

SHORT
COMMUNICATIONS

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

Ethyl 3-Nitroacrylate Reaction with Phenyldiazomethane

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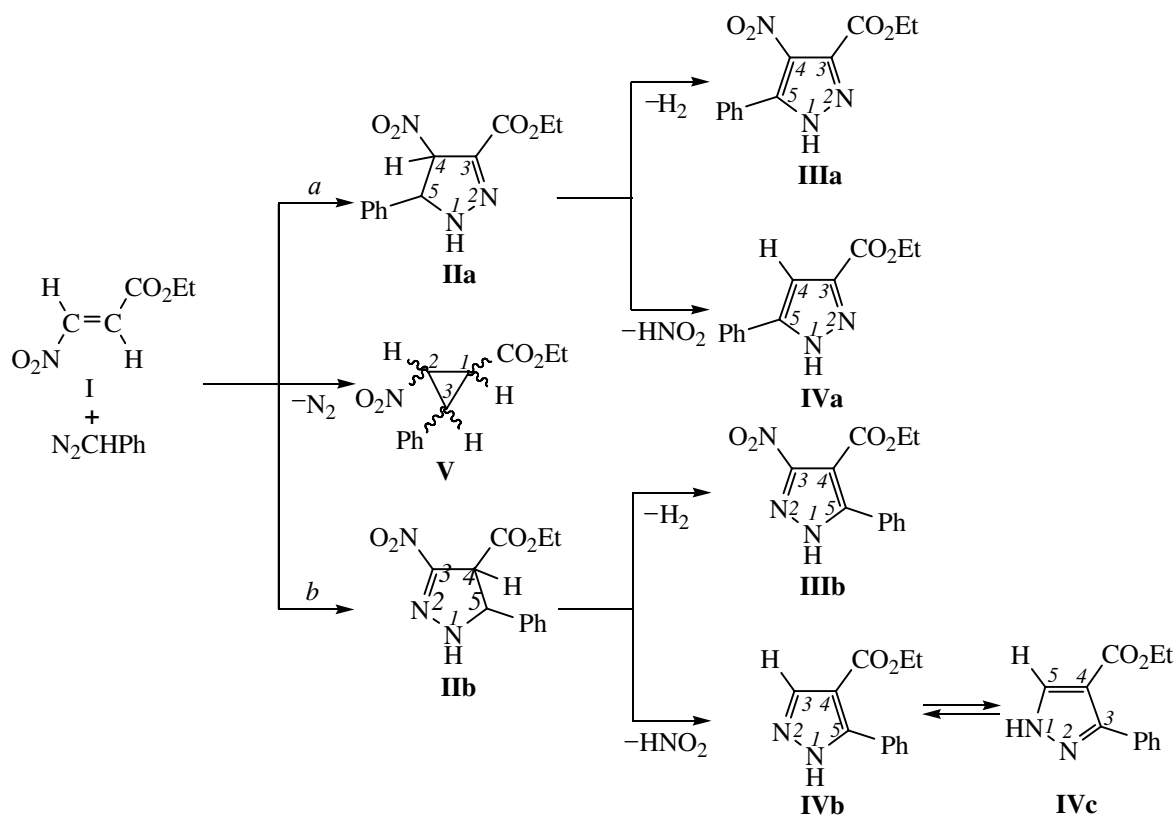
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We investigated for the first time a reaction of ethyl 3-nitroacrylate with phenyldiazomethane. The reaction proceeded along two concurrent routes (*a* and *b*) and in spite of mild conditions (18–20°C, ether) was accompanied with a number of intramolecular rearrangements. The primarily formed Δ^1 -pyrazolines suffered a prototropic isomerization into regioisomeric Δ^2 -pyrazolines **IIa** and **IIb**. The latter in their turn underwent

dehydrogenation or nitrous acid elimination converting into the corresponding Δ^2 -pyrazoles with a nitro group (**IIIa** and **IIIb**) or without it (**IVa** and **IVb**). In the mixture of regioisomeric pyrazoles **IVa** and **IVb** a tautomer **IVc** was also found.

