

SHORT  
COMMUNICATIONS

## Preparation of 2-Benzoyl-1-bromo-1-nitroethene

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Received April 20, 2004

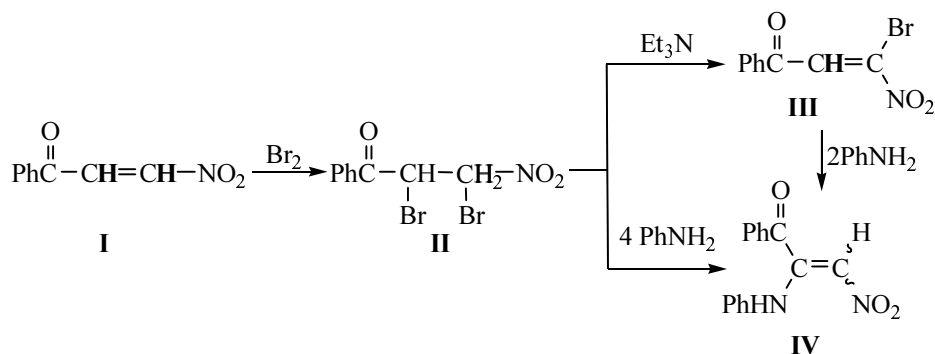
Halonitroalkenes belong to an interesting class of organic compounds with reach synthetic opportunities [1, 2]. A special attention are worth gem-halonitroethenes containing an electron-withdrawing substituent in a vicinal position to the nitro group. For instance, gem-halonitroethenes with a phosphonate function are highly active in reactions with nucleophilic reagents [3, 4], in diene synthesis [5, 6], and can be regarded as convenient “building blocks” for preparation of substances with specially designed structure.

We synthesized the first representative of carbonyl-containing gem-halonitroethenes, 2-benzoyl-1-bromo-1-nitroethene. The preparation procedure involves two stages: bromination of initial 2-benzoyl-1-nitroethene (**I**) with subsequent dehydrobromination of addition product **II**. Reaction of compound **I** with a double excess of bromine in the glacial acetic acid or in carbon tetrachloride afforded dibromide **II**, and the best yield (65%) was obtained at at bromination in carbon tetrachloride. Compound **II** is a light-yellow oily fluid.

Dehydrohalogenation of dibromide **II** in  $\text{CCl}_4$  was effected by triethylamine within 1 h at room temperature.

Bromonitroethenyl phenyl ketone (**III**) was isolated as light-yellow low-melting crystals (yield 63%). Reaction of bromonitroethenyl phenyl ketone (**III**) with double excess of aniline in anhydrous benzene furnishes nitroenamine **IV** that may be regarded as resulting from dehydrohalogenation of the primarily arising addition product. Nitroenamine **IV** was also prepared directly from dibromide **II**, and a mixed sample of nitroenamines obtained by both methods melted with no depression of the melting point.

The structure of compounds **II–IV** was proved by IR,  $^1\text{H}$  NMR, and UV spectroscopy. For instance, in the IR spectrum of compound **III** were present absorption bands corresponding to all functional groups; therewith the bands of nitrogroup stretching vibrations ( $\nu_{as}$  1560,  $\nu_s$  1320  $\text{cm}^{-1}$ ) appear with the difference  $\Delta\nu$  240  $\text{cm}^{-1}$  characteristic of conjugated nitroalkenes containing a halogen in the *gem*-position with respect to the nitro group [7]. In the  $^1\text{H}$  NMR spectrum the olefin proton is located downfield (8.48 ppm.) that corresponds to its *cis*-orientation regarding the nitro group [8]. The IR and electronic spectra of compound **IV** reveal a high polarization in its molecule.



The initial 2-benzoyl-1-nitroethene was prepared by a published procedure [9].

The reaction progress was monitored and homogeneity of compounds obtained was checked by TLC on Sulufol UV-254 plates, eluent hexane–acetone, 3:1, development in iodine vapor or under UV irradiation.

**2,3-Dibromo-3-nitro-1-phenylpropan-1-one (II).**  $R_f$  0.48. IR spectrum,  $\text{cm}^{-1}$ : 1690 (C=O), 1572, 1352 ( $\text{NO}_2$ ), 1600 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 8.05–7.56 (5H,  $\text{C}_6\text{H}_5$ ), 6.47–6.40 q (1H,  $\text{CHBrNO}_2$ ), 5.85–5.66 q (1H,  $\text{CHBrCO}$ ). Found, %: C 32.20, 32.26; H 2.58, 2.60; N 4.25, 4.23.  $\text{C}_9\text{H}_7\text{Br}_2\text{NO}_3$ . Calculated, %: C 32.05; H 2.08; N 4.15.

**2-Benzoyl-1-bromo-1-nitroethene (III).**  $R_f$  0.58, mp 25–26°C (from petroleum ether). IR spectrum,  $\text{cm}^{-1}$ : 1685 (C=O), 1560, 1320 ( $\text{NO}_2$ ), 1600, 1580 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 8.48 s (1H,  $\text{CHNO}_2$ ), 7.27–7.92 m (5H,  $\text{C}_6\text{H}_5$ ). UV spectrum:  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 253 (14300). Found, %: C 42.41, 42.43; H 2.03, 2.01; N 5.51, 5.53.  $\text{C}_9\text{H}_6\text{BrNO}_3$ . Calculated, %: C 42.35; H 1.96; N 5.49.

**2-Anilino-2-benzoyl-1-nitroethene (IV)**, mp 125–126°C (from heptane). IR spectrum,  $\text{cm}^{-1}$ : 1680 (C=O), 1595, 1583 (C=C, C=N<sup>+</sup>), 1370, 1282, 1257, 1190 ( $\text{NOO}^-$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 11.0 (1H, NH), 6.9–7.9 m (5H,  $\text{C}_6\text{H}_5$ ), 6.7 (1H,  $\text{CHNO}_2$ ). UV spectrum:  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 244 (16700), 362 (14900). Found, %: C 67.22, 67.25; H 4.68, 4.67; N 10.55, 10.54.  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$ . Calculated, %: C 67.16; H 4.47; N 10.44.

IR spectra were registered on spectrophotometer InfraLUM FT-O2 from chloroform solutions,  $c$  0.1–0.001 mol l<sup>-1</sup>,  $^1\text{H}$  NMR spectra were registered on

spectrometer Bruker AC-200 (200 MHz) from solutions in deuteriochloroform, external reference HMDS. Electron absorption spectra were obtained on spectrophotometer SF-121 from solutions in ethanol.

The study was carried out under financial support of the Ministry of Education of the Russian Federation (grant no. E02-5.0-138).

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