

Dedicated to Professor V.A.Ostrovskii on occasion of his sixtieth birthday

Reaction of 3-Nitro- and 3-Bromo-3-nitroacrylates with Sodium Azide

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Abstract—Reactions of 3-nitro- and 3-bromo-3-nitroacrylates with sodium azide proceed as 1,3-dipolar cycloaddition and lead to the formation of triazolyl- and nitrotriazolylcarboxylates, and also of azido- and azido-nitropropenoates.

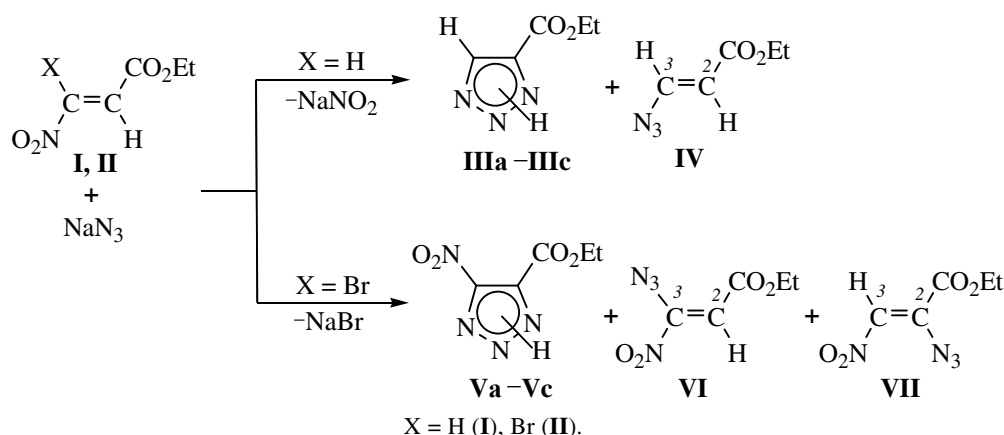
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The interest in reactions of 1,3-dipolar cycloaddition involving nitroalkenes is aroused by the possibility to prepare thereof heterocyclic compounds with a number of practically useful properties [1]. In particular, 1,2,3-triazoles are widely used in medicine [2–4], and among the triazoles containing a nitro group compounds have been found with fungicidal and tuberculostatic action [1, 5].

The analysis of published data on 1,3-dipolar cycloaddition of the azide ion to nitroalkenes revealed that the best understood is the reaction of sodium azide with β -nitrostyrene and its derivatives. The reaction between sodium azide and β -nitrostyrene in DMSO (80°C, 2 h) or methanol (20°C, 3 h) occurred with elimination of sodium nitrite and final formation of the corresponding

triazoles [6–8]. The formation of nitrotriazoles was demonstrated by an example of β -nitrostyrene derivatives possessing in the *gem*-position to the nitro group either a bromine atom or the second nitro group [9, 10]. In event the nitroalkenes contained the second electron-withdrawing substituent in the vicinal or the geminal position the opportunity existed to obtain not only triazole, but also vinylazides [11, 12].

In our study 3-nitro- and 3-bromo-3-nitroacrylates **I** and **II** reacted with sodium azide under relatively mild conditions (methanol, 18–20°C, 2 h), and from 3-nitroacrylate (**I**) and sodium azide we thus obtained triazolylcarboxylate **III** and vinylazide **IV**. 3-Bromo-3-nitroacrylate (**II**) reacted similarly to give nitrotriazolylcarboxylate **V** and regioisomeric vinylazides **VI** and **VII**.



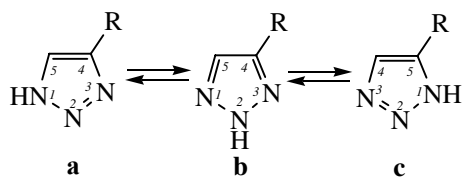
In keeping with [5, 11] the formation of triazoles and vinylazides occurs because of the elimination of easily departing nucleofuge substituent (nitro group or bromine atom) from the primary arising intermediate, azido-nitroanion.

In reaction carried out in acetonitrile at 60°C the yield of triazole **III** grew from 45 to 52%.

