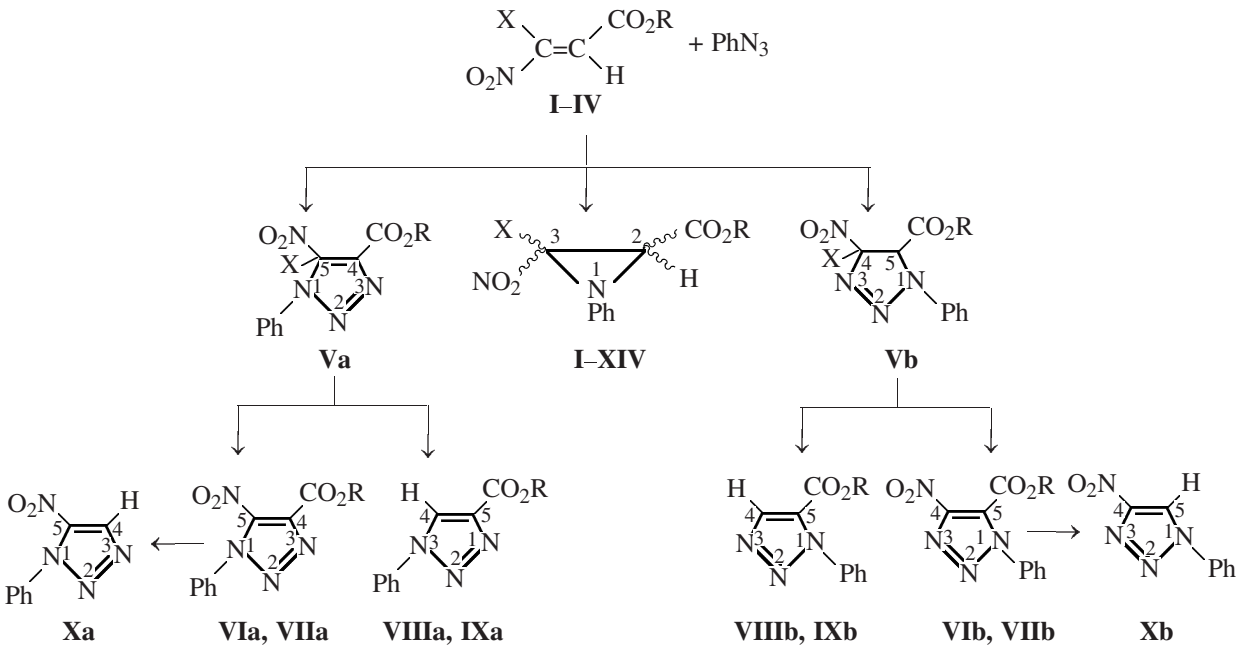
Interest in 1,3-dipolar cycloadditions involving nitroalkenes as dipolarophiles and azides as 1,3-dipoles originates from the synthetic potential of these reactions which lead to the formation of five-membered nitrogencontaining heterocycles, 1,2,3-triazoles. Triazole derivatives are used as photosensitizers and optical belaching agents, while nitrotriazoles exhibit antiviral, antiphlogistic, and antifungal activity [1–3].

According to published data, β-nitrostyrene reacts with phenyl azide at 20–100°C (in the absence of a solvent) to give only one regioisomeric triazole (or, in rare cases, dihydrotriazole) [4–7]; a small amount of another regioisomer was isolated only after prolonged heating (17–156 h) of the reactions mixture in toluene or cyclohexane [6, 8].

In the present work we examined reactions of alkyl 3-nitro- and 3-bromo-3-nitroacrylates **I**–**IV** with phenyl azide under different conditions. Unlike model β-nitrostyrene containing no additional electron-withdrawing groups, compounds **I** and **II** reacted with phenyl azide in ethanol (18–20°C, 14 days) or benzene (80°C, 2 h) at both reactive centers with formation of mixtures of regioisomeric alkyl 5(4)-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4(5)-carboxylates **Va** and **Vb** which were isolated in a yield of 6–7%. During the process, compounds **Va** and **Vb** underwent concurrent intramolecular transformations along three paths: (1) dehydrogenation leading to regioisomeric alkyl 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates **VIa/VIb** and **VIIa/VIIb**; (2) denitration with formation of regioisomeric 1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates **VIIIa/VIIIb** and **IXa/IXb**; and (3) elimination of nitrogen to give the corresponding alkyl 3-nitro-1-phenylaziridine-2-carboxylates **XI** and **XII**. The reactions of nitroalkenes **I** and **II** with phenyl azide in boiling toluene (1.5 h) afforded mainly triazoles **VIIIa/VIIIb** and **IXa/IXb**, whereas nitrotriazoles **VIa/VIb** and **VIIa/VIIb** and aziridines **XI** and **XII** were the minor products.

Variation of the reaction conditions showed that, regardless of the solvent nature (ethanol, benzene, DMSO, toluene), raising the temperature from 20 to 110°C leads to complete transformation of dihydrotriazoles into triazoles via predominant elimination of nitrous acid. In this case, the yields of triazoles **VIIIa/VIIIb** and **IXa/IXb** containing no nitro group increase from 15–17 to 48–54%, and the yields of aziridines **XI** and **XII** increase from 7–8 to 20–25%.

