Russian Journal of Organic Chemistry, Vol. 41, No. 6, 2005, pp. 941–943. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 6, 2005, pp. 957–958.

SHORT COMMUNICATIONS

Reaction of Ethyl 3-Nitroacrylate with Phenyl Azide

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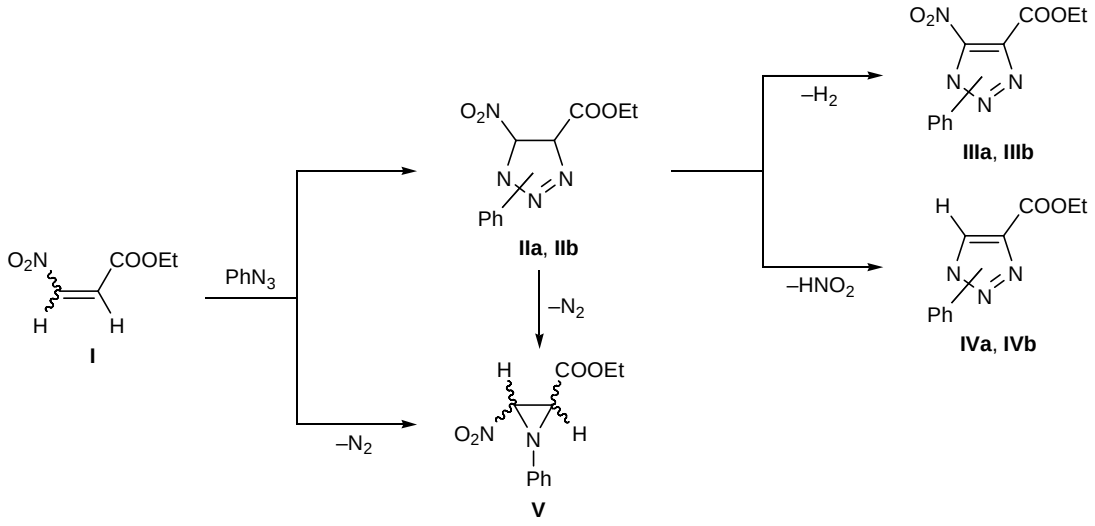
Received December 1, 2004

Nitrogen-containing heterocycles are known to exhibit a broad spectrum of practically useful properties [1–5]. In particular, triazole rings are structural fragments of a number of medicines possessing antifungal, antiphlogistic, and tuberculostatic properties [1, 2]. Dihydrotriazoles are used in manufacture of photostabilizers, optical bleaching agents, and incombustible materials [3–5].

Nitro-substituted 1,2,3-triazoles and dihydro-1,2,3-triazoles can be obtained by 1,3-dipolar cycloaddition of phenyl azide to nitroalkenes. As shown previously, nitroethenes having alkyl or aryl substituents in the β-position with respect to the nitro group slowly react with phenyl azide in polar solvents at room temperature; the reaction is regioselective, and the products are the corresponding 4,5-dihydro-1,2,3-triazoles. At elevated temperature (up to 130°C), these reactions are accompanied by denitration or dehydrogenation to produce the corresponding 1,2,3-triazoles [6, 7].

We were the first to study the reaction of ethyl 3-nitroacrylate (**I**) with phenyl azide. We found that the cycloaddition of phenyl azide to nitroalkene **I** in ethanol at room temperature takes 14 days. The process involves two concurrent pathways and finally leads to formation of a mixture of regioisomeric ethyl 5-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate (**IIa**) and ethyl 4-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-5-carboxylate (**IIb**), nitrotriazoles **IIIa** and **IIIb**, triazoles **IVa** and **IVb**, and aziridine **V**. The latter was isolated as a mixture of diastereoisomers. Regioisomers **IIIa** and **IVa** were isolated as individual products. Compounds **IIIa**, **IIIb**, **IVa**, and **IVb** are likely to result from intramolecular transformations of dihydrotriazoles **IIa** and **IIb** via dehydrogentation or elimination of nitrous acid molecule, respectively. Aziridine **V** can be formed either from dihydrotriazole **IIa**/**IIb** or directly by reaction of **I** with phenyl azide with elimination of nitrogen.

The structure of the products was confirmed by spectral methods. Their IR spectra contained absorption bands at 1750–1735 cm^{-1} due to stretching vibrations of the ester carbonyl group; nonconjugated nitro groups in molecules **IIa**, **IIb**, and **V** give rise to absorption bands at 1560–1545 and 1390 cm^{-1}, and



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stretching vibrations of conjugated nitro groups in **IIIa** and **IIIb** appear at 1540 and 1360 cm^{-1}.

The ^1H NMR spectral parameters of the isolated compounds are consistent with the assumed structures and are analogous to the spectra of structurally related model compounds [8–10]. The spectra contain two set of signals with different signal intensity ratios. The main criteria for the structure of isomer **a** or **b** were the chemical shifts of the CH (olefinic) and ethyl protons in the ester group. These groups in isomers **a** and **b** appear at different distances from the phenyl group. The phenyl and ethoxycarbonyl groups in isomers **b** are attached to the neighboring atoms, while the corresponding groups in isomers **a** are more distant from each other. Due to effect of the benzene ring, the 5-H proton in the spectrum of **IVa** resonates in a weaker field (δ 8.50 ppm) than the corresponding proton in **IVb** (δ 8.18 ppm). The CH_2 protons of the ester group in molecule **IVb** are located below the benzene ring plane (i.e., they fall into the area shielded by the benzene ring), and their signal appears in a stronger field (δ 4.20 ppm) relative to the corresponding signal of isomer **IVa** (δ 4.40 ppm) [11, 12]. Likewise, we distinguished between regioisomeric dihydrotriazoles **IIa** and **IIb** and triazoles **IIIa** and **IIIb**.

