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# 1-Nitro-2-thio(sulfonyl)alkenes in Reactions with Thiols

**N. V. Kuz'mina, E. S. Lipina, T. Yu. Kropotova, G. A. Berkova, and Z. F. Pavlova**

*Gertsen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia*

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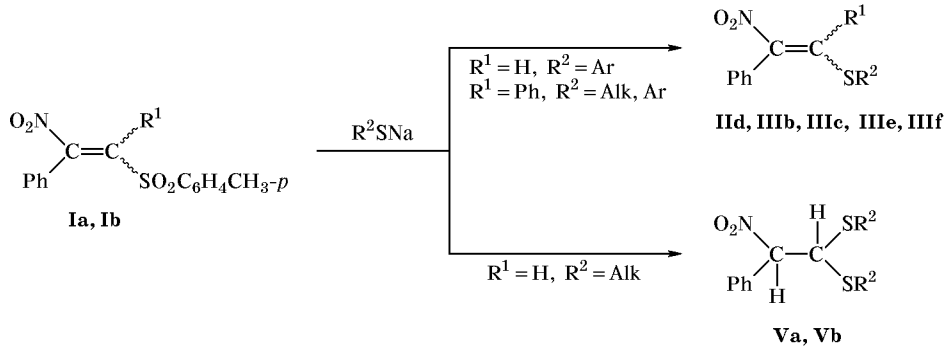
**Abstract**—Reactions of 1-nitro-2-sulfonylalkenes with arenethiolates result in replacement of the sulfonyl group; the reactions with alkanethiolates are accompanied by subsequent addition of the reagent at the double bond to afford thioacetals. Less reactive α-nitro-β-R-thiostyrenes with thiolates at reduced temperature form addition products which are converted into the corresponding substitution products on storage at room temperature, in keeping with the addition–elimination mechanism of nucleophilic vinyl substitution. Nitro(arylthio)- and nitro(heterylthio)alkenes react with alkanethiolates at room temperature, resulting in replacement of the arylthio (heterylthio) group by alkylthio.

The presence of a readily departing group in the β-position with respect to conjugated nitro group is responsible for the high reactivity of such nitroalkenes toward nucleophilic reagents and ready formation of the corresponding substitution products [1]. We previously described reactions of some 2-arylsulfonyl-1-nitroalkenes with *p*-halobenzenethiolates which resulted in formation of arylthio(nitro)alkenes. We also showed that 1-arylthio-2-nitroethenes and β-arylthio-α-nitrostyrenes react with the same compounds at 60°C to form products of replacement of the nitro group [2].

The goal of the present work was to examine reactions of sulfur-containing nitroalkenes with a series of alkane-, arene-, and hetarenethiolates. The results showed that these reactions are strongly influenced by the nature of the sulfur-containing group, structure of the nitroalkene, and nucleophilicity of the reagent. The reaction of 1-nitro-2-*p*-tolylsulfonyl-1,2-diphenylethene (**Ib**) with arene- and alkanethiolates leads to formation of the corresponding substitution products **IIb**, **IIIe**, and **IIIf**. Less sterically hindered styrene derivative **Ia** gives similar products (compounds **IIIb** and **IIIc**) only with arenethiolates. The reaction of **Ia** with stronger nucleophiles, sodium alkanethiolates, does not stop at the stage of formation of the substitution product; further addition of the reagent at the double bond (as in the case of alkoxide ions [2]) leads to formation of nitro-substituted thioacetals **Va** and **Vb** as the major products (Scheme 1, Table 1).

Taking into account that thioacetals were formed through addition of the second thiolate molecule to the substitution product (nitrothioalkene), we studied the reactions of nitrothiostyrenes and nitrothiostilbenes

**Scheme 1.**




**IId**, $R^1$ = Ph, $R^2$ = $C_{12}H_{25}$; **IIIa**, $R^1$ = H, $R^2$ = *p*-$ClC_6H_4$; **IIIb**, $R^1$ = H, $R^2$ = *p*-$CH_3C_6H_4$; **IIIe**, $R^1$ = Ph, $R^2$ = *p*-$CH_3C_6H_4$; **IIIf**, $R^1$ = Ph, $R^2$ = *p*-$ClC_6H_4$; **Va**, $R^1$ = H, $R^2$ = $C_2H_5$; **Vb**, $R^1$ = H, $R^2$ = $C_{12}H_{25}$.

