

SHORT  
COMMUNICATIONS

## 3-Nitro- and 3-Bromo-3-nitroacrylates in Reactions with 2-Phenyl-1,3-indanedione

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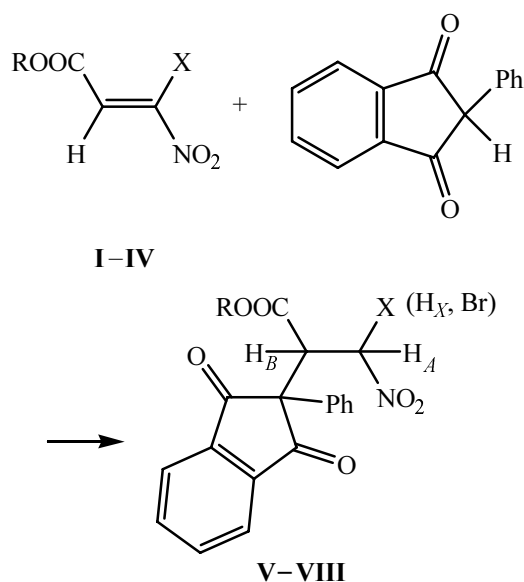
Alkyl 3-nitroacrylates are highly reactive reagents used in the designed synthesis of practically important substances. In particular methods were developed based on these compounds for preparation of oryzoxymycin antibiotic [1], and also for  $\beta$ -amino acids used in the synthesis of  $\beta$ -peptides [2, 3]. An introduction of a halogen into the molecules of alkyl 3-nitroacrylates a priori extends their synthetic opportunities [4, 5] and makes it possible to regard the halonitroacrylates as promising synthons in designing compounds with desired properties. In this respect the investigation of reactions of 3-nitro- and 3-bromo-3-nitroacrylates **I–IV** with C-nucleophiles is of a great interest, in particular, the reaction with 2-phenyl-1,3-indanedione which possesses its proper importance as

an anticoagulant and which is used in the treatment of thrombosis as a phenindione medicine [6, 7].

Our studies demonstrated that the mentioned substrates **I–IV** readily added 2-phenyl-1,3-indanedione (in benzene solution at equimolar reagents ratio in the presence of a catalytic amount of triethylamine) forming adducts of a Michael condensation **V–VIII**.

Compound **V** is a colorless viscous liquid, and compounds **VI–VIII** are crystalline substances; their structure is confirmed by spectral methods. For instance, the IR spectra of adducts **VII** and **VIII** contain the absorption bands of  $\beta$ -dicarbonyl ( $1715\text{--}1750\text{ cm}^{-1}$ ), nitro ( $1350, 1575\text{--}1580\text{ cm}^{-1}$ ) groups and multiple C=C bonds of the aromatic rings ( $1600\text{ cm}^{-1}$ ). It should be noted that the split bands in the region  $1700\text{--}1750\text{ cm}^{-1}$  are typical of the  $\beta$ -diketo fragments [8], and the observed large distance between the bands of the symmetric and antisymmetric vibrations of the nitro group ( $\Delta\nu \sim 230\text{ cm}^{-1}$ ) is characteristic of the geminal location of a nitro group and a halogen atom [9]. In the  $^1\text{H}$  NMR spectra all the signals from the structural fragments of the compounds were revealed. In particular, the  $^1\text{H}$  NMR spectrum of compound **VII** contained a double set of proton signals from the methine and methyl groups corresponding to the existence of the compound as a mixture of two diastereomers in a ratio (**VIIa**):(**VIIb**) = 12:1. According to the  $^1\text{H}$  NMR data the ethoxy analog **VIII** is stereo homogeneous. Compounds **V–VIII** obtained may be regarded as precursors of the  $\beta$ -alanine containing a pharmacophoric fragment of 2-phenyl-1,3-indanedione.

Initial nitroacrilates **I** and **II** were synthesized by a modified published procedure [10], and alkyl 3-bromo-



X = H, R = Me (**I**, **V**), Et (**II**, **VI**); X = Br, R = Me (**III**, **VII**), Et (**IV**, **VIII**).

3-nitroacrylates **III** and **IV** were prepared as described in [4].

**2-(1-Methoxycarbonyl-2-nitroethyl)-2-phenyl-1,3-indanedione (V)**. Yield 76% (eluent benzene),  $R_f$  0.36. IR spectrum,  $\text{cm}^{-1}$ : 1735, 1710 (C=O), 1600 (C=C), 1560, 1380 ( $\text{NO}_2$ ).  $^1\text{H}$ ,  $\delta$ , ppm: 3.56 s (3H,  $\text{OCH}_3$ ), 5.13 d.d (1H,  $\text{H}_A$ ,  $J_{AB}$  14.6,  $J_{AX}$  9.2 Hz), 4.33 d.d (1H,  $\text{H}_B$ ,  $J_{AB}$  14.6,  $J_{BX}$  2.7 Hz), 4.74 d.d (1H,  $\text{H}_X$ ,  $J_{AX}$  9.2,  $J_{BX}$  2.7 Hz), 7.31–8.06 m (9H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). Found, %: C 64.68, 64.64; H 4.41, 4.40; N 3.95, 3.94.  $\text{C}_{19}\text{H}_{15}\text{NO}_6$ . Calculated, %: C 64.59; H 4.28; N 3.96.