Compounds **V**–**IX**, **XI**, and **XII** were isolated by column chromatography on silica gel. Surprisingly, chromatographic separation of the products on aluminum oxide was accompanied by transformation of alkyl nitrotriazolecarboxylates **VIa/Vb** and **VIIa/VIIb** into 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazoles **Xa/Xb** as a result of hydrolysis and decarboxylation. We succeeded in isolating individual isomers **Xa** and **Xb** by



R = Et: X = H (**I, Va, Vb, VIa, VIb, VIIIa, VIIIb, XI, XIII**), Br (**III, XIII**), R = Me (**II, VIIa, VIIb, IXa, IXb, XII**), Br (**IV, XIV**).

repeated chromatography of their mixture, and isomer **Xb** turned out to be identical in the melting point to that reported in [9, 10]. By repeated chromatography of regioisomer mixtures **VIIa/VIIb**, **VIIIa/VIIIb**, and **IXa/IXb** were isolated pure isomers **VIIa**, **VIIIa**, **IXa**, and **IXb**. Compounds **VIIIa**, **IXa**, **IXb**, and **Xb** were identical in their physical constants and spectral parameters to the corresponding samples described in [11, 12], which were synthesized by different methods.

Unlike halogen-free nitroalkenes **I** and **II**, alkyl 3-bromo-3-nitroacrylates **III** and **IV** reacted with phenyl azide under more severe conditions, presumably due to greater steric requirements of the dipolarophile. Compounds **III** and **IV** failed to react with phenyl azide at 20°C, and the reaction successfully occurred only on heating in boiling benzene (2 h). Under these conditions, dehydrobromination of the initially formed halonitrotriazoles was faster than elimination of nitrous acid therefrom; as a result, the nitro group was retained in the triazole ring, and nitrotriazoles **VIa/VIb** and **VIIa/VIIb** were isolated in 48–51% yield. In addition, as in the reactions with dipolarophiles **I** and **II**, 5–7% of aziridine derivatives **XIII** and **XIV** (as mixtures of diastereoisomers) and nitrotriazoles **Xa** and **Xb** (after separation of the reaction mixture on aluminum oxide) was obtained. The products were isolated by column chromatography on silica gel (**VIa/VIb**, **VIIa/VIIb**) or aluminum oxide (**Xa/Xb**), and their properties were identical to those of samples synthesized from alkenes **I** and **II**. Repeated chromatographic separation of regioisomer mixture **VIIa/VIIb** gave pure nitrotriazole **VIIa** (18%).

The structure of products **V**–**XIV** was proved by the data of elemental analysis (Table 1) and IR and ^{1}H NMR spectroscopy (Table 2), which were compared with the corresponding data for structurally related compounds reported in the literature (dihydrotriazoles [13–15], triazoles [11, 12, 16, 17], and aziridines [18, 19]). The IR spectra of V–XIV contained absorption bands assignable to all functional groups present in their molecules. The ester moiety was characterized by strong absorption bands at 1745–1725 ($\nu_{C=O}$) and 1190–1140 and 1025–1010 cm^{-1} (ν_{C-O-C}). Symmetric and antisymmetric stretching vibrations of the conjugated nitro group in compounds **VIa**, **VIb**, **VIIa**, **VIIb**, **Xa**, and **Xb** give rise to absorption at 1360–1355 and 1560–1540 cm^{-1}, respectively, and bands at 1575 and 1365 cm^{-1} were assigned to the nonconjugated nitro group in dihydrotriazoles **Va** and **Vb**.

The most useful information on the structure of all compounds of the above series was derived from their ^{1}H NMR spectra. The isomer structure was determined on the basis of the signal intensity ratios and chemical shifts of the $C_{sp^3}H$ (dihydrotriazoles, aziridines) and olefinic CH= protons (triazoles). Different effects of functional groups, N=N and C=N bonds, neighboring endocyclic nitrogen atom, and magne-

Table 1. Elemental analyses of compounds **V**–**XIV**

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
Va, Vb	–	–	21.60 21.64	$C_{11}H_{12}N_4O_4$	–	–	21.21
VIa, VIb	50.29 50.30	4.00 4.02	21.40 21.41	$C_{11}H_{10}N_4O_4$	50.38	3.82	21.37
VIIa, VIIb	48.34 60.85	3.26 5.28	22.50 19.65	$C_{10}H_8N_4O_4$	48.39	3.23	22.58
VIIIa, VIIIb	60.81 60.85	5.27 5.28	19.69 19.65	$C_{11}H_{11}N_3O_2$	60.83	5.07	19.35
IXa, IXb	59.17 59.18	4.65 4.63	20.57 20.52	$C_{10}H_9N_3O_2$	59.11	4.43	20.69
Xa, Xb	50.66 50.71	3.19 3.15	29.39 29.37	$C_8H_6N_4O_2$	50.53	3.16	29.47
XI	55.78 55.69	4.97 4.94	11.76 11.89	$C_{11}H_{12}N_2O_4$	55.93	5.08	11.86
XII	54.18 54.18	4.69 4.70	12.71 12.65	$C_{10}H_{10}N_2O_4$	54.05	4.50	12.61
XIII	–	–	8.87 8.88	$C_{11}H_{11}BrN_2O_4$	–	–	8.89
XIV	–	–	9.40	$C_{10}H_9BrN_2O_4$	–	–	9.30

