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α-Nitro-β-iodo(sulfanyl)ethenes in Reactions with N,S-Binucleophiles

A. V. Mikova, E. S. Lipina, T. Yu. Kretser, and N. V. Kuzmina

Herzen Russian Pedagogical University, St. Petersburg, 191186 Russia
e-mail: chemis@herzen.spb.ru

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Abstract—α-Nitro-β-iodo(sulfanyl)ethenes were brought into reactions with N,S-binucleophiles that completed with the replacement of the β-functional group. Iodonitroethenes with thiourea and *N,N'*-diphenylthiourea provided products of S-substitution. The reaction of less reactive sulfanylnitrostyrene with *N,N'*-diphenylthiourea and also of iodonitrostyrene with 5-amino-benzothiazolyl-2-thiol required longer time and led to the formation of more stable products of N-substitution. The reactions with 5-aminobenzothiazolyl-2-thiolate in all events resulted in the products of S-substitution.

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The objects of the present study, 1-nitro-2-iodo-(sulfanyl)ethenes **I**, **II**, **VI**, **IX**, and **X**, are representatived of highly polarized systems with substituents of a pronounced nucleofugal character. Their specific feature consists in the presence alongside the nitro group of the second nucleofugal substituent (I, SAr), endowed with a considerable mesomeric effect.

Reactions of α-nitro-β-sulfanylethenes with mono-N- and -S-nucleophiles: aliphatic, aromatic, and alicyclic amines [1], and also aromatic and aliphatic thiols [2] were thoroughly investigated formerly. As a result the products of replacement of the β-functional group were obtained, and also the products of the nucleophile addition. Among the nitroiodo derivatives the reactions with this type nucleophiles were carried out only with 1-iodo-2-nitro-1,2-diphenylethene [3].

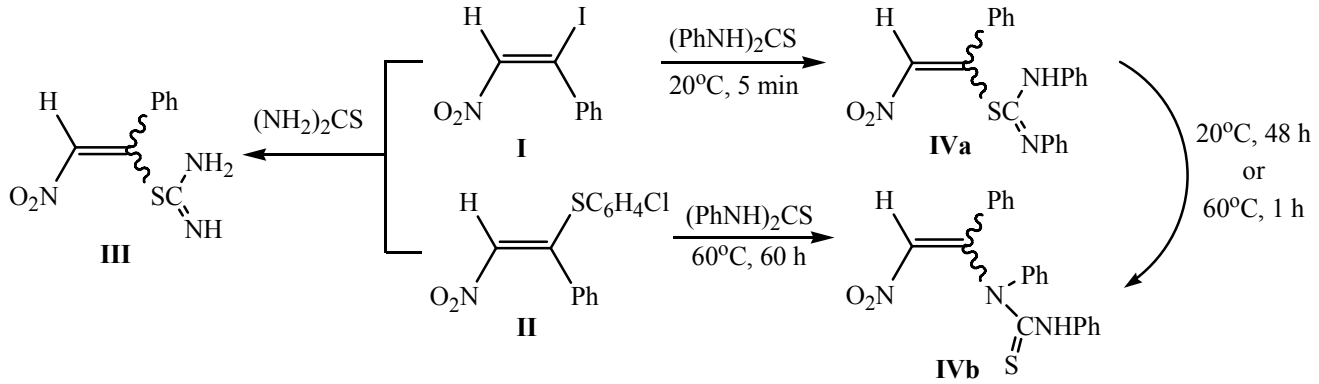
No published data exist on the reactions of N,S-binucleophiles capable of dual reacting either with α-nitroalkenes or with their β-functionalized derivatives. The mentioned substances were brought into reactions with the following N,S- binucleophiles: thiourea, *N,N'*-diphenylthiourea, and 5-aminobenzothiazolyl-2-thiol. The interesting feature of these reagents is the presence in them of two potential reaction centers. According to published data in the thiourea the sulfur atom is more nucleophilic as a result of a significant contribution of a bipolar resonance structure [4]. Therefore in the majority of described reactions of alkylation, addition, and also substitution in the systems containing α,β-diactivated multiple bonds [5] the thiourea behaves as S-nucleophile. The diphenylthiourea depending on the conditions can react both at the S- and the N-center [6]. We found no published data on the nucleophilic activity of aminobenzothiazolylthiol.

