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Reactions of 2-Benzylidenemalononitrile and 2-Nitro-3-phenylacrylonitrile with Aryl Azides

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Abstract—Reactions of 2-benzylidenemalononitrile and 2-nitro-3-phenylacrylonitrile with aryl azides in diethyl ether at room temperature gave mixtures of regioisomeric 1(3)-aryl-5-phenyl-4,5-dihydro-1(3)*H*-1,2,3-triazole-4,4-dicarbonitriles and 1-aryl-5(4)-phenyl-1*H*-1,2,3-triazole-5(4)-carbonitriles, respectively. 2-Benzylidenemalononitrile reacted with the same arylazides on heating in boiling chloroform to produce 1-aryl-2-phenylaziridine-2,2-dicarbonitriles.

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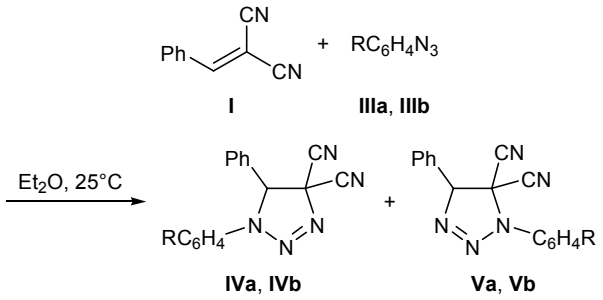
Chemistry of substituted cyanoethenes is a promising line in modern organic chemistry. Chemical transformations of these compounds include 1,3-dipolar cycloaddition to nitrogen-containing 1,3-dipoles, which occupies an important place among synthetic tools of organic chemists. Nitrogen-containing heterocycles formed as a result of such transformations exhibit a broad spectrum of practically important properties. In particular, 1,2,3-triazole ring constitutes a structural fragment of a number of drugs [1]. 1,2,3-Triazole derivatives are used in the manufacture of photosensitizers [2], optical bleaching agents [3], and noncombustible materials [4].

Chemical transformations of 2-benzylidenemalononitrile (**I**) as substituted cyanoethene were poorly studied. It is known that its reactions with aldehydes and imidic acids on heating follow 1,3-dipolar cycloaddition pattern leading to the formation of substituted pyrroles [5] and that three-component heterocyclization of **I** with aldehydes and L-proline gives pyrrolizine derivatives [6]. In continuation of our studies in this line, in the present work we examined 1,3-dipolar cycloaddition reactions of 2-benzylidenemalononitrile (**I**) and its analog, 2-nitro-3-phenylacrylonitrile (**II**), with phenyl and 4-tolyl azides **IIIa** and **IIIb** with a view to elucidate how the nature of 1,3-dipoles affects the direction of their reactions with substituted 2-phenyl-1-cyanoethenes. The reactions of 2-benzylidenemalononitrile (**I**) with azides **IIIa** and **IIIb** were carried out in diethyl ether at 25°C (reaction time 20 days). As a result, we isolated the corresponding regioisomeric cycloaddition products, dihydro-1,2,3-triazoles **IVa**/**Va** and **IVb**/**Vb** (Scheme 1).

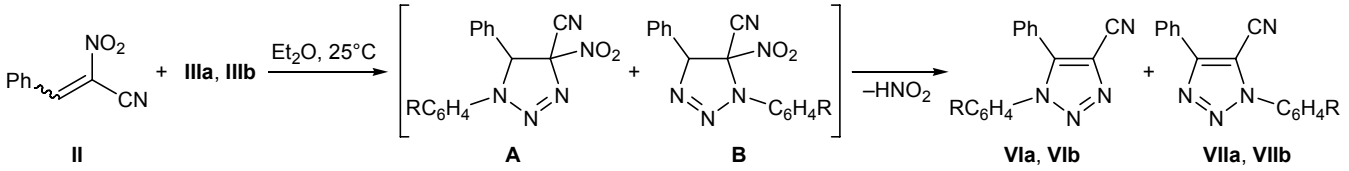
Scheme 1.



