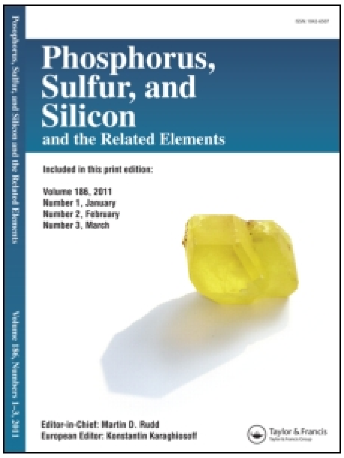

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REDUCTIVE SPLITTING REACTIONS OF AROMATIC BIVALENT SULFUR DERIVATIVES

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The inclination of aromatic derivatives of bivalent sulfur towards reductive splitting with trichlorosilane in tri-*n*-propylamine or with triethylsilane in trifluoroacetic acid or at an electron transfer from cyclooctatetraene dianion in THF is determined by the nature of sulfur-containing, i.e. sulfenether, sulfeneamide or rhodanic groups. When at the same time a nitro group is present in the aromatic ring, the sulfur-containing group becomes inactive in such reactions, which start directly with an electron transfer stage. At this stage the neutral molecules yield nitro-anion-radicals, whose raised stability renders difficult further transformations.

Reductive splitting reactions of bivalent sulfur derivatives are not only of synthetic interest,[1] but also are involved in mechanisms of a transformation in biological systems.[2]

The present work deals with a comparison of the behavior of the following aromatic bivalent sulfur derivatives: rhodanides, sulfeneamides, sulfeneethers and sulfenechlorides. Trichlorosilane in tri-*n*-propylamine and triethylsilane in trifluoroacetic acid were used as reducing agents.

Diphenyl disulfide is obtained in nearly 70% yield when treating propylbenzenesulfenate with triethylsilane in trifluoroacetic acid, while 2-rhodanothiophene remains altogether unchanged. A mixture of 2,2′-dithienyl disulfide and the initial rhodanoderivative is obtained by the interaction of rhodanothiophene with tri-*n*-propylamine and trichlorosilane in absolute benzene. It would appear that the reduction should proceed deeper introducing also an electron acceptor nitro group in the aromatic ring besides the existing rhodano group. Such aromatic compounds used were 2- and 4-nitrorhodanobenzene (see Table I, compounds I, II). Besides these, other nitroaromatic bivalent sulfur derivatives were studied also (Table I, compounds III–V). It turned out unexpectedly, that in the tri-*n*-propylamine-trichlorosilane system nitrorhodanobenzenes do not yield reduction products and are recovered unchanged. Under these conditions methylnitrobenzenesulfenate (III) and nitrobenzenemorpholylsulfeneamide (IV) also do not undergo reduction.

From data in Table I it is clear that the presence of a nitro group in derivatives III and IV does not interfere with the reduction of the sulfur-containing group by the help of triethylsilane and trifluoroacetic acid. However, the question whether in tri-*n*-propylamine-trichlorosilane system the compounds in consideration are recovered unchanged because of no reaction taking place between them remains open. It is well known that the interaction of trichlorosilane with tri-*n*-propylamine brings about the formation of trichlorosilylic anion.[4] Possibly, the reduction in this system starts with an electron transfer from trichlorosilylic anion to the bivalent sulfur derivative (ArSX) according to the following scheme 1:

$$
\begin{aligned}
&HSiCl_3 + Pr_3N \rightarrow {}^{\ominus}SiCl_3 + Pr_3\overset{+}{N}H\\
&ArSX + {}^{\ominus}SiCl_3 \rightarrow (ArSX)^{\dot{-}} + \cdot SiCl_3\\
&(ArSX)^{\dot{-}} + Pr_3\overset{+}{N}H \rightarrow ArSSAr + HX + Pr_3N\\
&\cdot SiCl_3 \rightarrow \text{Polymers}
\end{aligned}
\qquad (1)
$$

It is apparent from this scheme, that the final result of the reaction should depend on the stability of the intermediate $(ArSX)^{\dot{-}}$ anion-radical.

