

SHORT
COMMUNICATIONS

Methyl 3-Nitroacrylate Reaction with 2-(2-nitroethenyl)furan

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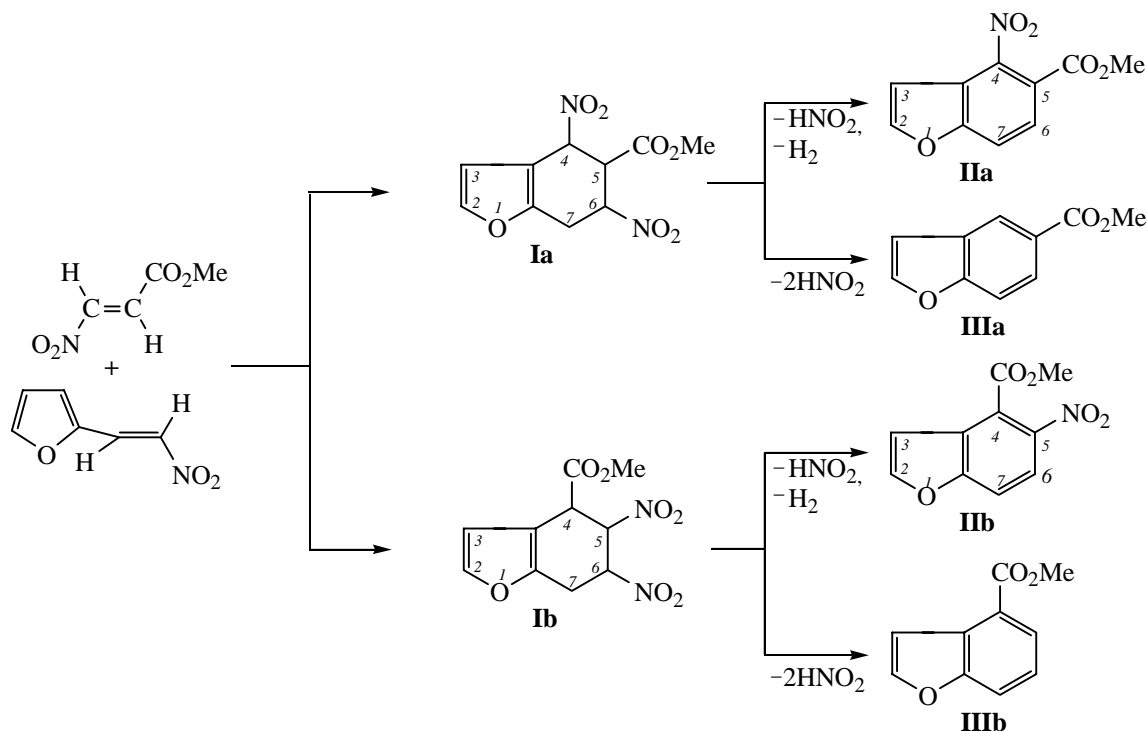
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Benzofuran fragment frequently appears in compounds from vegetable kingdom origin (carotenoids, alkaloids) [1], it is contained in the structure of enzymes inhibitors [2, 3], plant growth regulators [4], and also of synthetic drugs [5–7]. The modified benzofuran ring is a structural fragment of a molecule of fungicidal antibiotic Griseofulvin [8].

One of the known methods for preparation of benzofuran derivatives is Diels–Alder reaction between β -furylnitroethene (diene component) and methyl acrylate or acrylonitrile (dienophiles) [1]; the process requires severe conditions (100–140°C, pressure reactor) and results in

formation of disubstituted tetrahydrobenzofurans which further under treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone undergo aromatization into the corresponding benzofurans.

We studied for the first time the reaction of methyl 3-nitroacrylate with β -furylnitroethene. It turned out that in this case the cycloaddition occurred readily at boiling the equimolar mixture of then reagents (0.008 mol) in 10 ml of toluene for 6 h. The reaction takes two routes to give regioisomeric tetrahydrobenzofurans **Ia** and **Ib** that on dehydrogenation and elimination of nitrous acid convert



into the corresponding benzofurans with a nitro group (**Ia** and **Ib**) and without it (**IIa** and **IIb**).

The structure of compounds obtained was confirmed by spectral methods. In their IR spectra absorption bands were observed in the region 1735–1740 cm^{-1} belonging to the vibrations of the carbonyl of ester group, absorption bands of nonconjugated nitro groups of compounds **Ia** and **Ib** appeared at 1570–1565 and 1360–1370 cm^{-1} , and those of conjugated nitro groups of compounds **IIa** and **IIb**, at 1540–1520 and 1350–1340 cm^{-1} . ^1H NMR spectra of all compounds obtained contained a double set of signals with different intensity ratio.

In tetrahydrobenzofurans **Ia** and **Ib** the signals of nitromethine protons of **Ia** isomer appear upfield at 4.10 and 4.40 ppm, whereas in the spectrum of **Ib** isomer they are shifted downfield (4.45 and 4.60 ppm) due to the effect of two contiguous nitro groups attached to atoms C^{5,6}. The cyclic proton H⁵ situated at the ester group is similarly affected and appeared in **Ia** isomer at 3.90 ppm downfield with respect to H⁴ proton in compound **Ib** which gives rise to a peak at 3.60 ppm.