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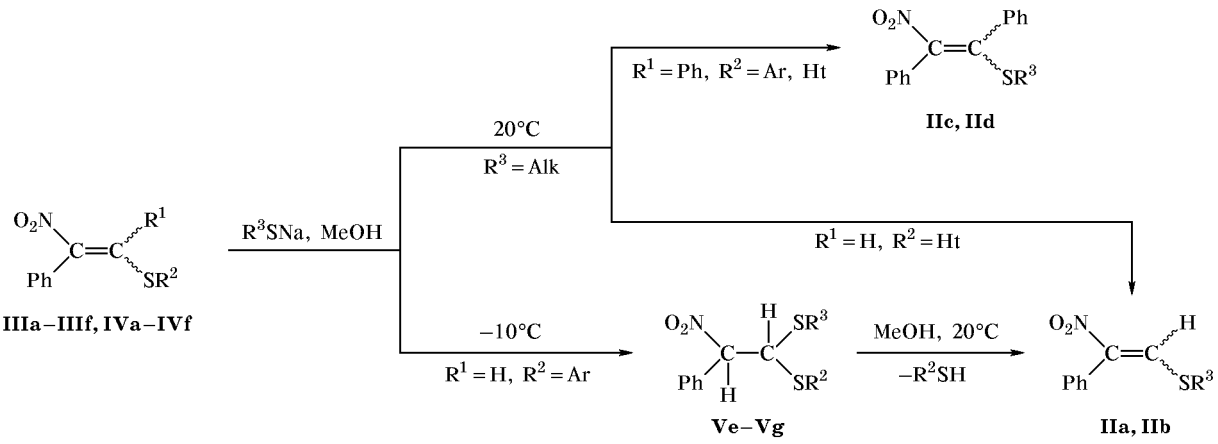
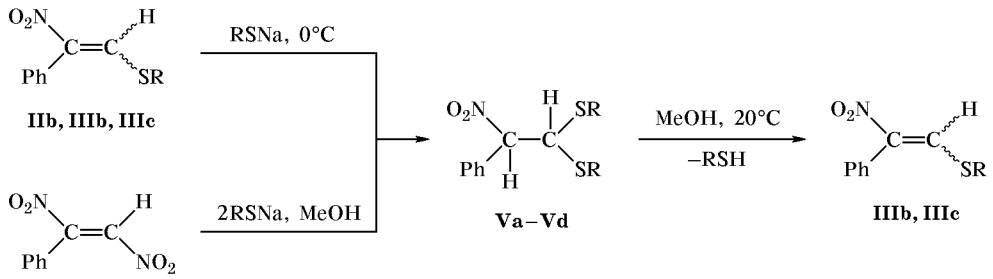
**Scheme 2.**

*a*. $R^2 \neq R^3$




**IIIa**, **IIId**, **Ve**, $R^2$ = Ph; **IIIb**, **IIIe**, **Vf**, $R^2$ = *p*-$CH_3C_6H_4$; **IIIe**, **IIIf**, **Vg**, $R^2$ = *p*-$ClC_6H_4$; **IVa**, **IVd**, $R^2$ = Ht; **IVb**, **IVe**, $R^2$ = HtOEt; **IVc**, **IVf**, $R^2$ = $HtNO_2$; **IIa**, **IIc**, $R^3$ = $C_8H_{17}$; **IIb**, **IId**, **Ve**, **Vg**, **Vf**, $R^3$ = $C_{12}H_{25}$.

*b*. $R^2 = R^3 = R$




**Va**, R = $C_2H_5$; **IIb**, **Vb**, R = $C_{12}H_{25}$; **IIIb**, **Vc**, R = *p*-$CH_3C_6H_4$; **IIIc**, **Vd**, R = *p*-$ClC_6H_4$.

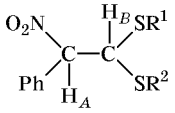
with thiolates under various conditions. Nitrothiostilbenes failed to react with thiolates at low temperature, while nitrothiostyrenes **IIb** and **IIIa**–**IIIc** with alkane- and arenethiolates gave rise to addition products **Vb**–**Vg**. The latter were converted into the corresponding substitution products on raising the temperature or by the action of bases. Scheme 2 shows the results of the reaction, depending on the temperature and nitroalkene structure.

