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Organic Sulfur Compounds. XIV. The Reactions of Sulfinic Esters and Related Compounds with Hydrazine

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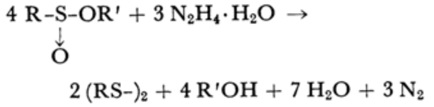
Anhydrous hydrazine reacted with sulfinic esters under mild reaction conditions to give disulfides, which were in turn, upon prolonged heating, reduced by hydrazine to mercaptans. Aromatic thiolsulfonates and sulfonyl chlorides were also reduced by hydrazine, whereas aromatic sulfoxides and sulfinic acids were not reduced under comparable reaction conditions. A mixture of hydrazine with a sulfinic ester or another of the reducible sulfur compounds described above can hydrogenate carbon-carbon double bonds and triple bonds. A mechanism involving the intermediate formation of diimide is proposed.

The reactions of hydrazine hydrate with ethyl benzenesulfinate and methyl β-naphthalenesulfinate have been described by Curtius,1) and the formation of nitrogen and disulfides has been observed. Although these reactions have been claimed to be expressed by the following equation, no details of the material balance have been given and no reaction mechanism has yet been discussed.

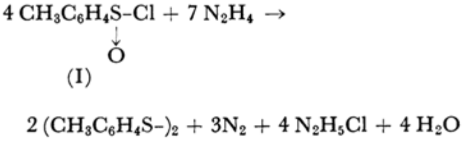


$$4\,\mathrm{R{-}\underset{\underset{O}{\downarrow}}{S}{-}OR'} + 3\,\mathrm{N_2H_4\cdot H_2O} \rightarrow 2\,\mathrm{(RS{-})_2} + 4\,\mathrm{R'OH} + 7\,\mathrm{H_2O} + 3\,\mathrm{N_2} \tag{1}$$

In an attempt to prepare the hitherto-unknown sulfinyl hydrazides, the reactions of anhydrous hydrazine with alkyl sulfinates and sulfinyl chlorides have been studied by the present authors. Ethyl *p*-toluenesulfinate and hydrazine reacted very slowly at room temperature, but vigorously at 60—80°C to form about one mole of gaseous product and *p*, *p*-ditolyl disulfide in an almost theoretical yield. Ethyl *p*-bromobenzenesulfinate reacted similarly to give 1.5 mole of gas and di-*p*-bromophenyl disulfide in a quantitative yield. Ethyl benzenesulfinate gave 1.25 mole of gas and diphenyl disulfide in good yields. The amounts of the gaseous product were always more than the calculated figures based on the equation 1.

Upon prolonged heating, the reaction proceeded further to give the thiophenols. For instance, *p*-bromobenzenesulfinic ester gave *p*-bromothiophenol in a good yield.

The reaction between *p*-toluenesulfinyl chloride (I) and hydrazine was very vigorous, even at −60°C; di-*p*-tolyl disulfide was the major product. This reaction could be expressed by the following formula:



$$4\,\mathrm{CH_3C_6H_4\underset{\underset{O}{\downarrow}}{S}{-}Cl} + 7\,\mathrm{N_2H_4} \rightarrow 2\,\mathrm{(CH_3C_6H_4S{-})_2} + 3\mathrm{N_2} + 4\,\mathrm{N_2H_5Cl} + 4\,\mathrm{H_2O} \tag{2}$$

(I)

In all the reactions described above, the formation of the desired sulfinyl hydrazide was not observed; this suggests the low stability of this class of compounds.

The reactions of several other organic sulfur compounds with anhydrous hydrazine were also examined. *p*-Toluenesulfinic acid did not react with hydrazine, and the acid was recovered unchanged upon the acidification of the reaction mixture. Diphenyl sulfoxide was also unreactive towards hydrazine.

p-Tolyl *p*-toluenethiolsulfonate (II) reacted very rapidly with hydrazine, in either the presence or absence of the solvent, to form a considerable quantity of gas, as well as di-*p*-tolyl disulfide and *p*-toluenesulfinic acid in good yields. When the reaction was carried out in ethanol for several hours at the boiling point, *p*-thiocresol and sulfinic acid were the products.