Table 2. IR and ^{1}H NMR spectra of compounds **V**–**X**

Comp. no.	^{1}H NMR spectrum ($CDCl_3$), δ, ppm					IR spectrum ($CHCl_3$), ν, cm^{-1}	
	C^4H	C^5H	CO_2R		Ph	NO_2	(C=O)
			OCH_2	CH_3			
			(OCH_3)				
Va	4.47 d $^3J_{4,5}$ 4.0 Hz	5.12 d	4.30 q	1.30 t	7.00–7.70 m	1575 1365	1745
Vb	5.24 d $^3J_{4,5}$ 6.0 Hz	4.35 d	4.20 q	1.26 t			
VIa	–	–	4.45 q	1.30 t	7.65 m	1540	1740
VIb			4.30 q	1.40 t	7.60 m	1360	
VIIa	–	–	(3.95 s)		7.40–7.70 m	1540	1745
VIIb			(3.90 s)			1360	
VIIIa	–	8.50 s	4.40 q	1.15 t	7.35–7.80 m	–	1735
VIIIb	8.18 s	–	4.20 q	1.35 t			
IXa	–	8.50	(4.00 s)		7.40–7.80 m	–	1740
IXb	8.25	–	(3.80 s)				
Xa	8.70	–	–		7.60–7.80 m	1540	–
Xb	–	8.82	–			1355	

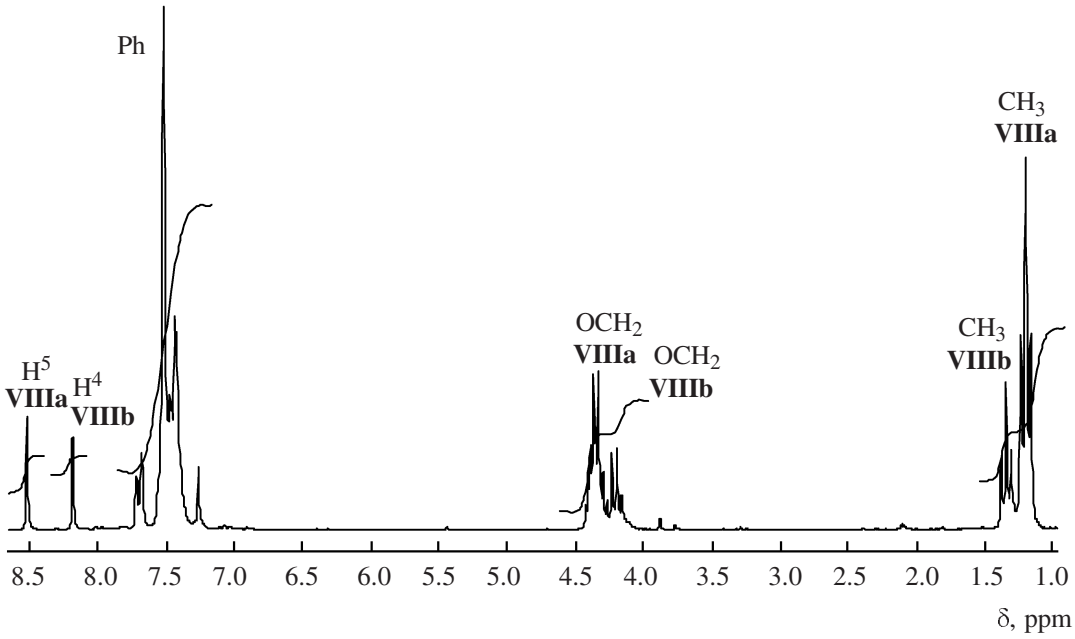


Fig. 1. ^{1}H NMR spectrum of a mixture of regioisomeric ethyl 1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates **VIIIa** and **VIIIb** in $CDCl_3$.

