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SHORT COMMUNICATIONS

Reactions of 1,2-Dinitro- and 1-Nitro-2-sulfonylethenes with Some Binucleophiles

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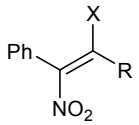
The presence in dinitroethene and nitrosulfonylethene molecules of a strong electron-withdrawing and nucleofugal substituent in the β-position with respect to the conjugated nitro group determines high reactivity of these compounds toward nucleophilic reagents and is responsible for predominant formation of replacement products in such reactions [1–3]. We previously reported on the reactions of dinitro- and nitrosulfonylethenes with such difunctional nucleophiles as hydrazine [4], thiourea, and *N*,*N*′-diphenylthiourea [5]. In the present communication we describe reactions of nitroethenes **I**–**IV** with phenylhydrazine, *o*-aminobenzenethiol, and 6-amino-1,3-benzothiazole-2-thiol. The two latter reagents are interesting due to the presence in their molecules of two potential reaction centers of different natures. We have found no published data on relative nucleophilic reactivity of these reagents.

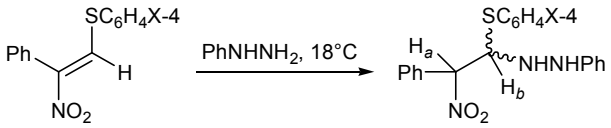


I–IV

I, **II**, R = H; **III**, **IV**, R = Ph; **I**, **III**, X = O_2N;
II, **IV**, X = 4-$ClC_6H_4SO_2$.

The reactions of compounds **I**–**IV** with phenylhydrazine (which is characterized by a fairly low oxidation potential) were accompanied by strong tarring, so that we failed to isolate and identify products of these reactions. We succeeded in avoiding side redox processes only by replacing electron-withdrawing β-substituent in the substrate by electron-donating phenyl- or 4-chlorophenylsulfanyl group; in these cases we obtained the corresponding addition products **VII** and **VIII**, the latter being formed as two stereoisomers (Scheme 1).

Scheme 1.



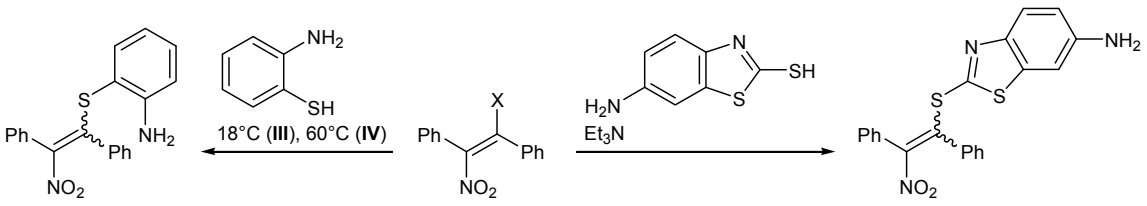
V, **VI** **VII**, **VIIIa**, **VIIIb**

V, **VII**, X = H; **VI**, **VIII**, X = Cl.

Unlike the reaction with phenylhydrazine, compounds **I**–**IV** reacted with N,S-binucleophiles, *o*-aminobenzenethiol and 6-amino-1,3-benzothiazole-2-thiol, following the nucleophilic replacement pattern. The reactions with nitrostilbene derivatives **III** and **IV** involved the sulfur reaction center of the binucleophile (Scheme 2). In the reactions with more electrophilic and less sterically loaded styrene derivatives **I** and **II**, unstable sulfanyl-substituted products **XI** and **XIII** were detected only spectrally as mixtures with isomeric nitro enamines **XII** and **XIV**. Compounds **XI** and **XIII** were converted with time or during the isolation procedure into thermodynamically more stable amino derivatives **XII** and **XIV** (Scheme 3). Compounds **XI** and **XIII** were identified by IR and UV spectroscopy; their IR and UV spectra were typical of 1-nitro-1-phenyl-2-arylsulfanylethenes [IR spectrum ($CHCl_3$): ν, cm^{-1}: 1620, 1595, 1520, 1320, 1310. UV spectrum ($CHCl_3$): λ_{max} 1360 nm] [6]. The spectral parameters of compounds **XII** and **XIV** were typical of nitro enamines [3].