It should be noted that only thioacetals with similar RS groups were reported previously; they were synthesized from α-nitroketones [3, 4]. The reaction under study can be regarded as a method for preparation of both symmetric (**Vb**–**Vd**) and mixed nitrothioacetals (**Ve**–**Vg**). The structure of compounds **Vb**–**Vd** was proved by independent synthesis from α,β-dinitrostyrene and 2 equiv of appropriate sodium thiolate without isolation of intermediate nitrothiostyrene (Scheme 2*b*). Table 1 contains spectral parameters of the newly synthesized nitrothioacetals **Va**–**Vg**.

The reaction of nitrothiostyrenes with alkanethiolates at room temperature is governed by the nature of the RS group (Table 2). In the reactions of arylthionitrostyrenes **IIIa**–**IIIc** with sodium dodecanethiolate both thioacetals **Ve**–**Vg** and substitution products **IIa** and **IIb** were isolated, whereas the latter were the only final products of the reactions of heterylthionitrostyrenes **IVa**–**IVc** with the same thiolate (Scheme 2*a*). Under similar conditions nitrothiostilbenes **IIId**–**IIIf** and **IVd**–**IVf** reacted with alkanethiolates to give 80–90% of substitution products **IIc** and **IId**, no thioacetals being detected during the process (Scheme 2*a*).

The observed formation of nitrothioacetals is the first example of nucleophilic addition reactions of nitroalkenes having a readily departing group in the β-position. The subsequent transformation of the adducts into substitution products can be regarded as an experimental proof of the addition–elimination mechanism of nucleophilic vinyl substitution. When

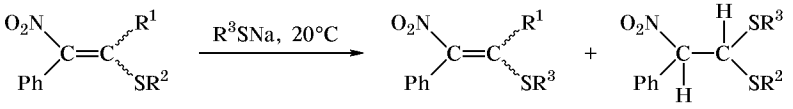
**Table 1.** Yields, melting points, and spectral parameters of 1-nitro-2,2-di-R-thioethanes (nitrothioacetals) **Va**–**Vg**



| Comp. no. | Yield, % | mp, °C | $^1$H NMR spectrum ($CDCl_3$), δ, ppm | | | | | IR spectrum,[a] $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Ph | $H_A$ | $H_B$ | $R^1$ | $R^2$ | $\nu_s NO_2$ | $\nu_{as} NO_2$ |
| **Va** | 30[b] | 25–27 | 7.28–7.45 m | 5.32 d | 4.54 d | 1.16 t, 2.67 q | | 1375 | 1580 |
| **Vb** | 41[b] | 27–28 | 7.12–7.29 m | 5.37 d | 4.59 d | 0.81, 1.19, 2.56 m | | 1375 | 1560 |
| **Vc** | 49[c] | 39–40 | 7.23–7.34 m | 5.37 d | 4.93 d | 2.23 s, 7.50–7.00 m | | 1355 | 1550 |
| **Vd** | 11[b] 33[b] | 37–39 | 7.26–7.32 m | 5.30 d | 4.93 d | 6.95–7.03 m | | 1360 | 1560 |
| **Ve** | 38[c] | 28–29 | 7.10–7.31 m | 4.80 d | 4.18 d | 7.09–7.30 m | 0.80–1.19 m | 1365 | 1560 |
| **Vf** | 10[c] | 35–37 | 7.09–7.30 m | 4.80 d | 4.18 d | 7.09–7.30 m, 1.37 s | 0.97–1.20 m | 1380 | 1570 |
| **Vg** | 44[c] | 36–37 | 7.18–7.24 m | 5.36 d | 4.56 d | 6.88, 6.95 m | 0.80–1.18 m | 1365 | 1560 |

[a] In $CHCl_3$.
[b] From dinitroalkene.
[c] From nitrothioalkene.