In the series of the studied nitroethenes the most reactive were 2-iodo-1-nitro-ethenes, in particular, the corresponding styrene **I**. This substrate reacted with thiourea and diphenylthiourea at normal conditions within several minutes giving the products of replacement of the β-functional by the S-center of the nucleophile **III** and **IVα**. The reactions of 2-arylsulfanyl-1-nitrostyrene **II** proceeded only at heating for several hours. Therefore in reaction with diphenylthiourea forms the more stable N-isomer **IVb** that presumably originated from the isomerization of the primarily arising S-product **IVa**; this assumption is consistent with the fact that the latter at heating or prolonged storage isomerized into **IVb**.

The attempts to carry out under similar conditions the isomerization of the reaction product **III** obtained from thiourea were unsuccessful.

The reactions of β-functionalized α-nitrostyrenes **I** and **II** with aminobenzothiazolylthiol occurred at different

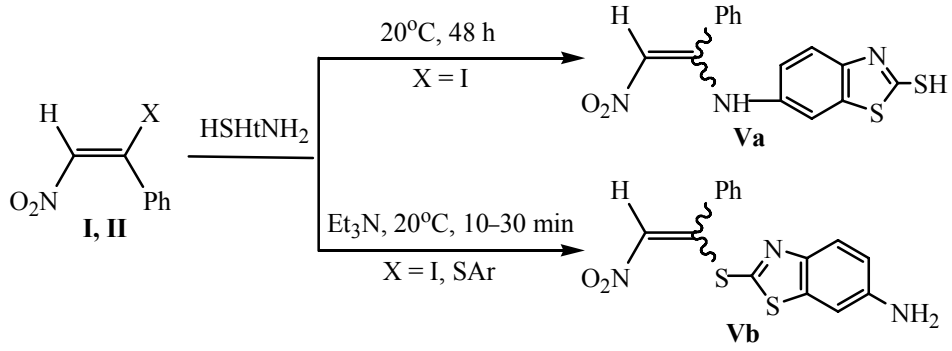
Scheme 1.



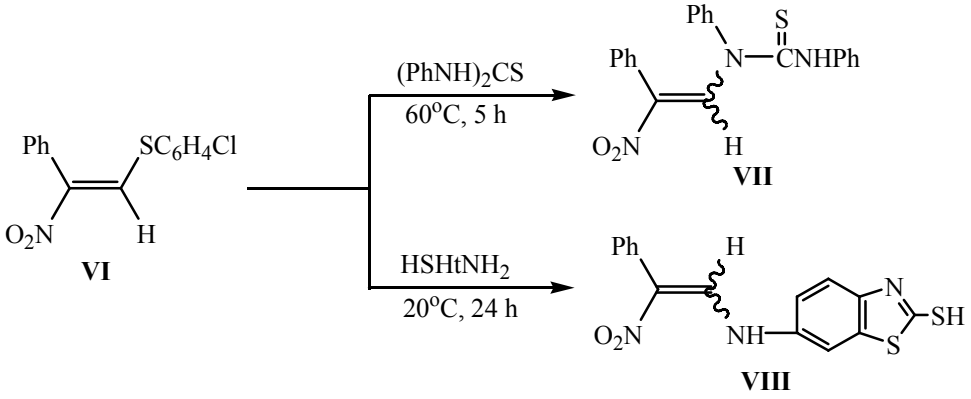
centers of the nucleophile depending on the reaction conditions. The most active 2-iodo-1-nitrostyrene (**I**) reacted with this nucleophile under normal conditions but at prolonged storage. The reaction occurred at the N-reaction site of the nucleophile and led to the formation of the more stable product of the N-substitution **Va**. The S-substitution product **Vb** was obtained at treating the above substrate with aminobenzothiazolylthiol in the presence of a base (triethylamine). The less reactive 2-aryl-sulfanyl-1-nitrostyrene **II** did not react with aminobenzothiazolylthiol even at prolonged heating, but in the presence of triethylamine also yielded compound **Vb**.