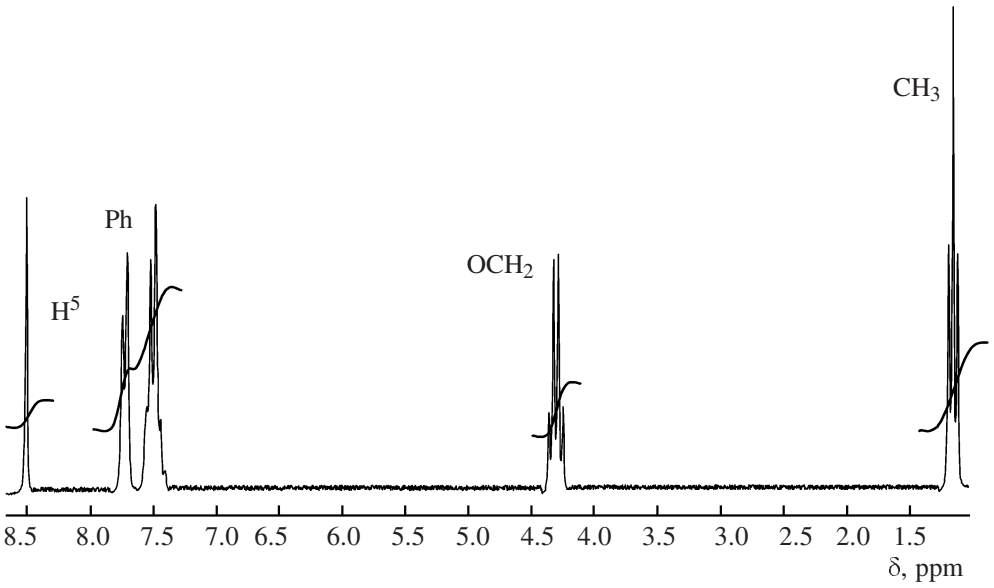


Fig. 2. ^{1}H NMR spectrum of ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (**VIIIa**) in $CDCl_3$.

tically anisotropic properties of the benzene ring (in molecules **VI**–**X**) were taken into account [16, 17]. The effect of the phenyl group in dihydrotriazoles **Va** and **Vb** on proton chemical shifts is likely to be insignificant (Table 2; Figs. 1, 2).

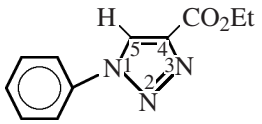
Regioisomers **a** and **b** of dihydrotriazoles **V** and triazoles **VI**–**X** differ by the distance from the 1-phenyl group to the ester moiety: the Ph and COOR substituents in series **a** regioisomers are the most distant from each other, whereas the corresponding groups in series **b** isomers are attached to the neighboring atoms. Their ^{1}H NMR spectra contain two sets of signals characterized by different intensity rations. In the ^{1}H NMR spectrum of regioisomer mixture **Va/Vb**, the 4-H proton of **Vb** resonates in a weaker

field (δ 5.24 ppm) relative to the corresponding signal from 5-H in isomer **Va** (δ 5.12 ppm) due to joint effect of the electron-withdrawing double N=N bond and nitro group. The second methine proton in **Vb** (5-H) gives a more upfield signal (δ 4.35 ppm), as compared to that of 4-H in **Va** (δ 4.47 ppm). Thus, the 4-H and 5-H signals in the spectrum of isomer **b** are most distant from each other (δ 5.24 and 4.35 ppm; Δδ = 0.89 ppm), whereas the corresponding signals in the spectrum of isomer a (δ 5.12 and 4.47 ppm; Δδ = 0.65 ppm) appear closer to each other.

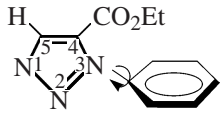
An analogous approach was applied by Huisgen et al. [13] to identify the structure of regioisomeric *N*-phenyldihydrotriazoles. The authors noted an upfield shift (by 0.2 ppm) of the methine proton signal of structures like a relative to the signal of regioisomers like **b**.

The spectra of phenyltriazoles **VI**–**X** were analyzed with account taken of the aromatic character of the planar triazole ring and specific effect of the phenyl substituent. It is known that a benzene ring is magnetically anisotropic, and its effect (shielding or deshielding) depends on the orientation of the benzene ring plane with respect to a given proton [20]. If the benzene ring is oriented by its plane toward an olefinic proton or protons of a functional group, the latter fall into the shielding cone, and the NMR signal shifts upfield. If the benzene is oriented by its edge toward an olefinic proton or functional group (deshielding area), the signal shifts downfield.

The molecules of isomeric triazoles **VIIIa/VIIIb** and **IXa/IXb** differ by the distance between the olefinic proton and double N=N and by the presence or absence of benzene ring in the vicinity of that proton. Undoubtedly, combined effect of the above factors on the olefinic proton chemical shifts must be taken into account while distinguishing the isomers. The benzene ring and triazole ring in molecule **VIIIa** are likely to lie in one plane since the olefinic proton on C^5 does not create steric hindrances to their planar arrangement.



VIIIa



VIIIb

In this case, the 5-H signal should appear in a weaker field (δ 8.50.ppm) due to deshielding effect of the benzene ring. Contrastingly, the 4-H proton in regioisomer **VIIIb** is remote from the benzene ring, and its signal is located in a stronger field (δ 8.18 ppm). Methylene protons in the ester group [C(O)OCH_2CH$_3$] of **VIIIa** are characterized by a larger chemical shift (δ 4.40 ppm) than those in molecule **VIIIb** (δ 4.20 ppm) due to effect of the endocyclic N=N bond (Figs. 1, 2). However, another factor is also important here: planar arrangement of the benzene and triazole rings in molecule **VIIIb** is hardly probable because of steric hindrances created by the ester substituent on C^5. As a result, protons in the ester group falls into the shielding cone of the benzene ring, which leads to upfield shift of the methylene proton signal. It should be noted that the effect on the cyclic proton of the N=N bond constituting a part of the π-electron system of the aromatic triazole heteroring is likely to be weaker than the "through-space" effect of the benzene ring.