**Table 2.** Exchange of the RS group

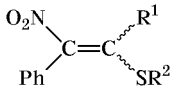


**IIIa–IIIf, IVa–IVf** **IIa–IId** **Ve–Vg**

| Initial alkene no. | $R^1$ | $R^2$ | $R^3$ | Reaction time, min | Yield, % (product) |
|---|---|---|---|---|---|
| **IIIc** | H | *p*-$ClC_6H_4$ | $C_{12}H_{25}$ | 5 | 33[a] (**IIb**) |
| **IIIa** | H | Ph | $C_{12}H_{25}$ | 10 | 25[b] (**IIb**) |
| **IIIb** | H | *p*-$CH_3C_6H_4$ | $C_{12}H_{25}$ | 20 | 18[c] (**IIb**) |
| **IVc** | H | 6-$NO_2$Ht | $C_{12}H_{25}$ | <5 | 15 (**IIb**) |
| **IVa** | H | Ht | $C_{12}H_{25}$ | 10 | 35 (**IIb**) |
| **IVb** | H | 6-EtOHt | $C_{12}H_{25}$ | 30 | 68 (**IIb**) |
| **IIIf** | Ph | *p*-$ClC_6H_4$ | $C_{12}H_{25}$ | 65 | 81 (**IId**) |
| **IIId** | Ph | Ph | $C_{12}H_{25}$ | 75 | 91 (**IId**) |
| **IIIe** | Ph | *p*-$CH_3C_6H_4$ | $C_{12}H_{25}$ | 95 | 80 (**IId**) |
| **IVf** | Ph | 6-$NO_2$Ht | $C_{12}H_{25}$ | 5 | 10 (**IId**) |
| **IVd** | Ph | Ht | $C_{12}H_{25}$ | 60 | 67 (**IId**) |
| **IVe** | Ph | 6-EtOHt | $C_{12}H_{25}$ | 25 h | 31 (**IId**) |
| **IVb** | H | 6-EtOHt | $C_8H_{17}$ | 60 | 50 (**IIa**) |
| **IIIe** | Ph | *p*-$CH_3C_6H_4$ | $C_8H_{17}$ | 120 | 68 (**IIc**) |

[a] Yield of **Vg** 44%.
[b] Yield of **Ve** 38%.
[c] Yield of **Vf** 10%.

**Table 3.** Yields, melting points, and spectral parameters of 1-nitro-2-R-thioethenes **IIa**–**IId** and **IVa**–**IVf**



| Comp. no. | $R^1$ | $R^2$ [a] | mp, °C | Yield, % | $^1$H NMR spectrum ($CDCl_3$), δ, ppm | | | IR spectrum,[b] ν, $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ph | $R^1$ | $R^2$ | $NO_2$ | C=C |
| **IIa** | H | $C_8H_{17}$ | 39–40 | 50[c] | 7.35–7.45 m | | 0.82, 1.45, 2.19 m | 1305, 1540 | 1610 |
| **IIb** | H | $C_{12}H_{25}$ | 48–49 | 67[c] | 7.35–7.45 m | | 0.83 t, 1.48 m, 2.22 m | 1305, 1540 | 1610 |
| **IVa** | H | Ht | 168–170 | 70[d] | 7.49 m, 7.53 m | 7.72 s | 7.44 d, 7.95 d, 8.00 d | 1310, 1505 | 1580, 1605 |
| **IVb** | H | 6-EtOHt | 172–173 | 69[d] | 7.52 m | 8.64 s | 7.43 t, 4.08, 4.10 q, 7.04, 7.49 m, 7.81 d | 1310, 1500 | 1600 |
| **IVc** | H | 6-$NO_2$Ht | 195–197 | 40[d] | 7.51, 7.54 m | 9.12 s | 8.10 d, 7.34 d, 8.75 s | 1355, 1535, 1545 | 1570 |
| **IIc** | Ph | $C_8H_{17}$ | 69–70 | 68[c] | 7.10–7.40 m | | 0.83 t, 1.46 m, 2.21 m | 1305, 1545 | 1605 |
| **IId** | Ph | $C_{12}H_{25}$ | 57–59 | 90[c] | 7.11–7.40 m | | 0.85 t, 1.44 m, 2.22 m | 1300, 1545 | 1605 |
| **IVd** | Ph | Ht | 169–170 | 75 | 7.30–7.51 m | | 7.30–7.51 m, 7.95, 8.01 m | 1315, 1540 | 1610, 1580 |
| **IVe** | Ph | 6-EtOHt | 162–164 | 61 | 6.95–7.35, 7.7 m | | 7.43 t, 3.95, 4.10 q, 6.95–7.35, 7.7 m | 1310, 1500 | 1595, 1560, 1470 |
| **IVf** | Ph | 6-$NO_2$Ht | 109–110 | 47 | 7.10–7.29 m | | 7.94 d, 8.26 d, 8.59 s | 1355, 1535 | 1560 |

[a] Ht is 2-benzothiazolyl.