A somewhat more reactive at the treatment with diphenylthiourea and aminobenzothiazolylthiol turned out to be the structural isomer of compound **II**, 2-arylsulfanyl-1-nitro-1-phenylethene (**VI**). The process with the first reagent required not so long heating, and the reaction with thiol proceeded without catalyst; in both cases the

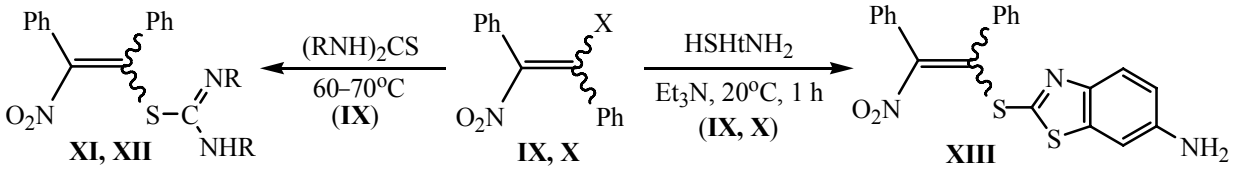
Scheme 2.



Scheme 3.



Scheme 4.



X = I (**I**), SC_6H_4Cl (**II**). R = H (**XI**), Ph (**XII**); X = I (**IX**), SC_6H_4Cl (**X**).

products of N-substitution were obtained, **VII** and **VIII** respectively.

2-Nitro-1-iodo(sulfanyl)stilbenes (**IX, X**) were less reactive presumably since they were sterically overloaded and less electrophilic compared to the corresponding styrenes. Reactions with thioureas proceeded only in the case of iodonitrostilbene **IX** and led to the formation of S-substitution products **XI** and **XII**; attempts to carry out their isomerization by heating failed. The reaction with aminobenzothiazolylthiol succeeded only in the presence of a base and, consequently, it occurred at the S-reaction site of the nucleophile.

All S-substituted compounds **II, III, IVa, Vb, XI–XIII** are characterized by the presence in the IR spectra of the absorption bands of a covalent conjugated nitro group in the region 1550–1500 and 1350–1300 cm^{-1}, and the position of the long-wave maximum at 320–340 nm corresponds to analogous bands of model compounds 1-nitro-2-phenylsulfanylstyrene [IR spectrum ($CHCl_3$), ν, cm^{-1}: 1530, 1310; UV spectrum ($CHCl_3$), λ, nm: 253, 355] and 1-nitro-2-phenylsulfanylstilbene [IR spectrum ($CHCl_3$), ν, cm^{-1}: 1550, 1310; UV spectrum ($CHCl_3$), λ, nm: 255, 345]. In the IR spectra of N-substituted compounds **IVb, Va, VII**, and **VIII** the bands of a ionized nitro group are present in the regions 1390–1325 and 1255–1135 cm^{-1}, and also the bands of the conjugated multiple bonds at 1630–1570 cm^{-1} ("nitroenamine bands" [7]). In the UV spectrum the long-wave maximum underwent a significant red shift (380–415 nm) in good agreement with the spectral behavior of the model compound 2-anilino-2-nitro-2-phenylethene [IR spectrum ($CHCl_3$), ν, cm^{-1}: 1640, 1390, 1313, 1155; UV spectrum ($CHCl_3$), λ, nm: 242, 395].

EXPERIMENTAL

^1H NMR spectra were registered on a spectrometer Bruker AC-200 (200 MHz) from solutions in deuterochloroform. IR spectra were recorded on a spectrophotometer Specord 75IR from solutions in chloroform (40 mg ml^{-1}) or pellets with KBr. UV spectra were taken on a spectrophotometer SF-200 in quartz celles from chloroform solutions. The reaction progress was monitored and the homogeneity of the products obtained was checked by TLC on Silufol UV-254 plates, eluent hexane–acetone, 2:1. Some reaction products were isolated and purified by column chromatography on silica gel L100/250μ, eluents according to Trappe eluotropic series.