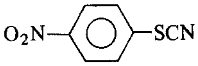
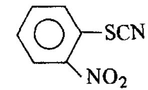
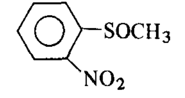
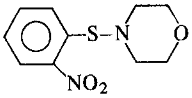
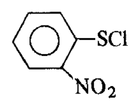
Unstable anion-radicals will decompose eliminating $X^{\ominus}$ and will form diaryldisulfides. Anion-radicals which are not inclined to splitting, may give their unpaired electrons to the oxidizer reversibly and may be converted to the initial derivatives (scheme 2) as if no reaction took place.

$$(ArSX)^{\dot{-}} + O_2 \rightarrow ArSX + O_2^{\dot{-}} \qquad (2)$$

Our experimental data indicate that unstable anion-radicals are formed from 2-rhodanothiophene and 2-

TABLE I

Reduction of aromatic bivalent sulfur derivatives in trichlorosilane-tri-*n*-propylamine system (a) (absolute benzene as solvent) and triethylsilane-trifluoroacetic acid system (b)

Compound	Formula	Products, obtained in systems (a) and (b)	Yield, %
I		(a) initial (b) initial	83 100
II		(a) initial (b) initial	90 100
III		(a) initial (b) 2,2'-dinitrodiphenyl-disulfide	60 96
IV		(a) initial (b) 2,2'-dinitrodiphenyl-disulfide	see note 65
V		(a) 2,2'-dinitrodiphenyl-disulfide (b) mixture of 2,2'-dinitro-diphenyldisulfide with 2-nitrothiophenole	93 76 + 18[3]

Note: The formation of a substance was established by thin-layer chromatography on alumina (in uv-light).

nitrobenzensulfenechloride. Nitroderivatives II–IV apparently yield stable anion-radicals. No paramagnetic particles were discovered by the esr method, when the reaction was carried out in argon. Single electron oxidation of anion-radicals II–IV might take place not only at the expense of the atmospheric oxygen but at the expense of a proton as well, according to the following scheme 3:

$$(ArSX)^{\dot{-}} + Pr_3\overset{+}{N}H \rightarrow ArSX + Pr_3N + \tfrac{1}{2}H_2 \qquad (3)$$

In the latter case, together with the regeneration of the initial nitrocompound, hydrogen should be eliminated too. Indeed, by means of GLC on molecular sieves of 5 Å we were able to indicate that during the reaction of nitro-aromatic derivatives II–IV with trichlorosilane and tri-*n*-propylamine hydrogen elimination occurred whose quantity increased continuously, while the same trichlorosilane-tri-*n*-propylamine mixture without II–IV yielded no hydrogen even on a very long standing.

In order to verify the predicted properties of the anion-radicals $(ArSX)^{\dot{-}}$ the electron transfer reactions were carried out between cyclooctatetraenedipotassium ($C_8H_8K_2$, 1 mole) and the derivatives of ArSX type (2 moles) in absolute THF in an atmosphere of argon. The reaction products were treated with dilute (25%) acetic acid. Under these conditions 2-rhodanothiophene, methyl- or *n*-propylbenzenesulfenates,[6] and 2-nitrobenzenesulfenechloride also yielded disulfides. Nitrosubstituted derivatives II–IV during the electron transfer according to scheme (4) were converted into anion-radicals whose structures were confirmed by their corresponding esr-spectra (Table 2). These esr-spectra were reproducible after several hours of standing also.

$$2(2\text{–}O_2NC_6H_4SX) + C_8H_8K_2 \rightarrow 2[(2\text{–}O_2NC_6H_4SX)^{\dot{-}} K^+] + C_8H_8 \qquad (4)$$

The reaction mixture containing anion-radicals, after being worked up with dilute acetic acid, gave up to 80% yield of the initial compounds. The same nitrocompounds were also obtained when oxygen was passed through the reaction mixture (up to 90% yield). 2-Nitrobenzenesulfenechloride V yielded an anion-radical only after S–Cl group reduction.[7] The same sulfenechloride V formed 2,2'dinitrodiphenylsulfide[8] by reacting with $C_8H_8K_2$ (reagent ratio 2 : 1).

Accordingly 2-nitrobenzenesulfenechloride V is smoothly converted to 2,2'-dinitrodiphenyldisulfide when treated with trichlorosilane and tri-*n*-propylamine in absolute benzene (Table 1).

TABLE 2

HFS-constants (a_i, G) for the potassium salts of the anion-radicals yielded by scheme (4)

Starting compounds	a_N	$a_H^{3\ 5}$	$a_H^{4\ 5}$
2-Nitrorhodanobenzene (II)	10.50	3.70	1.15
Methyl-2-nitrobenzenesulfenate (III)	10.75	3.31	0.30
2-Nitrobenzenemorpholylsulfenamide (IV)	10.10	3.88	1.25

Thus, the results obtained for electron transfer reactions involving bivalent sulfur derivatives are consistent with those characterizing the behavior of these derivatives in trichlorosilane-tri-*n*-propylamine system.