Many studies of the reactions between thiolsulfonates and anionoid reagents have been published.2) For instance, with cyanide anions or hydroxide anions:

$$\mathrm{RSO_2SR'} + \mathrm{CN^-} \rightarrow \mathrm{RSO_2^-} + \mathrm{R'SCN} \tag{3}$$

$$\mathrm{RSO_2SR'} + \mathrm{OH^-} \rightarrow \mathrm{RSO_2^-} + \mathrm{R'SOH} \tag{4}$$

with thiolate anions3):

$$\mathrm{RSO_2SR'} + \mathrm{R''SH} \rightarrow \mathrm{RSO_2H} + \mathrm{R'SSR''} \tag{5}$$

with amines4):

$$\mathrm{RSO_2SR'} + \mathrm{R''NH_2} \rightarrow \mathrm{RSO_2H} + \mathrm{R'SNHR''} \tag{6}$$

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1) T. Curtius and F. Lorenzen, *J. pr. Chem.*, [2] **58**, 160 (1898).

2) N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

3) T. F. Parsons, J. D. Buckman, D. E. Pearson and L. Field, *J. Org. Chem.*, **30**, 1923 (1965).

4) B. G. Boldyrev and S. A. Kolensnikova, *Zh. obshch. khim.*, **35**, 198 (1965).

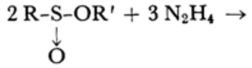
In all these reactions, the anionoid reagents attacked the thiolsulfonate on the sulfide sulfur. By analogy, the hydrazine molecule may be expected to react with the thiolsulfonate according to the following formula to give the sulfenyl hydrazide in the first stage:

$$RSO_2SR' + N_2H_4 \rightarrow RSO_2H + R'SNHNH_2 \qquad (7)$$

The overall reaction may then be expressed by the following equation:

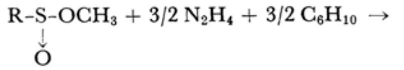
$$RSO_2SR' + 1/4\, N_2H_4 \rightarrow RSO_2H + R'SSR' + 1/4\, N_2 \qquad (8)$$

As has been described above, the volume of the gaseous products in the reactions of hydrazine with sulfinate esters exceeded the volume of nitrogen calculated on the basis of the reaction 1. This suggests the formation of some hydrogen molecule according to the reaction shown below:



$$2\,R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}OR' + 3\,N_2H_4 \rightarrow (RS\text{-})_2 + 3\,N_2 + 3H_2 + 2\,R'OH + 2\,H_2O \qquad (9)$$

This idea has led us to examine the reaction of sulfinate esters, or other reducible organic sulfur compounds, with hydrazine in the presence of cyclohexene. If the hydrogen in the reaction 9 is formed in a reactive state, cyclohexene would be reduced to cyclohexane. Actually, when a mixture of cyclohexene (60 mmole), hydrazine (30 mmole), and methyl *p*-toluenesulfinate (12 mmole) in ethanol was warmed, 9 mole% per ester of cyclohexane was formed. In the presence of a large excess of hydrazine, the formation of 1.5 mole of cyclohexane, 0.9 mole of di-*p*-tolyl disulfide, and 1.2 mole of gas was observed. These results may be expressed by the following formula:



$$R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}OCH_3 + 3/2\,N_2H_4 + 3/2\,C_6H_{10} \rightarrow 3/2\,C_6H_{12} + (RS\text{-})_2 + 3/2\,N_2 + CH_3OH + H_2O \qquad (10)$$

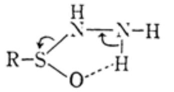
The reaction between di-*p*-tolyl disulfide, cyclohexene, and an excess of hydrazine also gave cyclohexane (75—87 mole% per mole disulfide). Cyclohexene was reduced by a mixture of *p*-tolyl *p*-toluenethiolsulfonate and hydrazine to give cyclohexane in a 50 mole% yield per thiolsulfonate and *p*-toluenesulfinic acid in a 83% yield. This reaction may be represented by the equation below:

$$2\,RSO_2SR + N_2H_4 + C_6H_{10} \rightarrow (RS\text{-})_2 + 2\,RSO_2H + N_2 + C_6H_{12} \qquad (11)$$

A mixture of *p*-toluenesulonyl chloride and hydrazine reduced cyclohexene to give 1.3 mole of cyclohexane per mole of sulfonyl chloride; *p*-toluenesulfinic acid was another major product.