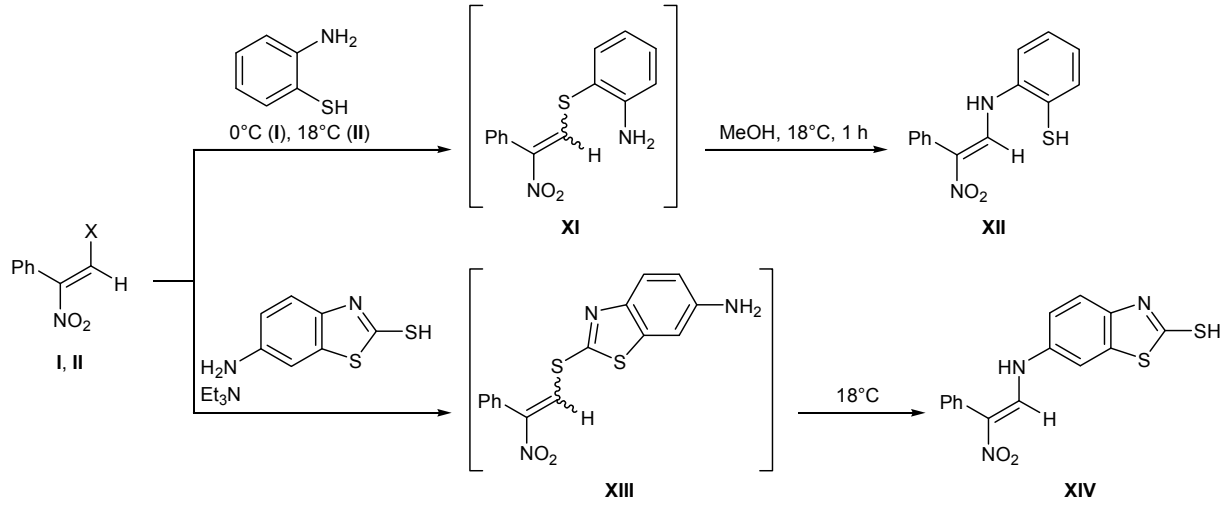
1-[2-Nitro-2-phenyl-1-(phenylsulfanyl)ethyl]-2-phenylhydrazine (VII). A solution of 0.108 g (1 mmol) of phenylhydrazine in 5 ml of ethanol was

Scheme 2.



III, X = O_2N; **IV**, X = 4-$ClC_6H_4SO_2$.

Scheme 3.



I, X = O_2N; **II**, X = 4-$ClC_6H_4SO_2$.

added to a suspension of 0.257 g (1 mmol) of compound **V** in 10 ml of ethanol. The mixture was kept for 3 days at 0°C, and the colorless needle-shaped crystals were filtered off. Yield 0.1 g (27%), mp 117–119°C (from ethanol). IR spectrum, ν, cm^{-1}: 1560, 1360 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.10 d (1H, H_b, J_{ab} = 11 Hz), 5.50 d (1H, H_a), 7.10–7.60 m (15H, H_{arom}). Found, %: C 65.10; H 5.21. $C_{20}H_{19}N_3O_2S$. Calculated, %: C 65.53; H 5.20.

1-[1-(4-Chlorophenylsulfanyl)-2-nitro-2-phenylethyl]-2-phenylhydrazines VIIIa and VIIIb were synthesized in a similar way from nitroethene **VI** at 20°C. After 30 min, isomer **VIIIa** separated from the solution as colorless solid with mp 127–130°C. Yield 0.084 g (21%). IR spectrum, ν, cm^{-1}: 1560, 1360 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.45 d (1H, H_a), 5.00 d (1H, H_b, J_{ab} = 11.5 Hz), 7.00 d and 7.15 d (4H, C_6H_4), 7.40 m (10H, C_6H_5). Found, %: C 60.10; H 4.70; N 10.41. $C_{20}H_{18}ClN_3O_2S$. Calculated, %: C 60.07; H 4.54; N 10.51.

The mixture was cooled to 0°C, and the colorless crystals of isomer **VIIIb** were filtered off. Yield 0.133 g (33%), mp 137–140°C. IR spectrum, ν, cm^{-1}: 1560, 1358 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.00 d (1H, H_b, J_{ab} = 8 Hz), 5.10 d (1H, H_a), 7.42 m (4H, C_6H_4), 7.55 m (10H, C_6H_5). Found, %: C 60.17; H 4.61; N 10.40. $C_{20}H_{18}ClN_3O_2S$. Calculated, %: C 60.07; H 4.54; N 10.51.

2-[(2-Nitro-1,2-diphenylvinyl)sulfanyl]aniline (IX). A solution of 0.125 g (1 mmol) of *o*-aminobenzenethiol in 10 ml of methanol was added dropwise at 18°C to a suspension of 0.27 g (1 mmol) of nitroethene **III** in 5 ml of methanol. After 30 min, the bright yellow crystals were filtered off. Yield 0.154 g (44%), mp 134–136°C. IR spectrum, ν, cm^{-1}: 1615 (C=C); 1530, 1305 (NO_2). UV spectrum ($CHCl_3$), λ, nm (ε, l mol^{-1} cm^{-1}): 255 (10000), 290 (7000), 338 (10000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.85 s (NH_2), 6.40–8.10 m (14H, C_6H_4, C_6H_5), Found, %: C 69.00; H 4.75; N 8.14. $C_{20}H_{16}N_2O_2S$. Calculated, %: C 68.96; H 4.63; N 8.04.

Compound **IX** was also synthesized in a similar way from nitrosulfonylethene (**IV**). The reaction mixture was heated until it became homogeneous, kept for

3 days at room temperature, and cooled to 0°C. Yield 0.07 g (38%), mp 133–135°C.