As analytical criterion of the regioisomer assignment of compounds **IIa** and **IIb** was used, like in [9–11], the comparative estimation of δ values of aromatic protons attached to atoms C^{6,7}. Under the effect of a nitro group these protons in the ^1H NMR spectrum of compound **IIb** appear downfield at 8.20 and 8.40 ppm respectively as compared to the position of the signals of analogous protons (7.90 and 8.10 ppm) in **IIa** isomer. The value of the coupling constant of protons H^{6,7} equal 7.9 Hz unambiguously indicates their *ortho*-orientation [12]. Similarly to [1] the protons of ester group CO_2CH_3 at 4.0 ppm should be assigned to **IIb** regioisomer, and protons at 3.9 ppm, to **IIa** isomer.

Spectral characteristics of **IIIa** isomer coincide with those published in [1] for this compound obtained by another method; the corresponding parameters of **IIIb** isomer have close values.

Initial β -nitroacrylate was obtained by refined procedure from [13], β -furylnitroethene was prepared as in [14].

4,6(5,6)-Dinitro-5(4)-methoxycarbonyl-4,5,6,7-tetrahydrobenzofurans Ia and Ib. Yield 30% (eluent chloroform), R_f 0.52, 0.58; ratio (**Ia**):(**Ib**) = 2:1. IR spectrum, cm^{-1} : 1750 (C=O), 1360, 1370, 1575, 1565 (NO_2). ^1H NMR spectrum, δ , ppm, isomer **Ia**: 7.52 d (1H, H²), 6.62 d (1H, H³), 4.00–4.45 m (3H, H⁴⁻⁶), 3.40–3.50 m (2H, H⁷), 4.10 s (3H, CH_3); isomer **Ib**: 7.52 d

(1H, H²), 6.42 d (1H, H³), 3.90 (1H, H⁴), 4.60 (1H, H⁵), 4.10 (1H, H⁶), 3.50–3.70 m (2H, H⁷), 3.90 s (3H, CH_3). Found, %: N 10.00, 10.03. $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_7$. Calculated, %: N 10.37.

5(4)-Methoxycarbonyl-4,5-nitrobenzofurans IIa and IIb. Yield 33% (eluent benzene), R_f 0.60, 0.65; ratio (**IIa**):(**IIb**) = 11:1. IR spectrum, cm^{-1} : 1740 (C=O), 1350, 1540 (NO_2). ^1H NMR spectrum, δ , ppm, isomer **IIa**: 7.80 d (1H, H², $J_{2,3}$ 7.5 Hz), 7.50 d (1H, H³, $J_{3,2}$ 7.5 Hz), 8.10 d (1H, H⁶, $J_{6,7}$ 7.9 Hz), 7.90 d (1H, H⁷, $J_{6,7}$ 7.9 Hz), 3.90 s (3H, CH_3); isomer **IIb**: 7.80 d (1H, H², $J_{2,3}$ 7.5 Hz), 7.50 d (1H, H³, $J_{3,2}$ 7.5 Hz), 8.40 d (1H, H⁶, $J_{6,7}$ 7.9 Hz), 8.20 d (1H, H⁷, $J_{7,6}$ 7.9 Hz), 4.00 s (3H, CH_3). Found, %: C 53.99, 54.10; H 3.13, 3.17; N 6.03, 6.09. $\text{C}_{10}\text{H}_7\text{NO}_5$. Calculated, %: C 54.30; H 3.17; N 6.33.

5(4)-Methoxycarbonylbenzofurans IIIa and IIIb. Yield 15% (eluent benzene), R_f 0.69, 0.75; ratio (**IIIa**):(**IIIb**) = 3:2. ^1H NMR spectrum, δ , ppm, isomer **IIIa**: 7.80 d (1H, H², $J_{2,3}$ 7.5 Hz), 7.60 d (1H, H³, $J_{2,3}$ 7.5 Hz), 7.30 m (1H, H⁴, $J_{4,6}$ 2.25 Hz), 7.50 m (1H, H⁶, $J_{6,7}$ 7.5 Hz, $J_{4,6}$ 2.25 Hz), 8.00 (1H, H⁷, $J_{7,6}$ 7.5 Hz), 3.80 s (3H, CH_3); isomer **IIIb**: 7.80 d (1H, H², $J_{2,3}$ 7.5 Hz), 7.60 d (1H, H³, $J_{2,3}$ 7.5 Hz), 7.30–7.50 m (2H, H⁵, H⁶), 7.90 d (1H, H⁷), 3.90 s (3H, CH_3). Found, %: C 68.01, 68.03; H 4.43, 4.47. $\text{C}_{10}\text{H}_8\text{O}_3$. Calculated, %: C 68.18; H 5.54.

IR spectra were recorded on a spectrophotometer Infra-LYuM 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) in deuteriochloroform, external reference HMDS.

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

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