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SHORT COMMUNICATIONS

Reaction of Methyl-3-nitroacrylate with 3-(2-Nitroethenyl)indole

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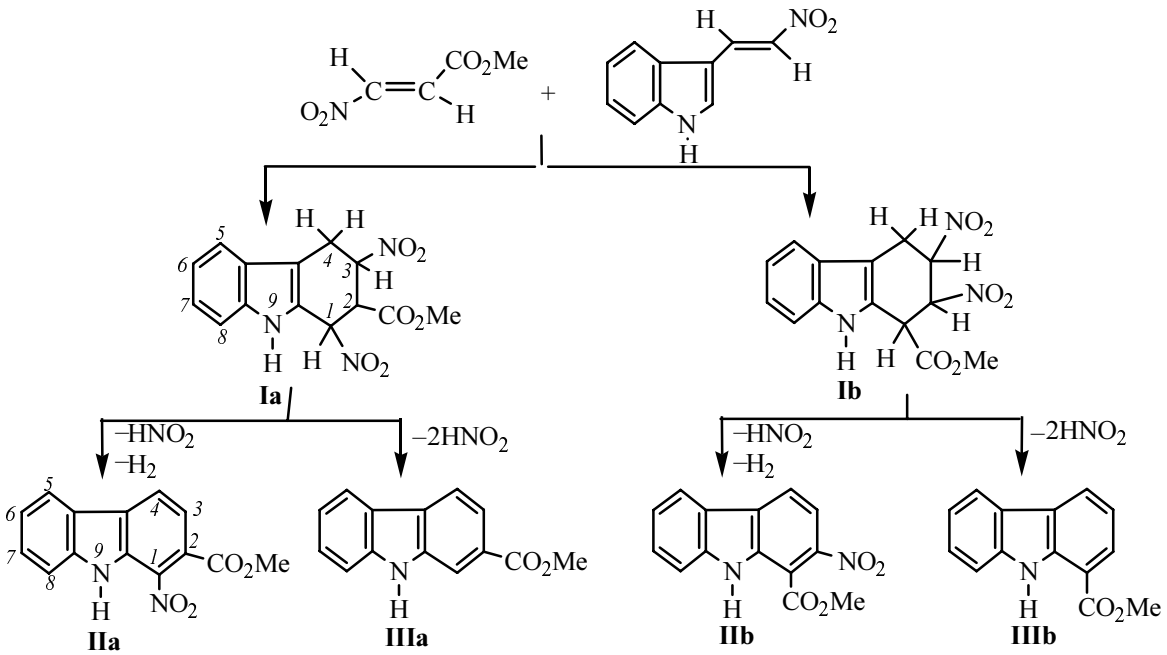
Carbazole is a structural fragment of many substances possessing useful properties [1]. This heterocycle attracts interest because it is widespread in the nature (being the key structural element of the carbazole alkaloids [2]) and is relatively easily available (being one of the components of coal-tar pitch [3]).

It is known that α- and β-nitrovinylindoles react with dienophiles (maleic anhydride, ethyl acrylate, acrylonitrile, cinnamic aldehyde) to form the corresponding substituted carbazoles [4, 5].

In order to prepare functionalized nitrocarbazoles we investigated for the first time a [4+2]-cycloaddition of methyl 3-nitroacrylate (dienophile) and 3-(2-nitroethenyl)-indole (diene). The reaction was carried out by boiling the reagents mixture in toluene in the presence of aluminum chloride for 2 h. The process proceeded along two paths and led to the formation of regioisomeric tetrahydrocarbazoles **Ia** and **Ib** which already under the reaction conditions suffered an intramolecular transformation (dehydration and denitration) into the corresponding carbazolylcarboxylates possessing a nitro group **IIa** and **IIb** or free of the nitro group **IIIa** and **IIIb**.

Applying the column chromatography we not only succeeded in isolation compounds **Ia, Ib**–**IIIa, IIIb** as mixtures of regioisomeric pairs, but we were also able to identify regioisomers **IIb** and **IIIa** as individual substances.

The structure of compounds **Ia, Ib**–**IIIa, IIIb** obtained was established by IR and ^{1}H NMR spectroscopy in comparison with the spectra of structurally similar compounds described in [6, 7]. The formation of regioisomeric pairs of these compounds follows from the appearance in the ^{1}H NMR spectrum of a double set of



signals from protons of the substituted ring, and from the ester group protons.

The assignment of the regioisomer structure of compounds **Ia, Ib**–**IIIa, IIIb** obtained was done basing on the different effect of the substituents on the ring protons in the compared structures using as an analytical criterion the difference in the chemical shifts and the integral intensities of methylene, methine (for compounds **Ia** and **Ib**), and aromatic (for compounds **IIa, IIb** and **IIIa, IIIb**) protons, and also the coupling constants values. For instance, in the ^{1}H NMR spectrum of the mixture of compounds **Ia** and **Ib** the more downfield nitromethine protons at 4.30 and 4.35 ppm attached to atoms C^2, C^3 were assigned to isomer **Ib** on the strength of the greater deshielding effect of the nitro groups compared to that (4.20 and 4.25 ppm) for the protons at C^1, C^3 in **Ia** isomer..