The syntheses of 1-nitro-2-iodo-2-phenylethene (**I**) and 1-nitro-2-iodo-1,2-diphenylethene (**IX**) were performed by procedure [8], 1-nitro-2-(4-chlorophenyl)sulfanyl-1-phenylethene (**VI**), 2-nitro-1-(4-chlorophenyl)sulfanyl-1,2-diphenylethene (**X**), by method [9], anilino-2-nitro-2-phenyl-1-ethenylanilinomethylthione (**VII**), by method [10].

2-Nitro-1-(4-chlorophenylsulfanyl)-1-phenylethene (II). To a solution of 0.145 g (1 mmol) of *p*-chlorophenylthiol in 2 ml of anhydrous ethanol was added 0.023 g (1 mmol) of sodium metal in 2 ml of anhydrous ethanol. The obtained thiolate was added dropwise to a solution of 0.275 g (1 mmol) of compound **I** in 2 ml of anhydrous ethanol. After 30 min the reaction mixture was cooled to 0°C, the precipitate was filtered off. Yield 0.198 g (72%). Bright yellow crystals, mp 108–109°C (ethanol). IR spectrum, ν, cm^{-1}: 1577, 1557 (C=C), 1500, 1328 (NO_2). UV spectrum, λ, nm (ε): 253 (4500), 335 (6000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.33 s (=CH), 7.26–7.05 m (Ph, C_6H_4). Found, %: C 57.68; H 3.52; N 4.86. $C_{14}H_{10}ClNO_2C$. Calculated, %: C 57.63; H 3.43; N 4.80.

Imino(2-nitro-1-phenyl-1-ethenylsulfanyl)-methylamine (III). To a solution of 0.275 g (1 mmol) of compound **I** in 3 ml of anhydrous ethanol was added dropwise a solution of 0.076 g (1 mmol) of thiourea in 3 ml of anhydrous ethanol. After 30 min the reaction mixture was concentrated on a rotary evaporator in a vacuum, and the precipitate was filtered off. Yield 0.16 g (72%), yellow crystals, mp 135–136°C (ether). The same compound was obtained from compound **II** by heating

on a water bath to 60°C for 48 h. Yield 81%, mp 134–136°C (ether). IR spectrum (KBr), ν, cm^{-1}: 1590, 1560 (C=C), 1550, 1324 (NO_2). UV spectrum, λ, nm (ε): 240 (7000), 332 (10000). ^1H NMR spectrum, δ, ppm: 7.91 s (=C–H), 7.84–7.56 m (Ph), 9.50 s (NH). Found, %: C 48.32; H 4.26; N 18.72. $C_9H_9N_3O_2C$. Calculated, %: C 48.43; H 4.03; N 18.83.

2-Nitro-1-phenyl-1-ethenylsulfanyl(phenylimino)methyl(phenyl)amine (IVa). To a solution of 0.275 g (1 mmol) of compound **I** in 3 ml of anhydrous ethanol was poured a suspension of 0.228 g (1 mmol) of *N,N'*-diphenylthiourea in 3 ml of anhydrous ethanol. After 5 min the precipitate was filtered off. Yield 0.257 g (68%), yellow crystals, mp 117–119°C (ether). IR spectrum, ν, cm^{-1}: 1628, 1589 (C=C), 1500, 1312 (NO_2). UV spectrum, λ, nm (ε): 232 (1670), 340 (4700). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.01 s (=CH), 7.31–7.27 m (Ph). Found, %: N 10.85. $C_{21}H_{17}N_3O_2S$. Calculated, %: N 11.19.