R = H (**a**), 4-Me (**b**).

The structure of compounds **IV** and **V** was determined on the basis of spectral data. The IR spectra of **IV** and **V** contained absorption bands at 2245–2250 cm^{-1}, typical of stretching vibrations of cyano group. The ^1H NMR spectra of these compounds were consistent with the assumed structures and were similar to the spectra of model dihydrotriazole derivatives [7]. Regioisomers **IVa** and **Va** were distinguished by the position of the 5-H signal which was observed in a weaker field (δ 4.68 ppm) in the ^1H NMR spectrum of **IVa**. The corresponding signal in the spectrum of **Va** was located at δ 4.47 ppm due to remoteness of the N-phenyl group. An additional proof for the structure of **IVa** is the presence in its mass spectrum of a strong peak with *m*/*z* 181 (87%) which belongs to the $[Ph–CHN–Ph]^{+\cdot}$ ion stabilized by two phenyl groups. No such peak was observed in the mass spectrum of

Scheme 2.



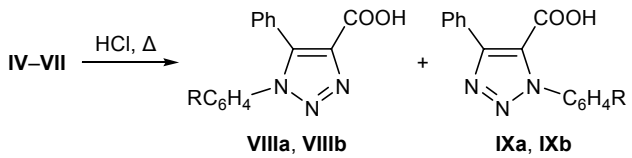
R = H (**a**), 4-Me (**b**).

Va. Regioisomeric compounds **IVb** and **Vb** were distinguished in a similar way.

Unlike 2-benzylidenemalononitrile (**I**), in the reactions of 2-nitro-3-phenylacrylonitrile (**II**) with azides **IIIa** and **IIIb** we isolated regioisomeric 1,2,3-triazolecarbonitriles **VIa**/**VIIa** and **VIb**/**VIIb** (Scheme 2). Obviously, compounds **VI** and **VII** were formed as a result of elimination of nitrous acid molecule from primary 1,3-dipolar cycloaddition products **A** and **B**. The structure of 1,2,3-triazoles **VIa**, **VIb**, **VIIa**, and **VIIb** was determined by IR and ^{1}H NMR spectroscopy and mass spectrometry. The IR spectra of **VI** and **VII** contained CN absorption band at 2250 cm^{-1}, and multiplet signals from aromatic protons were observed in their ^{1}H NMR spectra in the region δ 6.95–7.73 ppm. Compounds **VIa** and **VIIa** were assigned structures of particular regioisomers by analysis of the ^{1}H NMR spectra of their acid hydrolysis products.

By heating in boiling 18% hydrochloric acid isomeric 1,2,3-triazoles **VIa** and **VIIa** were converted into carboxylic acids **VIIIa** and **IXa** (Scheme 3). Regioisomeric structures **VIIIa** and **IXa** were distinguished by the chemical shifts of the COOH proton, taking into account different distances between that proton and phenyl substituent on the nitrogen atom. The COOH proton in isomer **IXa** appears under the phenyl ring plane and is shielded by the ring current in the latter, so that its signal is located in a stronger field (δ 13.23 ppm) relative to the corresponding signal of isomer **VIIIa** (δ 13.55 ppm) [8]. An additional proof for the structure of regioisomers **VIIIa** and **IXa** is their formation from 1,2,3-triazoledicarbonitriles **IVa** and **Va** under conditions of acid hydrolysis. Analogous approach was used to distinguish isomers **VIIIb** and **IXb**.

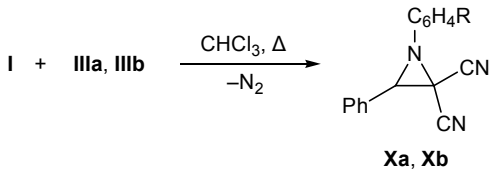
Scheme 3.



R = H (**a**), 4-Me (**b**).

When the reaction of 2-benzylidenemalononitrile (**I**) with azides **IIIa** and **IIIb** was carried out under more severe conditions, by heating in boiling chloroform, the process took a different pathway, and the products were dicyanoaziridines **Xa** and **Xb**, respectively (Scheme 4).