Based on the coupling constants of the vicinal protons equal to 7.5–8.0 Hz we ascribed the *ortho*-orientaion of aromatic protons at atoms C^3, C^4 in carbazole regioisomers **IIa** and **IIb** [4, 8]. The effect of the nitro group caused a downfield shift of the resonances of aromatic protons H^3, H^4 in carbazole **IIb** to 8.15 and 8.35 ppm, whereas in isomer **IIa** they appear in a stronger field, at 7.90 and 8.15 ppm respectively. In the ^{1}H NMR spectrum of regioisomer **IIIa** the aromatic proton at C^1 gives rise to a singlet at 8.30 ppm, and the signals of protons H^3, H^4 are observed as a multiplet in the region 7.90–8.10 ppm. The signals of the aromatic protons of regioisomer **IIIb** at the atoms C^2, C^3, C^4 appear in the range 7.90–8.15 ppm, with the coupling constant of the *ortho*-protons H^3, H^4 9.0 Hz, of *meta*-protons H^2, H^4 0.8–1.1 Hz.

The initial methyl 3-nitroacrylate was prepared by the procudure from [9] refined by us, the synthesis of 3-(2-nitroethenyl)indole was performed by method [10].

2-Methoxycarbonyl-1,3-dinitro- and 1-methoxycarbonyl-2,3-dinitro-1,2,3,4-tetrahydrocarbazoles (Ia and Ib). Yield 34% (eluent acetone), R_f 0.40, 0.45, mp 108–110°C, ratio **Ia**:**Ib** = 3:2. IR spectrum ($CHCl_3$), cm^{-1}: 1730 (S=O), 1328, 1536 (NO_2), 3460 (NH). ^{1}H NMR spectrum, δ, ppm: isomer **Ia**, 2.20–2.50 m (2H, C^4H, $J_{3,4}$ 16.5 Hz), 3.50 m (1H, C^2H), 3.90 s (3H, CH_3), 4.20 m (1N, C^3H), 4.25 (1H, C^1H), 7.20–7.60 m (4H, C_6H_4), 10.20 (1H, NH); isomer **Ib**, 2.20–2.50 m (1H, S^4H, $J_{3,4}$ 16.5 Hz), 3.30 m (1H, C^1H), 3.80 s (3H, CN_3), 4.30 m (1N, C^3H), 4.35 m (1N, C^2H), 7.20–7.60 m (4H, C_6H_4), 9.50 (1H, NH). Found, %: H 13.35, 13.39. $C_{14}H_{13}N_3O_6$. Calculated, %: N 13.17.

2-Methoxycarbonyl-1-nitro- and 1-methoxycarbonyl-2-nitrocarbazoles (IIa and IIb). Yield 8% (eluent benzene), ratio **IIa**:**IIb** = 1:10, R_f 0.49, 0.40, mp 133–135°S, isomer **IIb** (eluent at repeated chromatography benzene) mp 153–155°C. IR spectrum, cm^{-1}: 1730 (S=O), 1330, 1520 (NO_2), 3460 (NH). ^{1}H NMR spectrum, δ, ppm: isomer **IIa**, 3.90 s (3H, CN_3), 7.25–7.65 m (4H, C_6H_4), 7.90 d [1H, C^4H, $J_{3,4}$ 7.5 Hz], 8.15 d (1H, C^3H, $J_{3,4}$ 7.5 Hz), 10.50 (1H, NH); isomer **IIb**, 4.03 s (3H, CH_3), 7.25–7.65 m (4H, C_6H_4), 8.15 d (1H, C^4H, $J_{3,4}$ 8.0 Hz), 8.35 d [1N, C^3H, $J_{3,4}$ 8.0 Hz], 10.00 (1H, NH). Found, %: C 61.72, 61.77; H 3.30, 3.44; N 9.81, 9.82. $C_{14}H_{10}N_2O_4$. Calculated, %: C 62.22; H 3.70; N 10.37.

2-Methoxycarbonyl- and 1-methoxycarbonylcarbazoles (IIIa and IIIb). Yield 25% (eluent benzene), ratio **IIIa**:**IIIb** = 10:1, mp 165–168°C, isomer (**IIIa**) (eluent at repeated chromatography benzene) mp 171–173°C. IR spectrum, cm^{-1}: 1710 (C=O), 3465 (NH). ^{1}H NMR spectrum, δ, ppm: isomer **IIIa**, 4.20 s (3N, CN_3), 7.20–7.60 m (4H, C_6H_4), 7.80 (1H, NH), 7.90–8.10 m (2H ,C^3H ,C^4H), 8.30 s (1H, C^1H); isomer **IIIb**, 3.90 s (3H, CH_3), 7.20–7.60 m (4N, C_6H_4), 7.90 d.d (1H, C^3H, $J_{3,4}$ 9.0, $J_{3,2}$ 0.8 Hz), 8.10 d.d (1H, C^4H, $J_{3,4}$ 9.0, $J_{2,4}$ 0.8 Hz), 8.15 d.d (1H, C^2H, $J_{2,3}$ 7.9, $J_{2,4}$ 1.1 Hz), 8.70 (1H, NH). Found, %: C 74.27, 74.24; H 4.95, 4.97; N 6.92, 6.93. $C_{14}H_{11}NO_2$. Calculated, %: C 74.66; H 4.89; N 6.63.

IR spectra were recorded on a spectrophotometer Infra-LYuM FT-02 from solutions in chloroform, *c* 0.1–0.001 mol l^{-1}. ^{1}N NMR spectra were registered on a spectrometer Bruker AS-200 (200 MHz) in deuterochloroform, external reference HMDS.

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