Alongside the azoles the reaction mixture contained nitrocyclopropane (**V**) isolated as a mixture of diastereomers. Δ^2 -Pyrazolines **IIa** and **IIb**, nitropyrazoles



IIIa and **IIIb**, and pyrazoles **IVa** and **IVb** were obtained as mixtures of regioisomers and tautomers as showed their ^1H NMR spectra containing sets of two or three signals from the corresponding protons.

The structure of compounds obtained was established from their IR and ^1H NMR spectra referring to the known spectra of pyrazolines [1, 2], pyrazoles [3, 4], and cyclopropanes [5]. Besides the spectra of compound **IVa** were like those of 5-phenyl-3-ethoxycarbonyl- Δ^2 -pyrazole formerly prepared by another method [3].

^1H NMR spectra of the pairs of regioisomers (pyrazolines **IIa** and **IIb**, nitropyrazoles **IIIa** and **IIIb**, and pyrazoles **IVa** and **IVb**) are distinguished by the proton signals of the ring and of NH group. For instance, in the spectrum of pyrazoline **IIa** the signal of nitromethine proton at the atom C^4 appeared naturally downfield (at 4.75 ppm) compared to the analogous proton in pyrazoline **IIb** linked to the CO_2Et group (4.22 ppm). The signal of proton H^5 (5.22 ppm) in the spectrum of pyrazoline **IIa** also is shifted downfield due to the effect of the adjacent NO_2 group with respect to the corresponding signal in the spectrum of compound **IIb** (5.08 ppm). ^1H NMR spectrum of the mixture of pyrazoles **IVa–IVc** contains three signals from olefin protons of the ring at 7.25, 7.75, and 7.35 ppm. This signal (of the H^3 proton) in the spectrum of isomer **IVb** appeared at 7.75 ppm under the influence of the $\text{C}=\text{N}$ bond, the signal of analogous cyclic proton (H^5) was observed in the spectrum of isomer **IVc** at 7.35 ppm due to the effect of the contiguous atom N^1 . The signal of the cyclic proton at 7.25 ppm was assigned to pyrazole **IVa**.

The regioisomeric pyrazoles **IIIa** and **IIIb** were distinguished by the signals of the cyclic NH group: It was a singlet at 8.80 ppm in the spectrum of compound **IIIa**, and in pyrazole **IIIb** this signal was shifted downfield (11.0 ppm) due to the effect of the neighbor $\text{C}=\text{N}$ bond linked to NO_2 group.

In the IR spectra of compounds **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa–IVc**, and **V** the absorption bands of the ester carbonyl were observed at $1730\text{--}1738\text{ cm}^{-1}$, the unconjugated nitro group of compounds **IIa**, **IIb**, and **V** appeared as absorption bands in the regions $1560\text{--}1570$ and $1345\text{--}1380\text{ cm}^{-1}$, and the bands at $1540\text{--}1550$ and $1320\text{--}1350\text{ cm}^{-1}$ in the spectra of compounds **IIIa** and **IIIb** corresponded to the conjugated nitro group.

2-Nitroacrylate **I** [6] and phenyldiazomethane [7] were prepared by published procedures.

4-Nitro-3-ethoxycarbonyl- and 3-nitro-4-ethoxycarbonyl-5-phenyl-4,5-dihydro-1H-pyrazoles (IIa

and IIb). Yield 13% (eluent benzene), R_f 0.65, 0.70; ratio (**IIa**):(**IIb**) = 1:1. IR spectrum, ν , cm^{-1} : 1738 ($\text{C}=\text{O}$), 1545–1570, 1345–1380 (NO_2), 3435 (NH). ^1H NMR spectrum, δ , ppm, isomer **IIa**: 4.75 d (1H, H^4), 5.22 d (1H, H^5 , $^3J_{4,5}$ 10.0 Hz), 4.32 q (2H, OCH_2), 1.32 t (3H, CH_3), 7.00–7.50 m (5H, C_6H_5), 7.70 s (1H, NH); isomer **IIb**: 4.22 d (1H, H^4), 5.08 d (1H, H^5 , $^3J_{4,5}$ 13.0 Hz), 4.22 m (2H, OCH_2), 1.24 m (3H, CH_3), 7.00–7.50 m (5H, C_6H_5), 7.70 s (1H, NH). Found, %: C 54.68, 54.65; H 4.99, 4.96; N 15.76, 15.75. $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$. Calculated, %: C 54.75; H 4.94; N 15.97.