[b] In $CHCl_3$.

[c] Nitrothioethenes **IIa**–**IId** were obtained by RS-exchange reaction.

[d] According to the $^1$H NMR data, compounds **IIa** and **IIb** are *Z* isomers, and **IVa**–**IVc**, *E* isomers.

nitrothioacetals **Vc** and **Vd** were kept in methanol at room temperature, 30% of the corresponding substitution products (**IIIb** and **IIIc**) was formed via elimination of thiol (Scheme 2*b*).

According to the final result, i.e., replacement of one R-thio group by another, the above reaction of nitrothioalkenes with thiolates can be regarded as RS-exchange (by analogy with transamination reported in [5] for nitroenamines). The data obtained for β-alkyl-, β-aryl-, and β-heterylthio-α-nitroalkenes allowed us to formulate some general relations holding therein (Table 2):

(1) Alkanethiolate ions replace heteryl- and arylthio groups in nitrothioalkenes. Benzothiazole-2-thiolate and arenethiolate ions do not replace alkyl- and arylthio groups in the corresponding nitroalkenes.

(2) The presence of an acceptor substituent in the aryl(heteryl)thio group facilitates its replacement by more nucleophilic RS group; by contrast, donor substituents hinder the substitution.

We can recommend to use the reaction under study as a method of synthesis of alkylthionitroalkenes from aryl- and heterylthionitroalkenes; this procedure is superior to direct sulfurization of 1,2-dinitroalkenes, for it ensures preparation of purer products.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument. The $^1$H NMR spectra were obtained on a Tesla BS-487C spectrometer at 80 MHz. The progress of reactions was monitored by TLC on Silufol UV-254 plates using hexane–acetone (2:1) as eluent. Some products were isolated and purified by column chromatography on silica gel (L 100/400 μm) using the Trappe eluotropic series. Table 3 contains the melting points and spectral parameters of the newly synthesized 1-nitro-2-alkylthioethenes (**IIa**–**IId**) and 1-nitro-2-benzothiazolylthioethenes (**IVa**–**IVf**); the elemental analyses of new compounds **IIa**–**IId**, **IVa**–**IVf**, and **Va**–**Vg** are given in Table 4.

1-Nitro-2-*p*-tolylsulfonylethenes **Ia** and **Ib** were synthesized from the corresponding 1,2-dinitroethenes and *p*-toluenesulfinic acid by the procedure reported

**Table 4.** Elemental analyses of 1-nitro-2-R-thioethenes **IIa**, **IIb**, and **IVa**–**IVf** and nitrothioacetals **Va**–**Vg**