Anilino-2-nitro-1-phenyl-1-ethenylanilinomethanethione (IVb). To a solution of 0.12 g (0.4 mmol) of compound **II** in 3 ml of anhydrous ethanol was poured a suspension of 0.091 g (0.4 mmol) of *N,N'*-diphenylthiourea in 3 ml of anhydrous ethanol. The reaction mixture was heated at 60°C for 60 h, then cooled to 0°C and the precipitate was filtered off. Yield 0.05 g (45%), yellow crystals, mp 193–195°C (ether). IR spectrum, ν, cm^{-1}: 1611, 1594 (C=C, C=N), 1367, 1326, 1255 (NOO^-). UV spectrum, λ, nm (ε): 235 (7200), 293 (5000), 378 (12000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.63 s (=CH), 7.42–7.30 m (Ph), 8.01 s (NH). Found, %: C 67.02; H 4.78; N 10.77. $C_{21}H_{17}N_3O_2C$. Calculated, %: C 67.18; H 4.53; N 11.19.

Isomerization of S-substitution product IVa into N-substitution product IVb. In 20 ml of chloroform was dissolved 0.01 g of compound **IVa**. After 48 h the reaction mixture was concentrated on a rotary evaporator in a vacuum, and the yellow precipitate of compound **IVb** was filtered off. Yield 0.0056 g (56%), mp 195–197°C (ether). Similar result was obtained at heating compound **IVa** in ethanol solution at 50°C for 60 min. The mixed sample of compound **IVb** obtained by isomerization and by direct synthesis from iodonitroethene **I** melted without depression of the melting point.

6-(2-Nitro-1-phenyl-1-ethenylamino)-1,3-benzothiazole-2-thione (Va). To a solution of 0.275 g (1 mmol) of compound **I** in 2 ml of anhydrous ethanol was poured a suspension of 0.182 g (1 mmol) of 5-aminobenzothiazolyl-2-thiol in 3 ml of anhydrous methanol. After 48 h the orange-red precipitate was filtered off and subjected to purification by column chromatography. From the fraction eluted with ether we isolated 0.22 g (53%) of compound **Va**, mp 182–184°C. IR spectrum, ν, cm^{-1}: 1595, 1567 (C=C, C=N), 1362, 1333 (NOO^-). UV spectrum, λ, nm (ε): 304 (13000), 387 (19000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.74 s (=C–H), 7.30–7.16 m (Ph, Ht), 11.55 s (NH), 6.72 s (CH). Found, %: N 13.78. $C_{15}H_{11}N_3O_2C$. Calculated, %: N 14.14.

2-(2-Nitro-1-phenyl-1-ethenylsulfanyl)-1,3-benzothiazol-6-amine (Vb). To a suspension of 0.182 g (1 mmol) of 5-aminobenzothiazolyl-2-thiol in 3 ml of anhydrous methanol was poured 0.6 ml (1 mmol) of triethylamine. The obtained thiolate was slowly added dropwise to a solution of 0.275 g (1 mmol) of compound **I** in 2 ml of anhydrous methanol. After 10 min the dirty-yellow precipitate was filtered off and subjected to purification by column chromatography. From the fraction eluted with benzene we separated 0.16 g (46%) of yellow precipitate of compound **Vb**, mp 124–127°C, then elution was continued with ether, and 0.08 g (23%) of orange precipitate of compound **Va** was additionally isolated, mp 180–184°C. Nitrothioethene **Vb** was obtained in the similar way from compound **II**. After 30 min the reaction mixture was concentrated on a rotary evaporator in a vacuum, and the yellow precipitate of compound **Vb** was filtered off. Yield 20%, mp 124–127°C. IR spectrum, ν, cm^{-1}: 1619, 1600 (C=C), 1510, 1332 (NO_2). UV spectrum, λ, nm (ε): 263 (6600), 325 (8700). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.85 s (=CH), 7.38–7.24 m (Ph, Ht), 5.58 s (NH_2). Found, %: C 60.52; H 3.59. $C_{15}H_{11}N_3O_2C$. Calculated, %: C 60.60; H 3.70.