The reaction mixture was separated by column chromatography on silica gel. The structure of the compound series obtained was deduced from the spectral data. In the IR spectra of triazolylcarboxylates **III** and **V** and vinylazides **IV**, **VI**, and **VII** the strong bands at 1740–1735 cm⁻¹ correspond to the carbonyl group (C=O), and the bands at 1190–1140 and 1025–1010 cm⁻¹ belong to the C–O–C fragment of the ester group. The stretching vibrations of the free NH group of triazole and that involved in a hydrogen bond appear in the regions 3440–3400 and 3210–3205 cm⁻¹. The bands of the conjugated nitro groups in the spectra of compounds **V–VII** are observed at 1560–1540, 1360–1355 cm⁻¹, and the azide group of compounds **IV**, **VI**, and **VII** give rise to absorption bands in the region 2130–2125 cm⁻¹.

In the interpretation of the ¹H NMR spectra published spectral data were used of similar in structure triazoles [13–16] and vinylazides [17, 18].

According to published information [19–21] the triazoles containing a labile hydrogen atom frequently exist as a mixture of tautomers distinguished by the position of the hydrogen at one among the three nitrogens.



Triazoles we synthesized **III** and **V** contained a triple set of proton signals from the heterocycle indicating the presence of a mixture of three tautomers. For instance, in the ¹H NMR spectrum of triazole **III** protons H⁵ (H⁴) of the ring give rise to singlets at 7.25, 8.00, and 7.55 ppm. The most downfield signal among them (8.0 ppm) belonged to tautomer **b** evidently due to the effect of the electron-withdrawing moiety C=N. The signal of H⁴ proton of tautomer **c** affected by the N=N bond is located downfield (7.55 ppm) with respect to the signal of H⁵ proton (7.25 ppm) of tautomer **a**. The protons of NH groups of triazoles **III** and **V** appear as broadened singlets in the range 8.20–9.25 ppm,

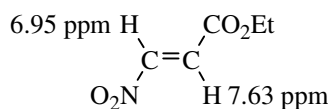
apparently suggesting the possibility of their involvement into intra- and intermolecular hydrogen bonds. In the ¹H NMR spectrum of the individual most stable tautomer triazole **IIIc** (obtained by reaction in acetonitrile at 60°C) the signal from the NH group was observed as a singlet at 8.85 ppm, the protons of OCH₂ and CH₃ groups of the ester function appeared in the regions 4.28–4.40 and 1.20–1.40 ppm respectively.

The tautomerism in alkoxy-carbonyl triazoles was formerly studied by dipole moments measurement [21], and to a sample of ethoxy-carbonyl triazole synthesized by another procedure and isolated in [22] was ascribed the structure **IIIa**.

Nitrotriazolylcarboxylate **V** like the unsubstituted ester **III** according to TLC and ¹H NMR spectrum also existed as a mixture of tautomers **Va–Vc**.

We obtained vinylazide **IV** only in a mixture with triazole **III** and therefore its presence was revealed only by spectral data. For instance, in the ¹H NMR spectrum of the mixture of compounds **III** and **IV** vinylazide **IV** is characterized by the presence of the signals from two olefin protons as doublets at 5.40 and 7.22 ppm with the coupling constant 13.0 Hz indicating their *trans*-location.

The ¹H NMR spectrum of the inseparable mixture of isomeric vinylazides **VI** and **VII** contained singlets from two olefin protons belonging to different compounds. The most downfield signal at 7.65 ppm was attributed to isomer **VI** because of the effect of the *cis*-located nitro group; the olefin proton signal at 7.28 ppm was assigned to nitrovinylazide **VII**. The validity of this assignment was confirmed by the close values of the chemical shifts δ of these signals to those observed in the spectrum of the initial ethyl 3-nitroacrylate.



Evidently in the molecules of both structural isomers of azidonitroacrylates like in their analogs with the phosphonate group formed geometric isomers with the *trans*-location of the nitro and carboxylate moieties.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Infraflum FT-02 (from solutions in chloroform, *c* 0.1–0.001 mol l⁻¹). ¹H NMR spectra were registered on a spectrometer Bruker AC-200 (200 MHz) from solutions in CDCl₃, chemical shifts were measured from an external reference HMDS with an accuracy ± 0.5 Hz. The homogeneity of compounds obtained was checked and

the reaction progress was monitored by TLC on Silufol UV-254 plates, eluent a mixture hexane–acetone, 3:2, development in iodine vapor. Isolation of individual products was performed by column chromatography on silica gel L 100/250, elution with Trappe solvent set [23].

Nitroalkene **I** was synthesized by procedure [24], and its brominated analog **II**, by method [25].