| Comp. no. | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|
| | C | H | N | | C | H | N |
| **IIa** | 65.21 | 7.92 | 5.05 | $C_{16}H_{23}NO_2S$ | 65.53 | 7.85 | 4.78 |
| **IIb** | 68.79 | 8.92 | 4.05 | $C_{20}H_{31}NO_2S$ | 68.77 | 8.88 | 4.01 |
| **IIc** | 71.44 | 7.27 | 3.89 | $C_{22}H_{27}NO_2S$ | 71.54 | 7.31 | 3.79 |
| **IId** | 73.11 | 8.45 | 3.20 | $C_{26}H_{35}NO_2S$ | 73.41 | 8.24 | 3.29 |
| **IVa** | 55.23 | 4.13 | 9.15 | $C_{15}H_{10}N_2O_2S_2$ | 55.25 | 3.94 | 4.21 |
| **IVb** | 56.68 | 3.98 | 7.75 | $C_{17}H_{14}N_2O_3S_2$ | 56.98 | 3.91 | 7.82 |
| **IVc** | 50.03 | 2.55 | 11.60 | $C_{15}H_9N_3O_4S_2$ | 50.14 | 2.51 | 11.69 |
| **IVd** | 57.27 | 3.24 | 8.87 | $C_{15}H_{10}N_2O_2S_2$ | 53.32 | 3.18 | 8.91 |
| **IVe** | 63.05 | 4.74 | 6.25 | $C_{22}H_{18}N_2O_3S_2$ | 63.30 | 4.59 | 6.42 |
| **IVf** | 57.81 | 3.17 | 9.57 | $C_{21}H_{13}N_3O_4S_2$ | 57.93 | 2.99 | 9.66 |
| **Va** | 53.09 | 6.08 | 5.43 | $C_{12}H_{17}NO_2S_2$ | 53.14 | 6.27 | 5.17 |
| **Vb** | 69.87 | 10.52 | 2.63 | $C_{32}H_{57}NO_2S_2$ | 69.69 | 10.34 | 2.54 |
| **Vc** | 65.98 | 5.55 | 3.37 | $C_{22}H_{21}NO_2S_2$ | 66.84 | 5.32 | 3.54 |
| **Vd** | 55.00 | 4.01 | 3.08 | $C_{20}H_{15}Cl_2NO_2S_2$ | 55.04 | 3.44 | 3.21 |
| **Ve** | 68.29 | 7.24 | 3.08 | $C_{26}H_{32}NO_2S_2$ | 68.12 | 6.99 | 3.06 |
| **Vf** | 68.41 | 8.17 | 3.21 | $C_{27}H_{39}NO_2S_2$ | 68.50 | 8.25 | 2.96 |
| **Vg** | 63.44 | 7.41 | 2.75 | $C_{26}H_{37}ClNO_2S_2$ | 63.22 | 7.29 | 2.83 |

in [6]. 1-Nitro-2-R-thioethenes **IIIa**–**IIIf** were synthesized by the procedure described in [7] from the corresponding dinitroethenes and sodium thiolates.

**2-(2-Benzothiazolylthio)-1-nitro-1-phenylethene (IVa).** A solution of 0.4 g (0.002 mol) of 1,2-dinitro-1-phenylethene in 7 ml of methanol was added to a solution of 0.4 g (0.002 mol) of benzothiazole-2-thiol in 5 ml of chloroform. The bright yellow precipitate was filtered off and recrystallized from ethanol. Yield of **IVa** 0.44 g.

**2-(6-Ethoxy-2-benzothiazolylthio)-1-nitro-1-phenylethene (IVb)** was synthesized in a similar way.

**2-(6-Nitro-2-benzothiazolylthio)-1-nitro-1-phenylethene (IVc).** To a suspension of 0.212 g (0.001 mol) of 5-nitrobenzothiazole-2-thiol in 5 ml of methanol we added at room temperature an equimolar amount of sodium methoxide in 3 ml of methanol. When the mixture became homogeneous, it was cooled to 0°C and was added to a solution of 0.2 g (0.001 mol) of 1,2-dinitro-1-phenylethene in 5 ml of methanol. The precipitate was filtered off and recrystallized from MeOH–$CHCl_3$ (2:1). Yield of **IVc** 0.22 g, yellow crystalline substance.

**2-(2-Benzothiazolylthio)-1-nitro-1,2-diphenylethene (IVd).** To a suspension of 0.5 g (1.9 mmol) of 1,2-dinitro-1,2-diphenylethene in 10 ml of methanol we added a suspension of 0.309 g (1.9 mmol) of benzothiazole-2-thiol in 10 ml chloroform and then 3 drops of triethylamine. When the mixture became homogeneous, it was cooled to 0°C. The yellow precipitate of nitrothioethene **IVd** was filtered off and recrystallized from ethanol.

**2-(6-Ethoxy-2-benzothiazolylthio)-1-nitro-1,2-diphenylethene (IVe)** was synthesized in a similar way. The product (bright yellow crystalline substance) was recrystallized from ethanol.

**2-(6-Nitro-2-benzothiazolylthio)-1-nitro-1,2-diphenylethene (IVf)** was synthesized by the procedure described above for compound **IVc**.

