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SHORT COMMUNICATIONS

Synthesis of 2-Morpholino(piperidino)-3-nitroacrylates

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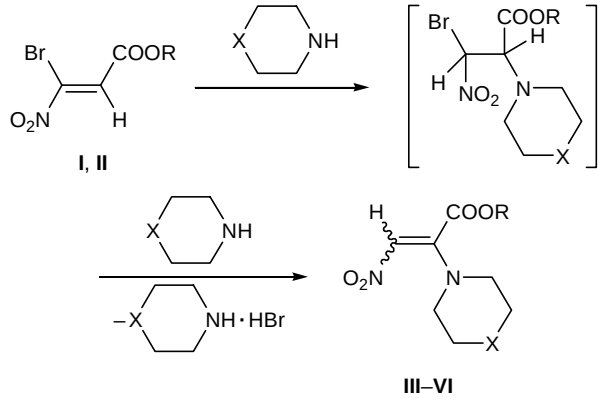
3-Nitroacrylates are highly reactive compounds which are important from the synthetic viewpoint as building blocks for design of practically useful structures, including fragments of natural substances and biologically active compounds [1, 2]. For example, oxanorbornene obtained on the basis of 3-nitroacrylate is the key intermediate product in the synthesis of compactin which is an important metabolite participating in the biosynthesis of chlolesterol [3, 4]; ethyl 3-nitroacrylate is used in the synthesis of α-methylenebutyrolactone which constitutes the main fragment of a number of sesquiterpenes [5]. Oryzoxymycin which exhibits antibacterial effect toward *Xanthomonas oryzae* was synthesized from 3-nitroacrylic acid [6]. Taking the above into account, various substituted alkyl 3-nitroacrylates may also be interesting.

We have developed a preparative procedure for the synthesis of 2-morpholino- and 2-piperidino-3-nitroacrylates by reaction of 3-bromo-3-nitroacrylates **I** and **II** [7] with morpholine and piperidine, respectively. The reactions were carried out with 2 equiv of the cyclic amine by heating in boiling benzene. The products, compounds **III**–**VI**, were isolated as slightly colored crystalline substances in 70–78% yield. The process is likely to follow the addition–elimination pattern. However, we failed to isolate intermediate addition product in reaction with equimolar amounts of the reactants. Presumably, the reason is the high basicity of morpholine and piperidine which promotes fast dehydrohalogenation of the primary adduct.



I, **III**, **V**, R = Me; **II**, **IV**, **VI**, R = Et; **III**, **IV**, X = O; **V**, **VI**, X = CH_2.

According to the spectral data, compounds **III**–**VI** are representatives of extensively studied nitroenamine series [8], which contain an alkoxycarbonyl group in the β-position with respect to the nitro group. The ^{1}H NMR spectra of **III**–**VI** indicate that these compounds are formed as a single stereoisomer and contain signals from protons of all structural fragments in molecules **III**–**VI**. In the electron absorption spectra we observed bands at λ_{max} 241–245 (ε = 3500–7700) and 355 nm (ε = 17800–23100). Compounds **III**–**VI** showed in the IR spectra strong absorption bands at 1365–1265 cm^{-1} due to vibrations of ionized nitro group and a strong broadened band at 1590–1575 cm^{-1}, which is typical of stretching vibrations of double C=C and C=N$^+$ bonds. These findings suggest a considerable contribution of a highly polar structure; the observed pattern is typical of nitroenamines [9, 10].

Initial methyl and ethyl 3-bromo-3-nitroacrylates **I** and **II** were synthesized by the procedure reported previously [6].

Methyl 2-morpholino-3-nitroacrylate (III). mp 168–170°C (from heptane). IR spectrum, ν, cm^{-1}: 1745, 1710 (C=O); 1590 (C=C, C=N$^+$); 1365, 1330, 1305, 1275 (NOO$^-$). ^{1}H NMR spectrum, δ, ppm: 6.62 (1H, $CHNO_2$), 3.95 (3H, OCH_3), 3.82 (4H, CH_2O), 3.26 (2H, CH_2N). UV spectrum: λ_{max}, nm (ε): 241 (12000), 355 (17800). Found, %: C 44.70; H 5.65; N 12.68. $C_9H_{12}N_2O_5$. Calculated, %: C 44.44; H 5.55; N 12.19.

Ethyl 2-morpholino-3-nitroacrylate (IV). mp 99–101°C (from heptane). IR spectrum, ν, cm^{-1}: 1740

(C=O); 1575 (C=C, C=N^+); 1335, 1305, 1275 (NOO^-). ^{1}H NMR spectrum, δ, ppm: 6.63 (1H, $CHNO_2$), 4.43 (2H, OCH_2), 3.79 (4H, CH_2OCH_2), 3.27 (4H, CH_2N), 1.38 (3H, CH_3). UV spectrum: λ_{max}, nm (ε): 245 (7100), 355 (21000). Found, %: C 46.94; H 6.08; N 12.21. $C_9H_{14}N_2O_5$. Calculated, %: C 46.96; H 6.08; N 12.17.

Methyl 2-piperidino-3-nitroacrylate (V). mp 91–93°C (from heptane). IR spectrum, ν, cm^{-1}: 1740 (C=O); 1575 (C=C, C=N^+); 1365, 1335, 1320, 1275 (NOO^-). ^{1}H NMR spectrum, δ, ppm: 6.65 (1H, $CHNO_2$), 3.94 (3H, OCH_3), 3.25 (4H, CH_2N), 1.69 [6H, $(CH_2)_3$]. UV spectrum: λ_{max}, nm (ε): 242 (3500), 356 (23100). Found, %: C 50.47; H 6.74; N 11.21. $C_9H_{14}N_2O_4$. Calculated, %: C 50.48; H 6.54; N 11.21.

Ethyl 2-piperidino-3-nitroacrylate (VI). mp 111–112°C (from heptane). IR spectrum, ν, cm^{-1}: 1740 (C=O); 1580 (C=C, C=N^+); 1335, 1320, 1265 (NOO^-). ^{1}H NMR spectrum, δ, ppm: 6.64 (1H, $CHNO_2$), 4.41 (2H, OCH_2), 3.26 (4H, CH_2N), 1.70 [6H, $(CH_2)_3$], 1.43 (3H, CH_3). UV spectrum: λ_{max}, nm (ε): 244 (7700), 356 (21600). Found, %: C 52.56; H 7.44; N 12.21. $C_{10}H_{16}N_2O_4$. Calculated, %: C 52.63; H 7.02; N 12.21.

The IR spectra were recorded on an InfraLYuM FT-02 spectrometer from solutions in chloroform (c = 0.1–0.001 M). The ^{1}H NMR spectra were obtained on a Bruker AC-200 instrument (200 MHz) from solutions in chloroform-*d*. The electron absorption spectra were measured on an SF-2000 spectrophotometer from solutions in ethanol.

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