

SHORT
COMMUNICATIONS

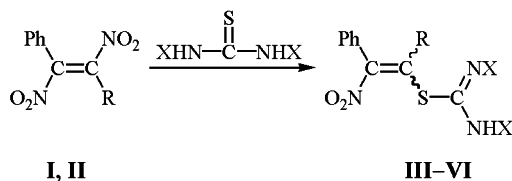
Reactions of 1,2-Dinitroethenes with Thiourea and *N,N'*-Diphenylthiourea

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Reactions of β -functionalized nitroethenes with mononucleophiles as a rule give products of Ad_N or $S_N\text{vin}$ [1, 2]. We were the first to study reactions of representatives of the mentioned series, 1,2-dinitroethenes, with *N,S*-binucleophiles, thiourea and *N,N'*-diphenylthiourea. We established that reactions of dinitrostyrene (**I**) and dinitrostilbene (**II**) with these binucleophiles occurred under mild conditions and afforded products of nucleophilic vinyl substitution, 2-isoureidothio-1-nitroethenes **III–VI** in 20–60% yield.



R = H (**I**), Ph (**II**); X = H: R = H (**III**), Ph (**IV**);
X = Ph: R = H (**V**), Ph (**VI**).

In this case the binucleophile molecule contains two different reactive sites. The fact of formation of C–S and not C–N bond is confirmed by spectral data. For instance, in the IR spectra appear the absorption bands of a conjugated nitro group at 1535–1510, 1320–1300 cm^{-1} (nonionized, in contrast to conjugation with amine nitrogen [3]), and these bands are located close to the position of the corresponding absorption bands in a model nitrothioethene, 2-(benzothiazol-2-yl)sulfanyl-1-nitro-1-phenylethene (1520, 1510, 1325 cm^{-1}) [2]. This conclusion is also valid for UV spectra which contain absorption bands in the region 335–390 nm characteristic of the above model compounds [370 nm ($6000 \text{ l mol}^{-1} \text{ cm}^{-1}$)] [2]. In the ^1H NMR spectra are observed signals from phenyl and olefin protons (6.80–7.60 ppm), and from

protons of amino groups (9.40–12.50 ppm). The chemical shift of the olefin proton (7.52 ppm) in the spectrum of compound **III** and the location of the phenyl protons signals in the spectrum of compound **V** suggest that the styrene derivatives **III** and **V** possess *Z*-configuration [4, 5].

(Z)- β -Nitrostyrylsulfanylcarboxamidine (III). To a solution of 0.19 g (1 mmol) of 1,2-dinitro-1-phenylethene (**I**) in 10 ml of ethanol was added a solution of 0.076 g (1 mmol) of thiourea in 10 ml of hot ethanol. In 20 min the reaction mixture was cooled to 0°C, the precipitated crystals were filtered off. Yield 0.05 g (23%), mp 171–172°C. UV spectrum (λ nm; ϵ , $\text{l mol}^{-1} \text{ cm}^{-1}$): 250 (4500), 377 (7000). IR spectrum, cm^{-1} : 1588, 1608 (C=C, C=N); 1520, 1310 (NO_2). ^1H NMR spectrum, δ , ppm: 7.52 s (=C–H), 7.42 s (Ph), 9.13 s, 9.48 s (NH). Found, %: C 48.41, 48.38; H 4.09, 4.10; N 18.72, 18.81. $\text{C}_9\text{H}_9\text{N}_3\text{O}_2\text{S}$. Calculated, %: C 48.43; H 4.03; N 18.83.

β -Nitro- α -phenylsulfanylcarboxamidine (IV) was prepared similarly in 55% yield, mp 93–95°C. UV spectrum (λ nm; ϵ , $\text{l mol}^{-1} \text{ cm}^{-1}$): 296 (9000). IR spectrum, cm^{-1} : 1600 (C=C, C=N); 1534, 1300 (NO_2). ^1H NMR spectrum, δ , ppm: 7.48 m (Ph), 9.48 s (NH). Found, %: C 60.11; H 4.74; N 14.37. $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$. Calculated, %: C 60.20; H 4.35; N 14.05.

(Z)-*N,N'*-Diphenyl- β -nitrostyrylsulfanylcarboxamidine (V) was prepared by the same procedure in 64% yield, mp 133–135°C. UV spectrum (λ nm; ϵ , $\text{l mol}^{-1} \text{ cm}^{-1}$): 261 (4050), 336 (4000). IR spectrum, cm^{-1} : 1638 (C=C, C=N); 1510, 1320 (NO_2). ^1H NMR spectrum, δ , ppm: 7.60–6.80 m (H, Ph). Found, %: C 66.53, 66.43; H 4.77, 4.70; N 11.38, 11.20. $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$. Calculated, %: C 66.12; H 4.68; N 11.57.

***N,N'*-Diphenyl- β -nitro- α -phenylsulfanylcarb-oxamidine (VI).** To a dispersion of 0.14 g (0.5 mmol) of 1,2-dinitro-1,2-diphenylethene (**II**) in 10 ml of ethanol was added a dispersion of 0.11 g (0.5 mmol) of diphenylthiourea in 5 ml of acetonitrile. The reaction mixture was heated for 5 min till dissolution of the reagents. In 20 min the solution was concentrated in a vacuum of a water-jet pump, and it was cooled to 0°C. After standing for 24 h the yellow crystals of compound **VI** were filtered off, yield 0.03 g (20%), mp 141–144°C. UV spectrum (λ nm; ϵ , l mol⁻¹ cm⁻¹): 246 (27500), 387 (30000). IR spectrum, cm⁻¹: 1660, 1585 (C=C, C=N); 1550, 1350 (NO₂). ¹H NMR spectrum, δ , ppm): 7.50–6.80 m (Ph), 12.45 m (NH). Found, %: C 70.55, 70.51; H 5.06, 5.00; N 9.10, 9.22. C₂₆H₂₁N₃O₂S. Calculated, %: C 71.07; H 4.78; N 9.57.

¹H NMR spectra were registered on spectrometer Bruker AC-200 (200 MHz) from solutions in CDCl₃,

internal reference HMDS. IR spectra were recorded on InfraLUM FT-02 instrument from solutions in chloroform. UV spectra were measured on spectrophotometer SF-121.

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