Scheme 4.



R = H (**a**), 4-Me (**b**).

Presumably, thermolysis of aryl azide **III** generates the corresponding nitrene [9] which adds at the double C=C bond of compound **I** to form aziridine **X**. The IR spectra of **Xa** and **Xb** contained absorption bands at 2250 cm^{-1} due to stretching vibrations of the CN group. Compounds **Xa** and **Xb** displayed in the ^{1}H NMR spectra multiplet signals belonging to aromatic protons and singlets from the CH proton in the aziridine ring (δ 4.51–4.52 ppm). The reaction of 2-nitro-3-phenyl-acrylonitrile (**II**) with aryl azides resulted in the formation of unidentified tarry material.

Thus, the results of the reaction of substituted 2-phenyl-1-cyanoethenes with aryl azides allow us to consider these compounds to be promising as substrates for both further functionalization and for studying biological activity.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer from solutions in chloroform with a concentration of 40 mg/ml (cell path length 0.1 mm). The ^{1}H NMR spectra were measured on a Tesla BS-487C spectrometer at 80 MHz using acetone-d_6 as solvent and hexamethyldisiloxane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan SSQ-7000 instrument with direct sample

admission into the ion source (vaporizer temperature 90–150°C). The progress of reactions and purity of the isolated compounds were monitored by TLC on Silufol UV-254 plates using acetone–hexane (2:3) as eluent; spots were visualized by treatment with iodine vapor.

2-Benzylidenemalononitrile (**I**) was synthesized by condensation of malononitrile with benzaldehyde in ethanol in the presence of a catalytic amount of piperidine [10]. 2-Nitro-3-phenylacrylonitrile (**II**) was prepared as described in [11], and aryl azides **IIIa** and **IIIb** were synthesized according to the procedure reported in [12].

Reactions of 2-benzylidenemalononitrile (I) and 2-nitro-3-phenylacrylonitrile (II) with aryl azides IIIa and IIIb (*general procedure***).** Compoundi **I** or **II**, 10 mmol, was dissolved in 50 ml of anhydrous diethyl ether, and a solution of 10 mmol of azide **IIIa** or **IIIb** in 30 ml of the same solvent was added at 25°C. The mixture was kept for 20 days at 25°C and evaporated under reduced pressure, and the residue was subjected to chromatography on a 500×10-mm column charged with silica gel (Silicagel 100–400 μm) using appropriate solvent systems as eluent.

1,5-Diphenyl-4,5-dihydro-1*H*-1,2,3-triazole-4,4-dicarbonitrile (IVa) was isolated by elution with carbon tetrachloride, followed by repeated chromatography using benzene as eluent. Yield 0.986 g (36%), R_f 0.68, mp 92–94°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 4.68 s (1H, CH), 7.61 m (10H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %): 273 (12) $[M]^+$, 272 (5) $[M - 1]^+$, 181 (87), 154 (100), 119 (22). Found, %: C 70.12; H 3.87; N 25.46. $C_{16}H_{11}N_5$. Calculated, %: C 70.33; H 4.03; N 25.64. *M* 273.32.

1,3-Diphenyl-4,5-dihydro-3*H*-1,2,3-triazole-4,4-dicarbonitrile (Va) was isolated by elution with diethyl ether. Yield 0.329 g (12%), R_f 0.62, mp 42–43°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 4.47 s (1H, CH), 7.72 m (10H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %): 273 (10) $[M]^+$, 272 (6) $[M - 1]^+$, 154 (100), 119 (18). Found, %: C 70.08; H 3.82; N 25.41. $C_{16}H_{11}N_5$. Calculated, %: C 70.33; H 4.03; N 25.64. *M* 273.32.