The above assignment is consistent with the observed signal intensity ratio for regioisomers **VIIIa** and **VIIIb** (2 : 1; Fig. 1). Presumably, isomer **VIIIa** is less sterically strained than **VIIIb**, and planar structure of the former ensures effective conjugation between the benzene and triazole rings. Following an analogous approach, we have distinguished regioisomeric triazoles **IXa** and **IXb** and **Xa** and **Xb**. The structure of triazoles **VIIIa**, **Xb**, **IXa**, and **IXb** is also confirmed by similarity of their spectral parameters and identity of their melting points to those reported in the literature [9–12].

Convincing proofs for the fine structure of the isolated triazoles were obtained by X-ray analysis of a single crystal of individual regioisomer **VIIIa** (Fig. 3). It is seen that the Ph and CO_2Et substituents in molecule **VIIIa** are attached to N^1 and C^4, respectively, and are therefore most distant from each other. Tables 3–5 contain the geometric parameters (torsion and bond angles and bond lengths) of molecule **VIIIa** in crystal. The torsion angles involving atoms of the triazole ring ($C^5N^1N^2N^3$, $N^1N^2N^3C^4$, $N^2N^3C^4C^5$, and $N^3C^4C^5N^1$) range from 0.05 to –0.13°, indicating that the triazole ring is virtually planar. The torsion angles $N^2N^1C^{10}C^{11}$ and $C^5N^1C^{10}C^{15}$ are –6.3(2) and –4.2(2)°, respectively; i.e., the triazole and benzene rings lie almost in one plane. Their orientation favors effective electronic interaction between the rings, as follows from the length of the C^{10}–N^1 bond (1.4294 Å); it is shorter than standard ordinary C–N bond (1.472 Å) but longer than standard double C=N bond (1.339 Å) [6].

The ester carbonyl group and the endocyclic C^4=C^5 bond form diene fragment C^5=C^4–C^6=O^6 having *s-cis* conformation with respect to the single C^4–C^6 bond. The latter (C^4–C^6, 1.461 Å) is appreciably shortened, which is typical of conjugated diene systems. The geometric parameters of the ethoxycarbonyl group do not differ from the corresponding standard values.

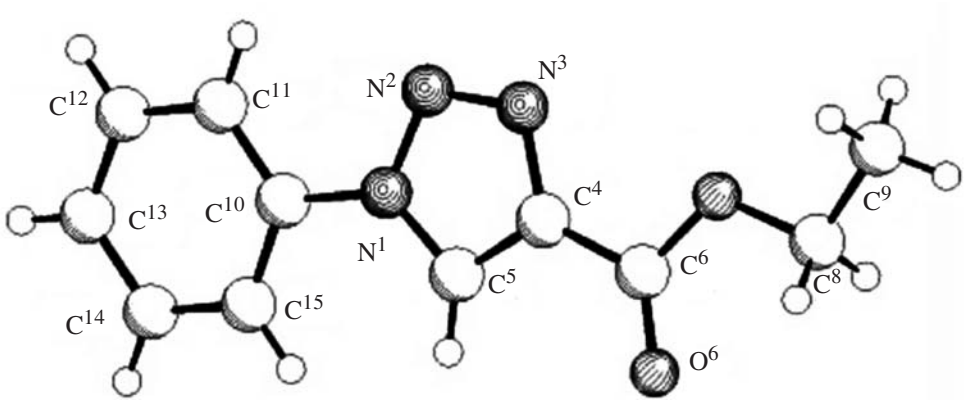


Fig. 3. Molecular geometry of 1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (**VIIIa**).

Due to asymmetric substitution pattern, aziridines **XI**–**XIV** possess chiral centers; therefore, they can be formed as mixtures of diastereoisomers. In fact, complicated character of their ^{1}H NMR spectra (Table 6) is consistent with the presence of different stereoisomers. However, we failed to distinguish signals from particular stereoisomers, and it seemed more reasonable to assign signals to specific groups of protons on the basis of general relations and comparison of chemical shifts with those reported for known analogs [18–22]. In the ^{1}H NMR of aziridine derivatives **XI** and **XII**, the most downfield were signals from the O^{2}NCH proton (δ 4.40–4.85 ppm) due to electron-withdrawing effect of the neighboring nitro group. The CH proton adjacent to less electron-withdrawing ester group resonated in a stronger field, at δ 2.75–3.30 ppm. The presence of a bromine atom in molecules **XIII** and **XIV** leads to a downfield shift of the 2-H signal to δ 3.50–3.85 ppm relative to the corresponding signals from compounds **XI** and **XII**.

EXPERIMENTAL

The IR spectra were recorded from solutions in chloroform (c = 0.1–0.001 M) on an InfraLYuM FT-02 spectrometer. The ^{1}H NMR spectra were measured on a Bruker AC-200 spectrometer at 200 MHz in chloroform-d or acetone-d_6; the chemical shifts were determined relative to hexamethyldisiloxane as external reference with an accuracy of ±0.5 Hz. The isomer ratios were determined from the corresponding signal intensities in the ^{1}H NMR spectra of samples isolated by column chromatography.