A sulfur-containing group undergoes reductive splitting both when treated with trichlorosilane and tri-*n*-propylamine in absolute benzene and by electron transfer from cyclo-octatetraene dipotassium in THF. Sulfeneetheric, sulfeneamidic and rhodanic fragments lose their ability for splitting in the presence of a nitro group in the aromatic ring. So molecules yield nitro-anion-radicals whose increased stability renders difficult further conversions.

In the case of the trichlorosilane-tri-*n*-propylamine system the reaction takes place through another path, i.e. through a catalytic evolution of hydrogen. 2-Nitrobenzenesulfenechloride yields a mixture of disulfide and mercaptane under the action of triethylsilane and trifluoroacetic acid (compare with Table I, V) while 2-nitrobenzenesulfeneamide and methyl-2-nitrobenzenesulfenate (IV and III in Table I) form 2,2′-dinitrodiphenyldisulfide only. In trifluoro-acetic acid sulfenechloride is specifically solvated at the expense of a hydrogen bond formation with chlorine atom.[3] Sulfeneamides and sulfeneethers yield in trifluoroacetic acid protonation products with positively charged atoms of nitrogen or oxygen. Protonated molecules further add the hydride ion and are converted into thiophenole. Thiophenole reacts with a protonated molecule of the starting compound and forms a disulfide, scheme 3:

$$\mathrm{ArSOR} \xrightarrow{\mathrm{H}^+} [\mathrm{ArS}\underset{+}{\mathrm{O}}(\mathrm{H})\mathrm{R}] \xrightarrow{\mathrm{H}^{\ominus}} \mathrm{ArSH} + \mathrm{ROH}$$

$$[\mathrm{ArS}\underset{+}{\mathrm{O}}(\mathrm{H})\mathrm{R}] + \mathrm{ArSH} \rightarrow \mathrm{ArSSAr} + \mathrm{ROH} + \mathrm{H}^+ \qquad (3)$$

A similar two-stage mechanism was formulated[3] for the transformation of arylsulfenechlorides into diaryldisulfides by triethylsilane and trifluoroacetic acid. Specifically solvated sulfenechloride molecules apparently interact with thiophenole less actively than do protonated sulfenate or sulfeneamide molecules. For this reason sulfenates and sulfeneamides form disulfides without thiophenole admixture when treated with triethylsilane and trifluoroacetic acid. Aromatic rhodanides are not reduced when treated with triethylsilane and trifluoroacetic acid (I, II in Table I). Trifluoroacetic acid, probably, is unable to protonize rhodanides and the polarization of the bond between the sulfur atom and the nitryl moiety is not so effective as that between sulfur and chlorine atoms in sulfenechlorides.

The hydride ion addition according to scheme (3) may be explained by a transfer of either one electron and a hydrogen atom or by two electrons (in succession) and one proton. Without discussing either of these possibilities we point out that both of them include an electron transfer. However, in these electron transfer reactions are involved not the initial molecules themselves but their interaction products with trifluoroacetic acid. The reduction course of aromatic bivalent sulfur derivatives depends on the mechanism of this reaction and, in particular, on which stage the electron transfer is observed, the first or the following ones.

EXPERIMENTAL

1. *Reduction by means of trichlorosilane and tri-n-propylamine*

2-Rhodanothiophene. To 0.3 g (0.0012 mole) of 2-rhodanothiophene[9] in absolute benzene was added 0.171 g (0.0012 mole) of tri-*n*-propylamine and 0.243 g (0.0018 mole) of trichlorosilane. The mixture was stirred for 4 hours at room temperature. TLC with an authentic specimen (alumina, hexene: ether 4 : 1) showed the presence of 2-rhodanothiophene and 2,2′-dithienyldisulfide. In the same conditions methylbenzenesulfenate and morpholyl benzenesulfenamide were converted into diphenyldisulfide (yields were 96 and 90% accordingly).