**Reaction of 1-nitro-2-*p*-tolylsulfonylethenes Ia and Ib with sodium thiolates.** To a suspension of 0.3 g (0.001 mol) of 1-nitro-2-*p*-tolylsulfonyl-1-phenylethene (**Ia**) in 5 ml of methanol we added at –5 to 0°C a solution of 0.001 mol of sodium ethanethiolate prepared from equimolar amounts of sodium methoxide and ethanethiol in methanol. After 1 h, the mixture was concentrated, the residue was treated with acetone, and 0.12 g of sodium *p*-toluenesulfinate was filtered off. The filtrate was subjected to column chromatography on silica gel using first cyclohexane as eluent. The eluate contained 0.08 g of 2,2-bis(ethylthio)-1-nitro-1-phenylethene (**Va**); colorless crystalline substance, mp 25–27°C. The subsequent elution with $CCl_4$ and $CHCl_3$ gave (according to the TLC and $^1H$ NMR data) a mixture of 2-ethylthio-1-nitro-1-phenylethene and nitrothioacetal **Va**.

Following the above procedure, the reaction with sodium dodecanethiolate was carried out at room temperature. The mixture was kept for 1 h at room temperature, evaporated by half, and frozen. The product, 2,2-bis(dodecylthio)-1-nitro-1-phenylethene (**Vb**), was filtered off. Colorless crystalline substance, mp 27–28°C.

The reactions with sodium *p*-toluenethiolate and sodium *p*-chlorobenzenethiolate were performed in a similar way. The products, 1-nitro-1-phenyl-2-*p*-tolylthioethene (**IIIb**), mp 83°C (published data [7]: mp 85°C), yield 61%, and 2-*p*-chlorophenylthio-1-nitro-1-phenylethene (**IIIc**), mp 112°C (published data [7]: mp 114°C [7]), yield 58%, were isolated as yellow crystalline substances.

The reaction of 1-nitro-2-*p*-tolylsulfonyl-1,2-diphenylethene (**Ib**) with an equimolar amount of sodium dodecanesulfonate was carried out in methanol at room temperature (see above). The mixture was kept for 1 h at room temperature and frozen. 1,2-Diphenyl-2-dodecylthio-1-nitroethene (**IId**) was isolated as a yellow crystalline substance. Yield 0.13 g (76%), mp 57–59°C.

The reaction with sodium *p*-chlorobenzenethiolate was carried out in a similar way. 2-*p*-Chlorophenylthio-1-nitro-1,2-diphenylethene (**IIIf**) was isolated in 60% yield; yellow crystalline substance, mp 132°C; published data [7]: mp 135°C.

**Reactions of 1-nitro-2-R-thioethenes with sodium thiolates at reduced temperature.** To a suspension of 0.22 g (0.9 mmol) of 2-*p*-chlorophenylthio-1-nitro-1-phenylethene (**IIIc**) in 7 ml of methanol we added at –10 to 0°C a solution of 0.9 mmol of sodium *p*-chlorobenzenethiolate prepared from equimolar amounts of sodium methoxide and *p*-chlorobenzenethiol in methanol. After 0.2 h, the solution was frozen to isolate 0.14 g of 2,2-bis(*p*-chlorophenylthio)-1-nitro-1-phenylethane (**Vd**) as a colorless crystalline substance.

**The reaction of 1-nitro-1-phenyl-2-*p*-tolylthioethene (IIIb) with sodium *p*-toluenethiolate** was carried out in a similar way. The product, 1-nitro-1-phenyl-2,2-bis(*p*-tolylthio)ethane (**Vc**) was isolated as a colorless crystalline substance with mp 39–40°C.

The reactions of 2-*p*-chlorophenylthio-1-nitro-1-phenylethene (**IIIc**) and 1-nitro-1-phenyl-2-*p*-tolylthioethene (**IIIb**) with sodium dodecanethiolate were carried out in a similar way. The mixture was kept for 1 h, and 2-*p*-chlorophenylthio-2-dodecylthio-1-nitro-1-phenylethane (**Vg**) and 2-dodecylthio-1-nitro-1-phenyl-2-*p*-tolylthioethane (**Vf**) were isolated in 50 and 25% yield, respectively. The filtrate was evaporated by half and frozen to isolate didodecyl disulfide (yield 40 and 25%, respectively), mp 32–33°C; published data [8]: mp 34°C.