5-(2-Nitro-2-phenyl-1-ethenylamino)-1,3-benzothiazole-2-thiol (VIII). To a suspension of 0.146 g (0.5 mmol) of 1-nitro-2-*p*-chlorophenylsulfanyl-1-phenylethene (**VI**) in 5 ml of methanol was poured a suspension of 0.091 g (0.5 mmol) of 5-aminobenzothiazolyl-2-thiol in 10 ml of methanol. After 24 h the dirty-yellow precipitate was filtered off and subjected to purification by column chromatography. From the fraction eluted with ether was isolated 0.16 g (90%) of bright-yellow precipitate of compound **VIII**, mp 228–229°C (ethanol). IR spectrum, ν, cm^{-1}: 1640, 1590 (C=C), 1377, 1136 (NOO^-). UV spectrum, λ, nm (ε): 336 (9800), 419 (17700). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.63 s (=CH), 7.54–7.24 m (Ph, Ht), 11.13 s (NH). Found, %: C 54.69; H 3.37; N 12.76. $C_{15}H_{11}N_3O_2C_2$. Calculated, %: C 54.71; H 3.34; N 12.76.

Imino(2-nitro-1,2-diphenyl-1-ethenylsulfanyl)-methylamine (XI). To a suspension of 0.17 g (0.5 mmol)

of 1-nitro-2-iodo-1,2-diphenylethene (**IX**) in 3 ml of anhydrous ethanol was added dropwise a solution of 0.038 g (0.5 mmol) of thiourea in 2 ml of anhydrous ethanol. The reaction mixture was heated at 50°C for 15 min, cooled to 0°C, and the precipitate was filtered off. Yield 0.059 g (40%). Yellow crystals, mp 94–96°C (2-propanol). IR spectrum, ν, cm^{-1}: 1600 (C=C), 1534, 1300 (NO_2). UV spectrum, λ, nm (ε): 258 (12400), 320 (10400). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.48 m (Ph), 12.55 s (NH). Found, %: C 60.11; H 4.74; N 14.37. $C_{15}H_{13}N_3O_2C$. Calculated, %: C 60.20; H 4.34; N 14.05.

2-Nitro-1,2-diphenyl-1-ethenylsulfanyl(phenylimino)methyl(phenyl)amine (XII). To a suspension of 0.351 g (1 mmol) of compound **IX** in 3 ml of anhydrous ethanol was poured a suspension of 0.228 g (1 mmol) of *N,N'*-diphenylthiourea in 3 ml of anhydrous ethanol. The reaction mixture was heated at 60°C for 10 min, then at 30°C for 30 min, cooled to 0°C, and the precipitate was filtered off. Yield 0.18 g (40%). Yellow crystals, mp 143–144°C (2-propanol). IR spectrum, ν, cm^{-1}: 1600, 1585 (C=C), 1550, 1350 (NO_2). UV spectrum, λ, nm (ε): 233 (11700), 338 (8000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.50–6.80 m (Ph), 12.45 s (NH). Found, %: C 71.09; H 5.00; N 9.23. $C_{27}H_{21}N_3O_2C$. Calculated, %: C 71.84; H 4.66; N 9.31.

2-(2-Nitro-1,2-diphenyl-1-ethenylsulfanyl)-1,3-benzothiazol-6-amine (XIII). To a suspension of 0.182 g (1 mmol) of 5-aminobenzothiazolyl-2-thiol in 3 ml of anhydrous methanol was poured 0.6 ml (1 mmol) of triethylamine. The thiolate obtained at 18°C was slowly added dropwise to a suspension of 0.351 g (1 mmol) of 1-nitro-2-iodo-1,2-diphenylethene (**IX**) in 3 ml of anhydrous methanol or acetonitrile. After 60 min the reaction mixture was cooled to 0°C, and the precipitate was filtered off. Yield 0.13 g (68%). Orange crystals, mp 143–144°C (2-fold from tetrachloromethane). By a similar procedure compound **XIII** was obtained from 1-nitro-2-*p*-chlorophenylsulfanyl-1,2-diphenylethene (**X**). Yield 40%, mp 143–144°C (2-fold from tetrachloromethane). IR spectrum, ν, cm^{-1}: 1620, 1600 (C=C), 1535, 1305 (NO_2). UV spectrum, λ, nm (e): 330 (19000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.60–6.70 m (Ph, Ht), 3.90 s (NH_2). Found, %: C 61.58; H 4.04; N 9.98. $C_{21}H_{15}N_3O_2C_2$. Calculated, %: C 62.22; H 3.70; N 10.37.

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