2-Nitrorhodanobenzene. To 0.1 g (0.0005 mole) of 2-nitrorhodanobenzene[10] in absolute benzene was added 0.0716 g (0.0005 mole) of tri-*n*-propylamine and 0.1 g (0.00075 mole) of trichlorosilane. The mixture was stirred for 4 hours at room temperature and the presence of hydrogen was detected all the time in the gas phase. For this purpose a gas chromatograph HT-63 (USSR) was used with a densitomer G-20 as detector, a column with molecular sieves of 5 A and 5.4 m long, inner diameter 4 mm, and column temperature 25°C. The gas carrier was nitrogen with a pressure of 0.35 atm. at the entrance of the column.

Nitrogen flow: general 150 ml/min, through the working camera 40 ml/min. Hydrogen formation was observed during the reaction. TLC of the sample of the reaction solution (alumina, hexane: ether 4 : 1) showed a spot of the initial 2-nitrorhodanobenzene. After removing the solvent, the starting 2-nitrorhodanobenzene was obtained with a melting point of 132–133°C. The yield was 90%. A sample mixed with the authentic specimen gave no depression in the melting point.

4-Nitrorhodanobenzene. To 0.1 g (0.0005 mole) of 4-nitrorhodanobenzene[11] in absolute benzene was added 0.0716 g (0.0005 mole) of tri-*n*-propylamine and 0.1 g (0.00075 mole) of trichlorosilane. The mixture was stirred for 4 hours at room temperature. The reaction solution contained the unchanged starting material which was recovered in 83% yield. No depression was observed in the melting point of a mixed sample.

Methyl-2-nitrobenzenesulfenate. To 0.1 g (0.0005 mole) of methyl-2-nitrobenzenesulfenate[12] in absolute benzene was added 0.0716 g (0.0005 mole) of tri-*n*-propylamine and 0.1 g (0.00075 mole) of trichlorosilane. The mixture was stirred for 4 hours at room temperature. Hydrogen was detected in the gas phase; its quantity was increasing faster than in the case of 2-nitrobenzenerhodanide. TLC of a sample of the reaction solution (alumina, hexane: THF 4 : 1) showed only a spot of the initial methylnitrobenzenesulfenate. After removal of the solvent, a viscous material remained which, on crystallization from hexane, yielded methyl-2-nitrobenzenesulfenate (0.06 g, mp 52°C, lit. mp 54°C,[12] 60%) and 2,2′-dinitrodiphenyldisulfide (0.02 g, mp 191–192°C, lit. mp 194°C,[13] yield 24%). Apparently part of the starting sulfenate was converted into the disulfide on air exposure. In a checking experiment methyl-2-nitrobenzenesulfenate on stirring in dilute hydrochloric acid yielded wholly 2,2′-dinitrodiphenyldisulfide. Trichlorosilane fumes in air and readily hydrolyzes.

2-Nitrobenzenemorpholylsulfeneamide. To 0.1 g (0.00041 mole) of 2-nitrobenzenemorpholylsulfeneamide[14] in absolute benzene was added 0.0587 g (0.00041 mole) of tri-*n*-propylamine and 0.0826 g (0.0006 mole) of trichlorosilane and the mixture was stirred for 4 hours. TLC (hexane: THF 4 : 1) showed only a spot of the initial compound.

2-Nitrobenzenesulfenechloride. To 0.189 g (0.001 mole) of 2-nitrobenzenesulfenechloride[15] in absolute benzene was added 0.143 g (0.001 mole) of tri-*n*-propylamine and 0.2 g (0.0015 mole) trichlorosilane. The mixture was stirred and treated as in the preceding experiments. 2,2′-Dinitrodiphenyldisulfide was obtained, 0.143 g (93%), mp 191–192°C. A mixed sample gave no depression in the melting point.

2. *Reduction by means of triethylsilane and trifluoroacetic acid*

n-Propylbenzenesulfenate. To 0.5 g (0.0029 mole) of *n*-propylbenzenesulfenate[16] in 4 ml of trifluoroacetic acid 0.16 g (0.0014 mole) of triethylsilane was added with stirring. The solution turned yellow first and soon a white precipitate deposited. Stirring was continued for 4 hours. Then the solvent was removed and 0.4 g (70%) of diphenyldisulfide was obtained melting at 58–59°C. A mixed sample with the authentic specimen gave no depression in the melting point. In runs with morpholylbenzenesulfenate diphenyldisulfide was obtained with the yield of 80%.

2-Rhodanothiophene. To 0.5 g (0.0035 mole) of 2-rhodanothiophene[9] in 4 ml of trifluoroacetic acid 0.2 g (0.001 mole) of triethylsilane was added and the mixture was stirred for 30 hours at room temperature. TLC on alumina (hexane: ether 4 : 1) showed only a spot of the initial rhodanoderivative. After removal of the solvent 2-rhodanothiophene (0.46 g, 93%) was obtained.