**Reactions of 1-nitro-2-R-thioethenes with sodium thiolates at room temperature.** To a suspension of 0.2 g (0.69 mmol) of nitrothiostyrene **IIIc** in 10 ml of methanol we added at room temperature a solution of sodium dodecanethiolate, prepared from equimolar amounts of dodecanethiol and sodium methoxide in 5 ml of methanol. The colorless flaky precipitate (0.15 g, nitrothioacetal **Vg**) was filtered off, the filtrate was evaporated by half, and the light yellow crystals of 2-dodecylthio-1-nitro-1-phenylethene (**IIb**), 0.08 g (33%), were filtered off. Freezing of the filtrate gave 0.02 g (7%) of didodecyl disulfide.

Following the same procedure, we performed reactions of sodium dodecanethiolate with styrenes **IIIa**, **IIIb** and **IVa**–**IVc** and stilbenes **IIId**–**IIIf** and **IVd**–**IVf**, as well as of sodium octanethiolate with styrene **IVc** and stilbene **IIIe**. The products were 1-nitro-2-octylthio-1-phenylethene (**IIa**), light yellow crystals, mp 38–40°C; styrene **IIb**, mp 48–49°C; 1-nitro-2-octylthio-1,2-diphenylethene (**IIc**), yellow crystals, mp 69–70°C; and stylbene **IId**, mp 57–59°C. For details, see Table 3.

In the reactions of **IVd** with sodium *p*-toluenethiolate and sodium *p*-chlorobenzenethiolate only the initial nitrothioalkene was isolated in 90% yield (reaction time 48 h). Likewise, the initial thiol was isolated in 91% yield in the reaction of 2-ethylthio-1-nitro-1-phenylethene with sodium benzothiazole-2-thiolate (reaction time 48 h).

**Transformation of nitrothioacetals Vc and Vd into nitrothioethenes.** Compound **Vc**, 0.18 g (0.14 mmol), was dissolved in 3 ml of methanol, and the solution was kept at room temperature. The initial compound dissolved, and the solution gradually turned yellow. After 30 min (TLC), the solvent was removed, the residue was treated with 2 ml of ethanol cooled to 0°C, *p*-toluenethiol was filtered off, and the filtrate was concentrated and frozen to isolate 0.1 g (33%) of nitrothioethene **IIIb**, mp 84°C. The reaction with compound **Vd** was carried out in a similar way; after 40 min, nitrothioethene **IIIc** was isolated in 21% yield, mp 112°C.

**Independent synthesis of nitrothioacetals from 1,2-dinitro-1-phenylethene.** *2,2-Bis(p-chlorophenylthio)-1-nitro-1-phenylethane (**Vd**).* To a solution of 0.3 g (1.54 mmol) of 1,2-dinitro-1-phenylethene in 5 ml of methanol we added at 0°C a solution of sodium *p*-chlorobenzenethiolate in 10 ml of methanol, prepared from 0.0708 g (3.8 mmol) of sodium and

0.445 g (3.8 mmol) of *p*-chlorobenzenethiol. After 10 min, the colorless precipitate of thioacetal **Vd** was filtered off. Yield 0.27 g (30%), mp 37–39°C.

Nitrothioacetals **Vb** and **Vc** were obtained in a similar way; **Vb**: yield 42%, mp 27–28°C; **Vc**: yield 31%, mp 39–40°C.

*2,2-Bis(ethylthio)-1-nitro-1-phenylethane (**Va**).* To a solution of 1 g (0.005 mol) of 1,2-dinitro-1-phenylethene in 5 ml of methanol we added at –10°C a solution of 0.01 mol of sodium ethanethiolate, prepared from equimolar amounts of ethanethiol and sodium methoxide in methanol. After 2 h, the mixture was concentrated, the residue was treated with acetone, the precipitate of sodium nitrite was filtered off, and the filtrate was subjected to column chromatography on silica gel. Using cyclohexane as eluent we isolated 0.43 g of 2,2-bis(ethylthio)-1-nitro-1-phenylethane (**Va**) as a colorless crystalline substance. The column was then eluted with $CCl_4$ and $CHCl_3$; according to the TLC and $^1H$ NMR data, the eluates contained a mixture of 2-ethylthio-1-nitro-1-phenylethene and nitrothioacetal **Va**. The yields and melting points of compounds **V** are given in Table 1.

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