X-Ray diffraction data for compound VIIIa. Monoclinic crystals, C11H11N3O2, space group

Table 3. Torsion angles τ in the molecule of ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (**VIIIa**)

Angle	τ	Angle	τ
$C^5N^1N^2N^3$	0.05 (18)	$C^4C^6O^7C^8$	178.97 (16)
$C^{10}N^1N^2N^3$	–177.70 (14)	$C^6O^7C^8C^9$	–167.74 (18)
$N^1N^2N^3C^4$	–0.13 (19)	$C^5N^1C^{10}C^{15}$	–4.2 (2)
$N^2N^3C^4C^5$	0.16 (19)	$N^2N^1C^{10}C^{15}$	173.09 (15)
$N^2N^3C^4C^6$	179.59 (15)	$C^5N^1C^{10}C^{11}$	176.50 (16)
$N^2N^1C^5C^4$	0.05 (17)	$N^2N^1C^{10}C^{11}$	–6.3 (2)
$C^{10}N^1C^5C^4$	177.53 (14)	$C^{15}C^{10}C^{11}C^{12}$	–0.8 (3)
$N^3C^4C^5N^1$	–0.13 (18)	$N^1C^{10}C^{11}C^{12}$	178.50 (16)
$C^6C^4C^5N^1$	–179.54 (15)	$C^{10}C^{11}C^{12}C^{13}$	0.6 (3)
$N^3C^4C^6O^6$	175.02 (17)	$C^{11}C^{12}C^{13}C^{14}$	–0.2 (3)
$C^5C^4C^6O^6$	–5.7 (3)	$C^{12}C^{13}C^{14}C^{15}$	–0.2 (3)
$N^3C^4C^6O^7$	–4.5 (2)	$C^{13}C^{14}C^{15}C^{10}$	0.0 (3)
$C^5C^4C^6O^7$	174.87 (15)	$C^{11}C^{10}C^{15}C^{14}$	0.5 (3)
$O^6C^6O^7C^8$	–0.5 (3)	$N^1C^{10}C^{15}C^{14}$	–178.80 (15)

Table 4. Bond angles ω in the molecule of ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (**VIIIa**)

Angle	ω	Angle	ω
$C^5N^1N^2$	109.67 (13)	$O^7C^6C^4$	113.17 (15)
$C^5N^1C^{10}$	129.84 (13)	$C^6O^7C^8$	116.04 (15)
$N^2N^1C^{10}$	120.45 (12)	$O^7C^8C^9$	108.4 (2)
$N^3N^2N^1$	107.61 (13)	$C^{15}C^{10}C^{11}$	120.56 (15)
$N^2N^3C^4$	108.83 (13)	$C^{15}C^{10}N^1$	119.64 (13)
$N^3C^4C^5$	108.27 (14)	$C^{11}C^{10}N^1$	119.80 (14)
$N^3C^4C^6$	124.63 (14)	$C^{12}C^{11}C^{10}$	119.11 (17)
$C^5C^4C^6$	127.10 (15)	$C^{11}C^{12}C^{13}$	121.12 (18)
$N^1C^5C^4$	105.63 (14)	$C^{12}C^{13}C^{14}$	119.22 (18)
$O^6C^6O^7$	124.02 (16)	$C^{15}C^{14}C^{13}$	120.40 (17)
$O^6C^6C^4$	122.80 (15)	$C^{14}C^{15}C^{10}$	119.58 (16)

$P2_1/c$. Unit cell parameters (20°C): a = 11.674(1), b = 11.273(1), c = 9.068(1) Å; β = 111.82(1)°; V = 1107.7(2) Å^3; Z = 4; d_{calc} = 1.302 g cm^{-3}. The unit call parameters and intensities of 14 832 reflections (2346 of which were independent, R_{int} = 0.0418) were measured on a Nonius KappaCCD automatic X-ray diffractometer (λMoK_α irradiation, graphite monochromator, θ ≤ 27.99°) at room temperature using COLLECT (Nonius B.V., 1998), Dirax/lsq (Duisenberg & Schreurs, 1989–2000), and EvalCCD programs (Duisenberg & Schreurs 1990–2000). An empirical correction for absorption was introduced. The structure was solved by the direct method using SHELXS-97 program [23] and was refined using SHELXL-97 software (G.M. Sheldrick, Universitat Gottingen, 1997). The final divergence factors were R = 0.045, R_W = 0.111 (from 1590 independent reflections with $F^2 \geq 2\sigma$).

Individual compounds were isolated and purified by column chromatography on silica gel (100–200 μm, Chemapol) or aluminum oxide using eluotropic solvent series [24]. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates (hexane–acetone, 3 : 2; development with iodine vapor).

Initial 3-nitroacrylates **I** and **II** were synthesized by an improved procedure [25], and 3-bromo-3-nitroacrylates **III** and **IV** were obtained as described in [26].

