

SHORT
COMMUNICATIONS

Synthesis of 3-Bromo-3-nitroacrylates

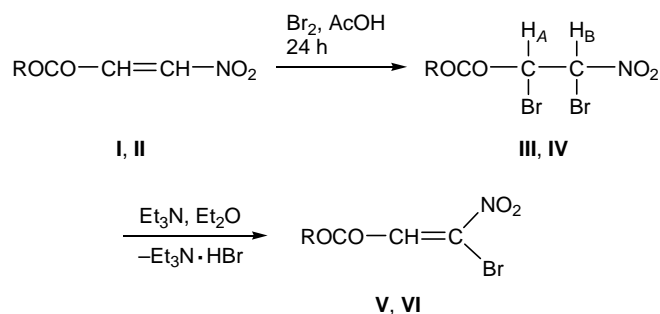
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Halonitroethenes are highly reactive synthons which are widely used for the preparation of a large number of nitro compounds of the acyclic, carbocyclic, and heterocyclic series [1, 2]. Introduction into a geminal halonitroethene molecule of one more electron-acceptor substituent enhances the electrophilicity of the double bond and should *a priori* extend the synthetic potential of unsaturated nitro compounds. In particular, this was convincingly demonstrated using 2-halo-2-nitroethenylphosphonates as examples [3–7].

We have synthesized new geminal halonitroalkenes containing an alkoxy carbonyl group. The procedure includes two steps: (1) halogenation of initial nitroacrylates **I** and **II** with an equimolar amount of bromine in glacial acetic acid and (2) dehydrohalogenation of dibromonitropropionates **III** and **IV** thus obtained by the action of triethylamine in anhydrous diethyl ether.



I, III, V, R = Me; II, IV, VI, R = Et.

3-Bromo-3-nitroacrylates **V** and **VI** are light yellow liquids with a sharp odor. Their structure was proved by the ^1H NMR, IR, and UV spectra. The downfield position of the 2-H signal in the ^1H NMR spectra of **V** and **VI** (δ 7.65–7.70 ppm) indicates its *cis* arrangement

with respect to the nitro group. This feature is widely used in structure determination of nitroalkenes [8, 9].

Initial nitroacrylates **I** and **II** were synthesized following a modified procedure [10].

Methyl 2,3-dibromo-3-nitropropionate (III). R_f 0.57. IR spectrum (CHCl_3), ν , cm^{-1} : 1580, 1350 (NO_2); 1750 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 3.84 (3H, CH_3O), 4.88 d (1H, H_A , $J_{AB} = 10.4$), 6.16 d (1H, H_B , $J_{AB} = 10.4$). Found, %: C 16.51, 16.55; H 1.90, 1.89; N 4.86, 4.87. $\text{C}_4\text{H}_5\text{Br}_2\text{NO}_4$. Calculated, %: C 16.49; H 1.71; N 4.81.

Ethyl 2,3-dibromo-3-nitropropionate (IV). R_f 0.94. IR spectrum (CHCl_3), ν , cm^{-1} : 1580, 1350 (NO_2); 1750 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 1.25 (3H, CH_3), 4.25 (2H, CH_2O), 4.85 d (1H, H_A , $J_{AB} = 10.4$), 6.20 d (1H, H_B , $J_{AB} = 10.4$). Found, %: C 19.29, 19.30; H 2.75, 2.70; N 4.67, 4.68. $\text{C}_5\text{H}_7\text{Br}_2\text{NO}_4$. Calculated, %: C 19.67; H 2.29; N 4.59.

Methyl 3-bromo-3-nitroacrylate (V). bp 102–104°C (10–12 mm), $n_D^{20} = 1.5110$, R_f 0.40. IR spectrum (CHCl_3), ν , cm^{-1} : 1560, 1305 (NO_2); 1630 ($\text{C}=\text{C}$); 1740 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 3.85 (3H, CH_3O), 7.70 (1H, CH). UV spectrum (EtOH), λ_{max} , nm (ϵ): 265 (4050). Found, %: C 22.79, 22.88; H 2.00, 2.01; N 6.60, 6.61. $\text{C}_4\text{H}_4\text{BrNO}_4$. Calculated, %: C 22.86; H 1.90; N 6.66.

Ethyl 3-bromo-3-nitroacrylate (VI). bp 70°C (2–3 mm), 110–112°C (10–11 mm); $n_D^{20} = 1.4940$; R_f 0.49. IR spectrum (CHCl_3), ν , cm^{-1} : 1560, 1310 (NO_2); 1630 ($\text{C}=\text{C}$); 1735 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.35 (3H, CH_3), 4.30 (2H, CH_2O), 7.65 (1H, CH). UV spectrum (EtOH), λ_{max} , nm (ϵ): 265 (4400). Found, %: C 26.59, 26.62; H 2.88, 2.85; N 6.30, 6.31. M^+ 225, 223. $\text{C}_5\text{H}_6\text{BrNO}_4$. Calculated, %: C 26.79; H 2.68; N 6.25. M 224.

The IR spectra were recorded on an InfraLYuM FT-02 spectrometer from solutions in chloroform ($c = 0.1\text{--}0.001\text{ M}$). The ^1H NMR spectra were obtained on a Bruker AC-200 instrument at 200 MHz from solutions in chloroform- d using HMDS as external reference. The electron absorption spectra were measured in ethanol on an SF-121 spectrophotometer.

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