4(5)-Ethoxycarbonyl-1H- and 4-ethoxycarbonyl-2H-1,2,3-triazoles (IIIa and IIIb), 5-ethoxycarbonyl-1H-1,2,3-triazole (IIIc), ethyl 3-azidopropenoate (IV).

a. To a solution of 0.7 g of ethyl 3-nitroacrylate (**I**) in 20 ml of anhydrous methanol was added at stirring 0.4 g of sodium azide. The reaction mixture was stirred for 2 h at 18–20°C, the precipitate was filtered off. The solvent was removed on a rotary evaporator, the residue was subjected to chromatography on silica gel. We obtained 0.30 g (45%) of a mixture of tautomers **IIIa–IIIc** (eluent benzene), R_f 0.50, 0.46, 0.32. ^1H NMR spectrum (CDCl_3), δ , ppm: isomer **a** 7.25 s (1H, H^5), 8.20 s (1H, NH), 4.28–4.30 m (2H, OCH_2), 1.35–1.40 m (3H, CH_3); isomer **b** 8.00 s (1H, H^4), 9.00 s (1H, NH), 4.28–4.30 m (2H, OCH_2), 1.35–1.40 m (3H, CH_3); isomer **c** 7.55 s (1H, H^4), 8.85 s (1H, NH), 4.28–4.30 m (2H, OCH_2), 1.35–1.40 m (3H, CH_3). Found, %: C 42.30, 42.35; H 5.33, 5.33; N 29.53, 29.53. $\text{C}_5\text{H}_7\text{N}_3\text{O}_2$. Calculated, %: C 42.55; H 4.96; N 29.79.

By elution with acetone (~100 ml) we isolated from the residue 0.02 g of a mixture of compounds **III** and **IV**. ^1H NMR spectrum (CDCl_3), δ , ppm, of compound **IV**: 7.22 d (1H, H^2), 5.40 d (1H, H^3 , $J_{2,3}$ 13.0 Hz), 4.22 m (2H, OCH_2), 1.23 t (3H, CH_3).

b. To a solution of 0.7 g of ethyl 3-nitroacrylate (**I**) in 20 ml of anhydrous acetonitrile was added at stirring 0.4 g of sodium azide. The reaction mixture was stirred for 1 h at 60°C, on cooling the precipitate was filtered off. The solvent was removed on a rotary evaporator, the oily residue was subjected to chromatography on silica gel. We obtained 0.35 g (52%) of tautomers mixture **IIIa–IIIc** (eluent benzene), R_f 0.50, 0.46, 0.32.

By elution with acetone we isolated 0.15 g of a mixture of vinylazide **IV** and triazole **IIIa–IIIc**.

By repeated chromatographic separation of the mixture **IIIa–IIIc** from the fraction eluted with benzene we isolated 0.07 g (10%) of individual 5-ethoxycarbonyl-1H-1,2,3-triazole (**IIIc**) as light-yellow crystals, mp 125–127°C; the compound which was assigned structure **IIIa** in [22] had mp 112–113°C. ^1H NMR spectrum (CDCl_3), δ , ppm, of compound **IIIc**: 7.55 s (1H, H^4), 8.85 s (1H, NH), 4.28 q (2H, OCH_2), 1.35 t (3H, CH_3).

5(4)-Nitro-4(5)-ethoxycarbonyltriazoles (Va–Vc), ethyl 3- and -2-azido-3-nitropropenoates (VI and VII) were prepared by procedure *a* from 0.7 g of ethyl 3-bromo-3-nitroacrylate (**II**) and 0.4 g of sodium azide.

We obtained 0.26 g (45%) of a mixture of compounds **Va–Vc**. Dark yellow oily substance, R_f 0.30, 0.24, 0.20. ^1H NMR spectrum (CDCl_3), δ , ppm: 8.30 s, 9.25 s, 8.75 s (NH), 4.28–4.40 m (2H, OCH_2), 1.20–1.35 m (3H, CH_3). Found, %: C 32.26, 32.22; H 3.29, 3.28; N 30.10, 30.10. $\text{C}_5\text{H}_6\text{N}_4\text{O}_4$. Calculated, %: C 32.26; H 3.23; N 30.11.

From the fraction eluted with chloroform we isolated 0.09 g of a mixture of nitrovinylazides **VI** and **VII**. ^1H NMR spectrum (CDCl_3), δ , ppm, compound **VI**: 7.65 s (1H, H^2), 4.30 m (2H, OCH_2), 1.30 m (3H, CH_3); compound **VII**: 7.28 s (1H, H^2), 4.30 m (2H, OCH_2), 1.30 m (3H, CH_3).

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