Ethyl 5(4)-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4(5)-carboxylates (Va/Vb), ethyl 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (VIa/VIb), ethyl 1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (VIIIa/VIIIb), and ethyl 3-nitro-1-phenylaziridine-2-carboxylate (XI). *a*. Ethyl 3-nitroacrylate (**I**), 0.7 g, was dissolved in 20 ml of anhydrous ethanol, 1.14 g of phenyl azide was added, and the mixture was kept for 14 days at 18–20°C, applied to silica gel, and subjected to column chromatography. Elution with hexane gave 0.57 g (45%) of a mixture of regioisomeric triazoles **VIa** and **VIb** at a ratio of 4 : 1 (R_f 0.77 and 0.71, respectively). Elution with carbon tetrachloride gave 0.3 g of a mixture of compounds **Va**, **Vb**, and **XI** at a ratio of 5 : 2 : 7. From the benzene fraction we isolated 0.16 g (15%) of a mixture of regioisomeric triazoles **VIIIa** and **VIIIb** at a ratio of 7 : 2 (R_f 0.73 and 0.65, respectively). Repeated chromatographic separation of the **Va/Vb/XI** mixture gave 0.08 g (7%) of aziridine **XI** (a mixture of diastereoisomers, R_f 0.64, 0.42; elution with carbon

Table 5. Bond lengths d in the molecule of ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (**VIIIa**)

Bond	d	Bond	d
N^1–C^5	1.3371(19)	O^7–C^8	1.450(2)
N^1–N^2	1.3607(18)	C^8–C^9	1.475(3)
N^1–C^{10}	1.4294(19)	C^{10}–C^{15}	1.377(2)
N^2–N^3	1.299(2)	C^{10}–C^{11}	1.378(2)
N^3–C^4	1.359(2)	C^{11}–C^{12}	1.373(3)
C^4–C^5	1.361(2)	C^{12}–C^{13}	1.373(3)
C^4–C^6	1.461(2)	C^{13}–C^{14}	1.379(3)
C^6–O^6	1.203(2)	C^{14}–C^{15}	1.375(2)
C^6–O^7	1.3281(19)		

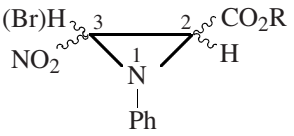


Table 6. Yields, R_f values, and IR and ^{1}H NMR spectra of aziridines **XI**–**XIV**

Comp. no.	Yield, %	R_f	IR spectrum ($CHCl_3$), ν, cm^{-1}			^{1}H NMR spectrum ($CDCl_3$), δ, ppm			
			NO_2	C=O	COC	C^2H	C^3H	R	Ph
XI	7	0.64, 0.42	1550 1370	1750	1160 1015	2.75–3.16 m	4.40–4.70 m	4.25 q, 1.25 t	7.20–7.70 m
XII	22	0.68, 0.63	1550 1370	1740	1155 1020	2.60–3.30 m	4.50–4.85 m	3.50–3.70 m	7.30–7.70 m
XIII	7	0.30, 0.24	1595 1390	1750	1165 1020	3.50 m	–	4.45 q, 1.25 t	7.70 m
XIV	7	0.61, 0.42	1585 1385	1745	1165 1015	3.85 m	–	3.90 s	7.20–7.70 m

tetrachloride) and 0.09 g (7%) of a mixture of dihydrotriazoles **Va** and **Vb** at a ratio of 5 : 2 (R_f 0.56 and 0.52, respectively; elution with benzene). Repeated chromatography of regioisomer mixture **VIa/VIb** gave 0.30 g (24%) of nitrotriazole **VIa** (elution with carbon tetrachloride) as an oily substance (R_f 0.77) which crystallized on storage, mp 33–35°C.

By repeated chromatography of regioisomer mixture **VIIIa/VIIIb** using benzene as eluent we isolated 0.08 g (8%) of triazole **VIIIa** as yellow crystals with mp 75–76°C, R_f 0.73; published data [11]: mp 76–77°C.

b. Phenyl azide, 1.14 g, was added to a solution of 0.7 g of ethyl 3-nitroacrylate (**I**) in 20 ml of DMSO. The mixture was heated for 5 min at 60°C and applied to silica gel, and the solvent was evaporated at room temperature. By column chromatography we isolated 0.42 g (33%) of a mixture of nitrotriazoles **VIa** and **VIb** at a ratio of 4 : 1 (elution with hexane; R_f 0.77, 0.71), 0.14 g (12%) of aziridine **XI** (a mixture of diastereoisomers; elution with carbon tetrachloride; R_f 0.64, 0.42), and 0.29 g (28%) of triazole mixture **VIIIa/VIIIb** (ratio 7 : 2; elution with benzene; R_f 0.73, 0.65).

c. Phenyl azide, 1.14 g, was added to a solution of 0.7 g of ethyl 3-nitroacrylate (**I**) in 20 ml of anhydrous benzene, and the mixture was heated for 2 h under reflux. The solvent was removed on a rotary evaporator, and the oily residue was subjected to chromatography on silica gel. Elution with hexane gave 0.13 g (10%) of triazole mixture **VIa/VIb** (5 : 1). Elution with carbon tetrachloride gave 0.25 g (22%) of aziridine **XI** (mixture of diastereoisomers, R_f 0.64, 0.42). Elution with benzene gave 0.48 g (46%) of triazole mixture **VIIIa/VIIIb** (9 : 2, R_f 0.73, 0.65).