1-(4-Methylphenyl)-5-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4,4-dicarbonitrile (IVb) was isolated by elution with carbon tetrachloride, followed by repeated chromatography using benzene as eluent. Yield 1.119 g (39%), R_f 0.65, mp 105–107°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 4.67 s (1H, CH), 6.96–7.27 m (4H, C_6H_4), 7.65 m (5H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %); 287 (10) $[M]^+$, 286 (6) $[M - 1]^+$, 195 (52), 154 (100), 133 (18). Found, %: C 70.97; H 4.36; N 24.22. $C_{17}H_{13}N_5$. Calculated, %: C 71.08; H 4.53; N 24.39. *M* 287.35.

3-(4-Methylphenyl)-5-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4,4-dicarbonitrile (Vb) was isolated by elution with diethyl ether. Yield 0.344 g (12%), R_f 0.59, mp 56–58°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 4.47 s (1H, CH), 6.97–7.26 m (4H, C_6H_4), 7.73 m (5H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %): 287 (15) $[M]^+$, 286 (10) $[M - 1]^+$, 154 (100), 133 (20). Found, %: C 70.87; H 4.32; N 24.18. $C_{17}H_{13}N_5$. Calculated, %: C 71.08; H 4.53; N 24.39. *M* 287.35.

1,5-Diphenyl-1*H*-1,2,3-triazol-4-carbonitrile (VIa) was isolated by elution with carbon tetrachloride, followed by repeated chromatography using benzene as eluent. Yield 0.369 g (15%), R_f 0.75, mp 78–80°C. IR spectrum: ν 2250 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 7.73 m (10H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %): 246 (15) $[M]^+$, 245 (8) $[M - 1]^+$, 127 (100), 119 (39). Found, %: C 73.04; H 3.92; N 22.58. $C_{15}H_{10}N_4$. Calculated, %: C 73.17; H 4.07; N 22.76. *M* 246.29.

1,4-Diphenyl-1*H*-1,2,3-triazole-5-carbonitrile (VIIa) was isolated by elution with diethyl ether. Yield 0.246 g (10%), R_f 0.70, mp 55°C. IR spectrum: ν 2250 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 7.72 m (10H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %): 246 (20) $[M]^+$, 245 (10) $[M - 1]^+$, 127 (100), 119 (45). Found, %: C 73.96; H 3.85; N 22.51. $C_{15}H_{10}N_4$. Calculated, %: C 73.17; H 4.07; N 22.76. *M* 246.29.

1-(4-Methylphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carbonitrile (VIb) was isolated by elution with benzene, followed by repeated chromatography using the same solvent. Yield 0.464 g (18%), R_f 0.71, mp 96–98°C. IR spectrum: ν 2250 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 2.10 s (3H, CH_3), 6.95–7.25 m (4H, C_6H_4), 7.70 m (5H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %), 260 (18) $[M]^+$, 259 (5) $[M - 1]^+$, 133 (25), 127 (100). Found, %: C 73.69; H 4.44; N 21.37. $C_{16}H_{12}N_4$. Calculated, %: C 73.85; H 4.62; N 21.54. *M* 260.32.

1-(4-Methylphenyl)-4-phenyl-1*H*-1,2,3-triazole-5-carbonitrile (VIIb) was isolated by elution with diethyl ether. Yield 0.258 g (10%), R_f 0.64, mp 75°C. IR spectrum: ν 2250 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 2.13 s (3H, CH_3), 6.96–7.26 m (4H, C_6H_4), 7.71 m (5H, C_6H_5). Mass spectrum, *m*/*z* (I_{rel}, %); 260

(15) $[M]^+$, 259 (10) $[M - 1]^+$, 133 (30), 127 (100). Found, %: C 73.63; H 4.38; N 21.31. $C_{16}H_{12}N_4$. Calculated, %: C 73.85; H 4.62; N 21.54. *M* 260.32.

Hydrolysis of 4,5-dihydro-1,2,3-triazole-4,4-dicarbonitriles IV and V and 1*H*-1,2,3-triazolecarbonitriles VI and VIIa (*general procedure***).** A solution of 6 mmol of compound **IV**–**VII** in 50 ml of concentrated hydrochloric acid was heated for 10 h under reflux. The mixture was evaporated, and the residue was subjected to column chromatography (see above) using diethyl ether as eluent.