4-Nitro-3-ethoxycarbonyl- and 3-nitro-4-ethoxycarbonyl-5-phenylpyrazoles (IIIa and IIIb). Yield 15% (eluent CCl_4), R_f 0.55, 0.45; ratio (**IIIa**):(**IIIb**) = 3:2. IR spectrum, ν , cm^{-1} : 1730 ($\text{C}=\text{O}$), 1540–1550, 1320–1350 (NO_2), 3430, 3250 (NH). ^1H NMR spectrum, δ , ppm; isomer **IIIa**: 4.25 m (2H, OCH_2), 1.20 m (3H, CH_3), 7.20–7.60 m (5H, C_6H_5), 8.80 s (1H, NH); isomer **IIIb**: 4.25 m (2H, OCH_2), 1.20 m (3H, CH_3), 7.20–7.60 m (5H, C_6H_5), 11.0 s (1H, NH). Found, %: C 55.11, 55.10; H 4.30, 4.27; N 16.41, 16.44. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4$. Calculated, %: C 55.17; H 4.21; N 16.09.

5-Phenyl-3-ethoxycarbonyl-, 5-phenyl-4-ethoxycarbonyl-, and 4-ethoxycarbonyl-3-phenylpyrazoles (IVa–IVc). Yield 38% (eluent CCl_4), R_f 0.47, 0.40, 0.32; ratio (**IVa**):(**IVb**):(**IVc**) = 4:1:2. IR spectrum, ν , cm^{-1} : 1730 ($\text{C}=\text{O}$), 3434, 3260 (NH). ^1H NMR spectrum, δ , ppm, isomer **IVa**: 7.25 s (1H, H^4), 4.32 q (2H, OCH_2), 1.32 t (3H, CH_3), 7.00–7.70 m (5H, C_6H_5), 10.30 s (1H, NH); isomer **IVb**: 7.75 s (1H, H^3), 4.38 q (2H, OCH_2), 1.40 t (3H, CH_3), 7.00–7.70 m (5H, C_6H_5), 9.05 s (1H, NH); isomer **IVc**: 7.35 s (1H, H^5), 4.38 q (2H, OCH_2), 1.40 t (3H, CH_3), 7.00–7.70 m (5H, C_6H_5), 8.95 s (1H, NH). Found, %: C 65.22, 65.34; H 5.06, 5.14; N 12.62, 12.65. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$. Calculated, %: C 66.67; H 5.56; N 12.96.

2-Nitro-3-phenyl-1-ethoxycarbonylcyclopropane (V). Yield 8% (eluent acetone), mixture of diastereomers, R_f 0.24, 0.16. IR spectrum, ν , cm^{-1} : 1735 ($\text{C}=\text{O}$), 1560, 1370 (NO_2). ^1H NMR spectrum, δ , ppm: 2.10 m (1H, H^3), 3.52 m (1H, H^1), 4.35 m (1H, H^2), 4.22 q (2H, OCH_2), 1.24 t (3H, CH_3), 7.00–7.50 m (5H, C_6H_5). Found, %: N 5.98, 5.99. $\text{C}_{12}\text{H}_{13}\text{NO}_4$. Calculated, %: N 5.96.

IR spectra were recorded on a spectrometer InfraLUM 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 deuteriochloroform, external reference HMDS.

The isolation and purification of individual compounds was performed by column chromatography on silica gel Chemapol (100/200 μm). The reaction progress was monitored by TLC on Silufol-254 plates, eluent hexane–acetone, 3:2, development in iodine vapor.

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