d. Phenyl azide, 0.6 g, was added to a solution of 0.7 g of ethyl 3-nitroacrylate (**I**) in 20 ml of anhydrous toluene, and the mixture was heated for 1.5 h under reflux (110°C). The solvent was removed on a rotary evaporator, and the oily residue was subjected to chromatography on silica gel. From the hexane fraction we isolated 0.06 g (5%) of a mixture of nitrotriazoles **VIa** and **VIb** at a ratio of 5 : 1 (R_f 0.77 and 0.71, respectively). From the carbon tetrachloride fraction we isolated 0.28 g (25%) of aziridine **XI** as a mixture of diastereoisomers (R_f 0.64, 0.42). From the benzene fraction we isolated 0.56 g (54%) of triazole mixture **VIIIa/VIIIb**.

Methyl 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (VIIa/VIIb), methyl 1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (IXa/IXb), 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazoles (Xa/Xb), and methyl 3-nitro-1-phenylaziridine-2-carboxylate (XII). *a*. Phenyl azide, 0.63 g, was added to a solution of 0.7 g of methyl 3-nitroacrylate (**II**) in 20 ml of anhydrous toluene. The mixture was heated for 1.5 h under reflux (110°C), the solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel. From the hexane fraction we isolated 0.07 g (5%) of a mixture of triazoles **VIIa** and **VIIb** at a ratio of 4 : 1 (R_f 0.76, 0.70). From the benzene fraction we isolated 0.54 g (50%) of a mixture of triazoles **IXa** and **IXb** at a ratio of 9 : 2 (R_f 0.60, 0.54). From the chloroform fraction we isolated 0.26 g (22%) of aziridine **XII** as a mixture of diastereoisomers (R_f 0.68, 0.63) with mp 90–92°C. By repeated chromatography of regioisomer mixture **IXa** and **IXb** using carbon tetrachloride as eluent we isolated 0.37 g (35%) of triazole **IXa** as light yellow crystals with mp 119–120°C; published data [12]: mp 120–121.5°C.

b. The procedure was the same as in *a*, but the oily residue was subjected to chromatography on aluminum oxide. Elution with benzene gave 0.49 g (45%) of triazole mixture **IXa/IXb** (5 : 1, R_f 0.60, 0.54). Elution with chloroform gave 0.30 g (25%) of aziridine **XII** (a mixture of diastereoisomers) as orange crystals with mp 90–92°C. Elution with acetone gave 0.18 g (18%) of triazole mixture **Xa/Xb** (1 : 2, R_f 0.86, 0.80). Elution with diethyl ether gave 0.05 g (5%) of triazole **Xa** with mp 120–122°C. By repeated chromatography of triazole mixture **Xa/Xb** using acetone as eluent we isolated isomer **Xb** with mp 132–134°C; published data [9, 10]: mp 134°C.

Ethyl 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (VIa/VIb) and ethyl 3-bromo-3-nitro-1-phenylaziridine-2-carboxylate (XIII). Phenyl azide, 0.37 g, was added to a solution of 0.7 g of ethyl 3-bromo-3-nitroacrylate (**III**) in 20 ml of anhydrous benzene. The mixture was heated for 2 h under reflux, the solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel. From the hexane fraction we isolated 0.39 g (48%) of a mixture of triazoles **VIa** and **VIb** at a ratio of 4 : 1 (R_f 0.77, 0.71). From the acetone fraction we isolated 0.07 g (7%) of aziridine **XIII** as a mixture of diastereoisomers (R_f 0.30, 0.24).

Methyl 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazole-4(5)-carboxylates (VIIa/VIIb), 5(4)-nitro-1-phenyl-1*H*-1,2,3-triazoles (Xa/Xb), and methyl 3-bromo-3-nitro-1-phenylaziridine-2-carboxylate (XIV). *a*. Phenyl azide, 0.39 g, was added to a solution of 0.7 g of methyl 3-bromo-3-nitroacrylate (**IV**) in 20 ml of anhydrous benzene. The mixture was heated for 2 h

under reflux and evaporated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Elution with hexane gave 0.41 g (50%) of a mixture of nitrotriazoles **VIIa** and **VIIb** at a ratio of 4 : 1 (R_f 0.76, 0.70). Elution with chloroform gave 0.07 g (7%) of aziridine **XIV** as a mixture of diastereoisomers (R_f 0.61, 0.42). By repeated chromatography of isomer mixture **VIIa/VIIb** using hexane as eluent we isolated 0.15 g (18%) of nitrotriazole **VIIa** as a crystalline substance with mp 70–72°C.

b. The procedure was the same as in *a* (benzene, 80°C), but the oily product mixture was separated by column chromatography on aluminum oxide. From the chloroform fraction we isolated 0.07 g (7%) of aziridine **XIV** as a mixture of diastereoisomers (R_f 0.61, 0.42). From the acetone fraction we isolated 0.28 g (45%) of a mixture of nitrotriazoles **Xa** and **Xb** at a ratio of 4 : 1 (R_f 0.86, 0.80).

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