1,5-Diphenyl-1*H*-1,2,3-triazole-4-carboxylic acid (VIIIa). Yield 0.782 g (52%), mp 131–132°C. IR spectrum, ν, cm^{-1}: 3560 br (OH), 1740 s (C=O). ^1H NMR spectrum, δ, ppm: 7.70 m (10H, C_6H_5), 13.55 s (OH). Found, %: C 67.74; H 4.01; N 15.67. $C_{15}H_{11}N_3O_2$. Calculated, %: C 67.92; H 4.15; N 15.85.

1,4-Diphenyl-1*H*-1,2,3-triazole-5-carboxylic acid (IXa). Yield 0.827 g (55%), mp 111–112°C. IR spectrum, ν, cm^{-1}: 3560 br (OH), 1740 s (C=O). ^1H NMR spectrum, δ, ppm: 7.72 m (10H, C_6H_5), 13.23 s (OH). Found, %: C 67.70; H 4.96; N 15.68. $C_{15}H_{11}N_3O_2$. Calculated, %: C 67.92; H 4.15; N 15.85.

1-(4-Methylphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid (VIIIb). Yield 0.928 g (58%), mp 152–153°C. IR spectrum, ν, cm^{-1}: 3560 br (OH), 1740 s (C=O). ^1H NMR spectrum, δ, ppm: 2.10 s (3H, CH_3), 6.95–7.25 m (4H, C_6H_4), 7.67 m (5H, C_6H_5), 13.56 s (OH). Found, %: C 67.65; H 4.51; N 14.89. $C_{16}H_{13}N_3O_2$. Calculated, %: C 68.82; H 4.66; N 15.05.

1-(4-Methylphenyl)-4-phenyl-1*H*-1,2,3-triazole-5-carboxylic acid (IXb). Yield 0.842 g (53%), mp 120°C. IR spectrum, ν, cm^{-1}: 3560 br (OH), 1740 s (C=O). ^1H NMR spectrum, δ, ppm: 2.11 s (3H, CH_3), 6.95–7.25 m (4H, C_6H_4), 7.67 m (5H, C_6H_5), 13.25 s (OH). Found, %: C 67.62; H 4.48; N 14.85. $C_{16}H_{13}N_3O_2$. Calculated, %: C 68.82; H 4.66; N 15.05.

Aziridine-2,2-dicarbonitriles Xa and Xb (*general procedure***).** A solution of 10 mmol of aryl azide **IIIa** or **IIIb** in 50 ml of chloroform was added at 25°C to a solution of 10 mmol of compound **I** or **II** in 100 ml of chloroform. The mixture was heated for 5 h under reflux and evaporated under reduced pressure, and the residue was subjected to chromatography as described above using carbon tetrachloride–benzene as eluent (benzene was used as eluent for repeated chromatography).

1,3-Diphenylaziridine-2,2-dicarbonitrile (Xa). Yield 0.181 g (7%), R_f 0.54, mp 42–43°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 4.51 s (1H, CH), 7.74 m (10H, C_6H_5). Found, %: C 78.19; H 4.32; N 16.98. $C_{16}H_{11}N_3$. Calculated, %: C 78.37; H 4.48; N 17.15.

1-(4-Methylphenyl)-3-phenylaziridine-2,2-dicarbonitrile (Xb). Yield 0.162 g (6%), R_f 0.42, mp 85–87°C. IR spectrum: ν 2250–2245 cm^{-1}, m (C≡N). ^1H NMR spectrum, δ, ppm: 2.10 s (3H, CH_3), 4.52 s (1H, CH), 6.95–7.25 m (4H, C_6H_4), 7.72 m (5H, C_6H_5). Found, %: C 78.59; H 4.84; N 16.04. $C_{17}H_{13}N_3$. Calculated, %: C 78.77; H 5.02; N 16.21.

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