Methyl-2-nitrobenzenesulfenate.

a) To 0.3 g (0.0015 mole) of methyl-2-nitrobenzenesulfenate in 2.5 ml of trifluoroacetic acid 0.092 g (0.0008 mole) of triethylsilane was added by stirring. Soon the solution acquired a lilac color. Stirring was continued for 4 hours. After removal of the solvent 2,2′-dinitrodiphenyldisulfide (0.24 g, 96%) was obtained melting at 192–193°C.

b) 0.1 g (0.0005 mole, of methyl-2-nitrobenzenesulfenate was mixed with 0.03 g (0.00025 mole) of triethylsilane in 0.5 ml of formic acid and the reaction mixture was stirred for 8 hours at room temperature to complete the reaction. The deposited residue was filtered out, washed with formic acid and dried in vacuum. 2,2′-Dinitrodiphenyldisulfide was obtained melting at 191–192°C (0.07 g, 85%).

2-Nitrobenzenemorpholylsulfeneamide. To 0.2 g (0.00683 mole) of 2-nitrobenzenemorpholylsulfeneamide in absolute ether 2.6 ml of trifluoroacetic acid and 0.048 g (0.00041 mole) of triethylsilane was added. The mixture was stirred for 4 hours at room temperature. After removal of the solvent 0.07 g (65%) of 2,2′-dinitrodiphenyldisulfide was obtained melting at 191–192°C. A mixed sample with the authentic specimen gave no depression in the melting point.

2- or 4-Nitrorhodanobenzenes. To 0.1 g (0.00055 mole) of 2- or 4-nitrorhodanobenzene in 1 ml of trifluoroacetic acid 0.03 g (0.00025 mole) of triethylsilane was added and the mixture was stirred for 14 hours at room temperature. After removing the solvent the initial substance was obtained in a quantitative yield. No change in the melting point was observed.

3. *Reduction by means of cyctooctatetraenedipotassium*

The reduction was performed at −60°C in a purified argon atmosphere. The solvent was absolute THF which was distilled under potassium-benzophenone before being used. Cyclooctatetraenedipotassium (COTDP) was prepared according to the method in Ref. 17.

After mixing the reagents, the temperature was raised to −5°C and 1 ml of 25% acetic acid free of air was added. ESR samples were taken before adding the acid; spectra represent by themselves a triplet of triplets; HFS constants are given in Table II.

Methyl-2-nitrobenzenesulfenate. On mixing the solutions of 0.181 g (0.0009 mole) of methyl-2-nitrobenzenesulfenate in THF and COTDP (from 0.0511 g or 0.0004 mole of cyclooctatetraene-COT) in THF a deep red color was formed. TLC on alumina (hexane: THF 4 : 1) showed only a spot of the initial methyl-2-nitrobenzenesulfenate. After removal of the solvent, the yellow oily residue was dissolved in hexane and passed through a column filled with alumina. Hexane was evaporated and 0.1 g (56%) of methyl-2-nitrobenzenesulfenate was obtained melting at 52°C. In a repeated run oxygen was passed through the resulting solution after mixing the electron donor and acceptor reagents. The initial sulfenate melting at 52°C was isolated in 80% yield. The mixed samples in all runs gave no depression in their melting points.

2-Nitrobenzenemorpholylsulfeneamide. Solutions of 0.6 g (0.0025 mole) of 2-nitrobenzenemorpholylsulfeneamide and COTDP (COT-0.13 g or 0.00125 mole) in THF were mixed. The orange color of the sulfeneamide solution turned to brown. After removing the solvent, the residue was crystallized from alcohol. The initial compound melting at 91°C was isolated (0.5 g, 83%). A mixed sample with an authentic specimen gave no depression in the melting point. The yield of COT was 100%.

2- or 4-Nitrorhodanobenzene. Solutions of 0.1 g (0.00055 mole) of 2- or 4-nitrorhodanobenzene and COTDP (0.0287 g or 0.000275 mole of COT) were mixed. The resulting solution became cherry colored. After removal of the solvent, the residue was crystallized from alcohol (2-isomer) or from heptane (4-isomer). From 0.08 g to 0.07 g (80–75%) of the initial nitrorhodanobenzene was obtained, which was identified with compound with corresponding structure. The yield of COT in each run was 100%.

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