

SHORT
COMMUNICATIONS

Specific Features of Reaction between 1,2-Dinitro- and 1-Nitro-2-Thioethenes and Hydrazine

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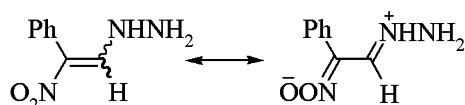
Conjugated nitroalkenes with a nucleofuge substituent in the β -position show high activity in reactions with nucleophilic reagents and therefore are used as convenient initial compounds for preparation of versatile functionalized nitro compounds along the routes S_NVin or Ad_N . For instance, from α , β -dinitro- and α -nitro- β -haloalkenes were obtained amino- and thionitroethenes [1, 2], and also bisthioethenes [3]. In the present study β -functionalized nitroethenes **I–V** were for the first time brought into reaction with a representative of *N,N*-binucleophiles, hydrazine.

It turned out that in reaction with hydrazine the expected product of nucleophilic substitution, 2-hydrazino-1-nitro-1-phenylethene (**VI**), formed successfully only from styrene derivatives, dinitro-**(I)** and nitrothioethenes **(III, IV)**. Among stilbene derivatives nitrothioethenes did not react with hydrazine, and the process occurred only with 1,2-dinitro-1,2-diphenylethene **(II)**; therewith at the use of excess reagent was obtained an unexpected result: Both nitro

groups were replaced to afford 1,2-dihydrazino-1,2-diphenylethene (**VII**). The same product was also obtained in reaction of 2-morpholino-1-nitro-1,2-diphenylethene (**V**) with excess hydrazine.

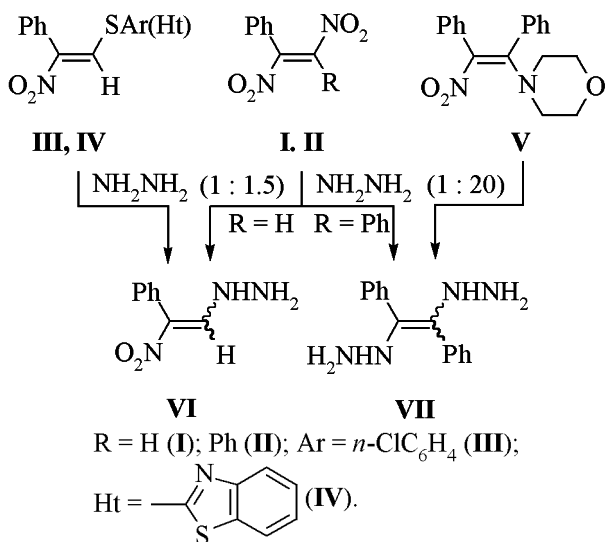
Note that the products of a conjugated nitro group substitution in reaction with *N*-nucleophile were not described in the literature.

The structure of compounds obtained was confirmed by spectral characteristics. Thus in the electronic spectrum of compound **VI** the absorption maxima in the longwave region λ_{max} 250 nm (ϵ 7950 l·mol⁻¹·cm⁻¹), 373 nm (ϵ 6970 l·mol⁻¹·cm⁻¹), 460 nm (ϵ 1000 l·mol⁻¹·cm⁻¹) indicate a significant contribution of a bipolar structure characteristic of conjugated nitroenamines [4].



In the spectrum of compound **VII** the longwave absorption is regularly lacking, and appears only a weak band at 280 nm (ϵ 500 l·mol⁻¹·cm⁻¹). In the spectrum of compound **VI** are present the typical “enamine” bands in the region 1640–1560 cm⁻¹ and also absorption bands from the ionized nitro group at 1350, 1200 cm⁻¹ [3–6] whereas the spectrum of dihydrazinoethene **VII** lacks the absorption bands of nitro group, but possesses a strong absorption band of conjugated multiple bonds (1600 cm⁻¹). In the ¹H NMR spectra of both compounds appear signals of phenyl and vinyl protons in the regions 7.60–7.80 ppm (**VI**) and 7.58–7.90 ppm (**VII**).

2-Hydrazino-1-nitro-1-phenylethene (VI). (a) To a solution of 0.388 g (2 mmol) of 1,2-dinitro-1-phenylethene (**I**) in 10 ml of anhydrous ether cooled to -10°C was added dropwise an emulsion of 0.15 ml (3 mmol) of hydrazine hydrate in 3 ml of an-



hydrous ether. In 1 min the solvent was evaporated, the oily residue was treated with a mixture ethanol-ether. We obtained orange crystals of compound **VI**, yield 0.059 g (16%), mp 88–89°C. Found, %: C 53.58; H 5.50; N 23.35. $C_8H_9N_3O_2$. Calculated, %: C 53.63; H 5.02; N 23.46.

(b) In the same fashion at 18–20°C was carried out a reaction with 1-nitro-1-phenyl-2-*p*-chlorophenylthioethene (**III**). The reaction mixture acquired the characteristic odor of *p*-chlorophenylthiol. In 10 min orange crystals of **VI** were filtered off, yield 0.259 g (72%).

(c) Ethene **VI** was also obtained from 2-(benzothiazol-2-yl)thio-1-nitro-1-phenylethene (**IV**) along procedure (b) in 53% yield. Mixed samples from compounds prepared by procedures (b) and (c) with that prepared by procedure (a) melted without depression of the melting point. The identity of these compounds was also proved by TLC on Silufol UV-254 plates, eluent hexane–acetone, 2:1.

1,2-Dihydrazin-1,2-diphenylethene (VII). (a) To a dispersion of 0.27 g (1 mmol) of dinitrostilbene (**II**) in 10 ml of ether was added a solution of 1 ml (20 mmol) of hydrazine hydrate in 10 ml of ethanol. In 20 min all the initial ethene dissolved. On removing the solvent the colorless amorphous residue was separated on a porous tablet, yield 0.2 g (85%), mp 94–97°C. Found, %: C 70.42; H 6.56; N 22.89. $C_{14}H_{16}N_4$. Calculated, %: C 70.00; H 6.67; N 23.33. M 240. Mass Spectrum: 240 M^+ , 224 [$-NH_2$], 209 [$-NH$], 193 [$-NH_2$], 178 [$-NH$], 119 [$PhCNHNH_2$], 89 [PhC], 77 [Ph].

(b) Under similar conditions the same compound was prepared from morpholinonitroethene **V**, yield 70%. The mixed sample of compounds obtained by procedures (a) and (b) melted without depression of the melting point.

1H NMR spectra were registered on spectrometer Bruker AC-200 (200 MHz), internal reference HMDS. IR spectra were recorded on spectrophotometer Specord 75IR from solutions in chloroform. UV spectra were measured on spectrophotometer SF-121. Mass spectrum was obtained on MKh 1321 instrument (direct admission of the sample into the ion source, ionizing voltage 70 V, ionizing chamber temperature 180°C).

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