**2-(2-Nitro-1-ethoxycarbonyl-ethyl)-2-phenyl-1,3-indanedione (VI)**. Yield 82%, mp 133–135°C (from ethanol). IR spectrum,  $\text{cm}^{-1}$ : 1750, 1730 (C=O), 1600 (C=C), 1560, 1380 ( $\text{NO}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.99 t (3H,  $\text{CH}_3$ ), 3.99 q (2H,  $\text{OCH}_2$ ), 5.13 d.d (1H,  $\text{H}_A$ ,  $J_{AB}$  14.6,  $J_{AX}$  9.8 Hz), 4.30 d.d (1H,  $\text{H}_B$ ,  $J_{AB}$  14.6,  $J_{BX}$  2.4 Hz), 4.70 d.d (1H,  $\text{H}_X$ ,  $J_{AX}$  9.8,  $J_{BX}$  2.4 Hz), 7.31–8.07 m (9H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). Found, %: C 65.44, 65.42; H 3.95, 3.99; N 3.89, 3.90.  $\text{C}_{20}\text{H}_{17}\text{NO}_6$ . Calculated, %: C 65.39; H 4.66; N 3.81.

**2-(2-Bromo-1-methoxycarbonyl-2-nitroethyl)-2-phenyl-1,3-indanedione (VIIa, b)**. Yield 22%, mp 174–176°C (from methanol); ratio of (VIIa):(VIIb) = 12:1. IR spectrum,  $\text{cm}^{-1}$ : 1740, 1715 (C=O), 1600 (C=C), 1580, 1350 ( $\text{NO}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: isomer VIIa 3.59 s (3H,  $\text{CH}_3\text{O}$ ), 6.33 d (1H,  $\text{H}_A$ ,  $J_{AB}$  4.9 Hz), 4.47 d (1H,  $\text{H}_B$ ,  $J_{AB}$  4.9 Hz), 7.33–8.07 m (9H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ); isomer VIIb 3.66 s (3H,  $\text{CH}_3\text{O}$ ), 6.42 d (1H,  $\text{H}_A$ ,  $J_{AB}$  4.3 Hz), 5.21 d (1H,  $\text{H}_B$ ,  $J_{AB}$  4.3 Hz), 7.33–8.07 m (9H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). Found, %: C 52.84, 52.85; H 3.32, 3.33; N 3.22, 3.23.  $\text{C}_{19}\text{H}_{14}\text{BrNO}_6$ . Calculated, %: C 52.80; H 3.26; N 3.24.

**2-(2-Bromo-2-nitro-1-ethoxycarbonyl-ethyl)-2-phenyl-1,3-indanedione (VIII)**. Yield 40% (eluent benzene), mp 133–136°C (from ethanol). IR spectrum,  $\text{cm}^{-1}$ : 1735, 1715 (C=O), 1600 (C=C), 1575, 1350 ( $\text{NO}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.14 t (3H,  $\text{CH}_3$ ), 4.09 q (2H,  $\text{CH}_2\text{O}$ ), 6.38 d (1H,  $\text{H}_A$ ,  $J_{AB}$  3.7 Hz), 5.19 d (1H,  $\text{H}_B$ ,  $J_{AB}$  3.7 Hz), 7.33–8.11 m (9H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ). Found, %: C 53.99, 54.00; H 3.91, 3.93; N 3.39, 3.38.  $\text{C}_{20}\text{H}_{16}\text{BrNO}_6$ . Calculated, %: C 53.83; H 3.61; N 3.14.

IR spectra were recorded on a spectrophotometer Infra-LYuM FT-02 from solutions in chloroform,  $c$  0.1–0.001 mol  $\text{l}^{-1}$ .  $^1\text{H}$  NMR spectra were registered on a spectrometer Bruker AC-200 (200 MHz) in deuteriochloroform; the chemical shifts were measured relative to an external reference HMDS with an accuracy  $\pm 0.5$  Hz. The purification and isolation of individual compounds was performed by recrystallization and column chromatography on silica gel Chemapol 100/250 using Trappe solvents series. The homogeneity of compounds obtained was checked and the reaction progress was monitored by TLC on Silufol UV-254 plates, eluent a mixture hexane–acetone, 2:1, development under UV irradiation and in iodine vapor.

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