2-[(2-Nitro-1,2-diphenylvinyl)sulfanyl]-1,3-benzothiazol-6-amine (X) was synthesized in a similar way from 0.135 g (0.5 mmol) of dinitroethene **III** and 0.091 g (0.5 mmol) of 5-amino-1,3-benzothiazole-2-thiol with addition of one drop of triethylamine. The mixture was kept for 1 h at 18°C, and the orange precipitate was filtered off. Yield 0.179 g (87%), mp 142–144°C (from CCl_4). IR spectrum, ν, cm^{-1}: 1600, 1620 (C=C, C=N); 1540, 1305 (NO_2). UV spectrum ($CHCl_3$), λ, nm (ε, l mol^{-1} cm^{-1}): 242 (16500), 328 (18700). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.70–7.60 m (13H, H_{arom}), 3.90 s (NH_2). Found, %: C 61.82; H 4.04; N 9.78. $C_{21}H_{15}N_3O_2S_2$. Calculated, %: C 62.20; H 3.73; N 10.37.

Compound **X** was also synthesized in a similar way from nitrosulfonylethene **IV**. Yield 0.016 g (57%).

2-{[(*E*)-2-Nitro-2-phenylvinyl]amino}benzenethiol (XII). A solution of 0.388 g (2 mmol) of dinitroethene **I** in 10 ml of anhydrous ethanol was cooled to 0°C, a solution of 0.25 g (2 mmol) of *o*-aminobenzenethiol in 10 ml of anhydrous ethanol was added, the mixture was kept for 40 min, and the yellow precipitate, 0.08 g (mp 85–150°C), was filtered off. According to the TLC, IR, and UV data, the product was a mixture of nitrosulfanylethene **XI** and nitroaminoethene **XII**.

2-[(2-Nitro-2-phenylvinyl)sulfanyl]aniline (XI). IR spectrum, ν, cm^{-1}: 1610 (C=C); 1525, 1310 (NO_2). UV spectrum ($CHCl_3$): λ_{max} 360 nm.

The filtrate was cooled to –5°C and kept for 48 h at that temperature, and red–orange crystals of compound **XII** were filtered off. Yield 0.077 g (14%), mp 170–173°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1587, 1634 (C=C, C=N); 1378, 1152 (NOO^-). UV spectrum ($CHCl_3$), λ, nm (ε, l mol^{-1} cm^{-1}): 250 (10900), 407 (8700). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.35–7.70 m (9H, H_{arom}), 8.10 s (1H, =CH), 11.50 s (NH). Found, %: C 62.02; H 4.78; N 9.97. $C_{14}H_{12}N_2O_2S$. Calculated, %: C 61.75; H 4.44; N 10.29.

According to the UV data, after 5 min the reaction mixture contained only sulfur derivative **XI**, and after 40 min, only compound **XII**.

6-{[(*E*)-2-Nitro-2-phenylvinyl]amino}-1,3-benzothiazole-2-thiol (XIV). A solution of 0.097 g (0.5 mmol) of dinitroethene **I** in 5 ml of methanol was added dropwise to a suspension of 0.091 g (0.5 mmol) of 6-amino-1,3-benzothiazole-2-thiol in 5 ml of methanol. After 5 min, the orange precipitate was filtered off and purified by column chromatography. Yield 0.11 g (67%), bright yellow crystals, mp 202–203°C (from benzene). IR spectrum (mineral oil), ν, cm^{-1}: 1645, 1600 (C=C, C=N); 1305, 1165 (NOO^-). UV spectrum ($CHCl_3$), λ, nm (ε, l mol^{-1} cm^{-1}): 336 (7500), 419 (15300). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.90–8.10 m (8H, H_{arom}), 8.15 s (1H, =CH), 11.26 (NH). Found, %: C 54.77; H 3.46; N 12.72. $C_{15}H_{11}N_3O_2S_2$. Calculated, %: C 54.70; H 3.37; N 12.76.

Compound **XIV** was also synthesized in a similar way from nitrosulfonylethene **II**. Yield 56%.

The reactions of 1,2-dinitro-1-phenylethene (**I**) with 6-amino-1,3-benzothiazole-2-thiol in the presence of triethylamine were performed according to an analogous procedure using an equimolar amount of triethylamine. After 10 min, 0.135 g of a brown–red solid was filtered off and subjected to column chromatography. Elution with benzene gave bright yellow crystals of compound **XIV**. Yield 0.1 g (31%), mp 201–203°C (from benzene). According to the spectral data, the chloroform eluate contained 2-[(2-nitro-2-phenylvinyl)-sulfanyl]-1,3-benzothiazol-6-amine (**XIII**). IR spectrum, ν, cm^{-1}: 1639, 1591 (C=C, C=N); 1517, 1339 (NO_2). UV spectrum ($CHCl_3$), λ_{max}, nm: 229, 335.

The ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer at 200 MHz. The IR spectra were measured on a Shimadzu IR Prestige-21 spectrometer from solutions in $CHCl_3$ with a concentration of 40 mg/ml. The UV spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using hexane–acetone (2 : 1) as eluent.

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