Initial nitroalkene **I** was synthesized by improved procedure [13], and phenyl azide was prepared as described in [14].

Ethyl 5-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate (IIa) and ethyl 4-nitro-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (IIb). Yield 7%. Isomer mixture **IIa**/**IIb** was isolated by repeated chromatographic separation of a mixture of compounds **IIa**, **IIb**, and **V** using benzene as eluent. R_f 0.56, 0.52; ratio **IIa**:**IIb** = 5:2. IR spectrum, ν, cm^{-1}: 1745 (C=O); 1545, 1390 (NO_2). ^1H NMR spectrum, δ, ppm: **IIa**: 1.26 t (3H, CH_3), 4.30 q (2H, OCH_2), 5.24 m (1H, 5-H, $J_{4,5}$ = 4.0 Hz), 4.41 m (1H, 4-H, $J_{4,5}$ = 4.0 Hz), 7.20–7.60 m (5H, C_6H_5); **IIb**: 1.30 t (3H, CH_3), 4.20 q (2H, OCH_2), 4.47 m (1H, 5-H, $J_{4,5}$ = 6.0 Hz), 5.12 m (1H, 4-H, $J_{4,5}$ = 6.0 Hz), 7.20–7.60 m (5H, C_6H_5). Found, %: N 21.60, 21.64. $C_{11}H_{12}N_4O_4$. Calculated, %: N 21.21.

Ethyl 5-nitro-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (IIIa) and ethyl 4-nitro-1-phenyl-1*H*-1,2,3-triazole-5-carboxylate (IIIb). Yield 45% (eluent hexane), R_f 0.77, 0.71; ratio **IIIa**:**IIIb** = 4:1. IR spectrum, ν, cm^{-1}: 1740 (C=O); 1540, 1360 (NO_2). ^1H NMR spectrum, δ, ppm: **IIIa**: 1.30 t (3H, CH_3), 4.45 q (2H, OCH_2), 7.65 m (5H, C_6H_5); **IIIb**: 1.40 t (3H, CH_3), 4.30 q (2H, OCH_2), 7.60 m (5H, C_6H_5). Found, %: C 50.29, 50.30; H 4.00, 4.02; N 21.40, 21.41. $C_{11}H_{10}N_4O_4$. Calculated, %: C 50.38; H 3.82; N 21.37. Pure isomer **IIIa** was isolated in 35% by repeated chromatographic separation of a mixture of compounds **IIIa** and **IIIb** using carbon tetrachloride as eluent. R_f 0.77, mp 33–35°C.

Ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (IVa) and ethyl 1-phenyl-1*H*-1,2,3-triazole-5-carboxylate (IVb). Yield 15% (from benzene fraction), R_f 0.73, 0.65; ratio **IVa**:**IVb** = 7:2. IR spectrum, ν, cm^{-1}: 1735 (C=O). ^1H NMR spectrum, δ, ppm: **IVa**: 1.15 t (3H, CH_3), 4.40 q (2H, OCH_2), 7.60 m and 7.80 m (5H, C_6H_5), 8.50 s (1H, 5-H); **IVb**: 1.40 t (3H, CH_3), 4.20 q (2H, OCH_2), 7.30–7.60 m (5H, C_6H_5), 8.18 s (1H, 4-H). Found, %: C 60.41, 60.45; H 5.27, 5.28; N 19.69, 19.65. $C_{11}H_{11}N_3O_2$. Calculated, %: C 60.83; H 5.07; N 19.35. Pure isomer **IVa** was isolated in 10% yield by repeated chromatography of a mixture of isomers **IVa** and **IVb** using benzene as eluent. R_f 0.73, mp 75–77°C.

Ethyl 2-nitro-1-phenylaziridine-3-carboxylate (V) was isolated in 7% yield as an inseparable mixture of diastereoisomers (by repeated chromatographic separation of a mixture of compounds **IIa**, **IIb**, and **V** using carbon tetrachloride as eluent), R_f 0.64, 0.42. IR spectrum, ν, cm^{-1}: 1750 (C=O); 1550, 1385 (NO_2). ^1H NMR spectrum, δ, ppm: 1.25 t (3H, CH_3), 4.25 q (2H, OCH_2), 2.75–3.16 m (1H, 2-H), 4.45–4.80 m (1H, 3-H), 7.20–7.70 m (5H, C_6H_5). Found, %: C 55.78, 55.69; H 4.84, 4.87; N 11.76, 11.89. $C_{11}H_{12}N_2O_4$. Calculated, %: C 55.93; H 5.08; N 11.86.

The IR spectra were recorded on an InfraLYuM FT-02 spectrometer from solutions in chloroform (c = 0.1–0.001 M). The ^1H NMR spectra were measured on a Bruker AC-200 instrument (200 MHz) using chloroform-*d* as solvent. The chemical shifts were measured relative to hexamethyldisiloxane (external reference) with an accuracy of ±0.5 Hz. The products were isolated and purified by column chromatography on silica gel (Chemapol, 100/200 μm) using the Trappe solvent series. The purity of the products was checked, and the progress of the reaction was monitored, by thin-layer chromatography on Silufol UV-254 plates using hexane–acetone (3:2) as eluent; development with iodine vapor.

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