Acetylenic triple bonds can be hydrogenated, too. When a solution of tolan (3.3 mmole), ethyl *p*-toluenesulfinate (2.60 mmole), and a large excess of hydrazine in ethanol was refluxed for 5 hr., the formation of bibenzyl (65 mole%) and *trans*-stilbene (19 mole%) was observed.

As the common reactive hydrogenator in the above reductions, diimide (III) is considered the most plausible. In the reaction with sulfinate esters and sulfinyl chlorides, a sulfinyl hydrazide (IV) could be formed as an intermediate; this could in turn decompose to give the sulfenic acid and diimide:

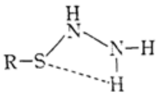


$$\longrightarrow RSOH + HN{=}NH \qquad (12)$$

IV III

In the next step, the sulfenic acid could be reduced with excess hydrazine, not with diimide, to give the disulfide.

In the case of thiolsulfonates, the sulfenyl hydrazide formed in the reaction 7 would decompose to the sulfide and diimide:



$$\longrightarrow RSH + HN{=}NH \qquad (13)$$

The disulfide could also give the sulfenyl hydrazide according to the reaction shown below:

$$RSSR + N_2H_4 \rightarrow RSH + RSNHNH_2 \qquad (14)$$

By assuming the reactions 12—14, the amount of cyclohexane formed may be seen to correspond well with the calculated yield of diimide in these reactions. It has also been confirmed that no reduction of cyclohexene is observed, even upon prolonged boiling, with hydrazine in ethanol except when a sulfur compound is added.

Recently there have been many investigations on the reduction with diimide.[5-15] Diimide has

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[5] a) E. J. Corey, W. L. Mock and D. J. Pasto, *Tetrahedron Letters*, **1961**, 347. b) E. J. Corey, D. J. Pasto and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

[6] a) S. Huenig, H. R. Mueller and W. Thier, *Tetrahedron Letters*, **1961**, 353. b) S. Huenig and H. R. Mueller, *Angew. Chem.*, **74**, 215 (1962).

[7] E. J. Corey and W. L. Mock, *J. Am. Chem. Soc.*, **84**, 685 (1962).

[8] R. Appel and W. Buechner, *Angew. Chem.*, **73**, 807 (1961); *Ann.*, **654**, 1 (1962).

[9] J. K. Stille and T. Anyos, *J. Org. Chem.*, **27**, 3352 (1962).

[10] E. E. van Tamelen, R. S. Dewey and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

[11] R. S. Dewey and E. E. van Tamelen, ibid., **83**, 3729 (1961).

[12] E. E. van Tamelen, R. S. Dewey, M. F. Lease and W. H. Pirkel, ibid., **83**, 4302 (1961).

[13] E. E. van Tamelen and R. J. Timmons, ibid., **84**, 1067 (1962).

[14] R. Buyle, A. V. Overstraeten and F. Eloy, *Chem. Ind.*, **1964**, 839.

[15] E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965).

been produced by several methods, including the oxidation of hydrazine, the decomposition of hydroxylamine-*O*-sulfonic acid, and the decomposition of azodicarboxylate, but the methods particularly related to the present investigation are the decomposition of the sulfonylhydrazine[6a,11,15] and the alkaline decomposition of chloroacetylhydrazide.[14] The reaction of the sulfonylhydrazine in the presence of a base to give diimide and a sulfinic acid is especially reminiscent of the reactions investigated in this paper:

$$RSO_2NHNH_2 \rightarrow RSO_2H + NH{=}NH \qquad (15)$$

Most probably, in the reaction of sulfonyl chlorides with hydrazine described above, this sulfonylhydrazine is formed in the first stage of the reaction.

The steric course of the hydrogenation by diimide has been shown to be *cis*.[5b,6a,7] In the reduction of tolan with ethyl sulfinate and hydrazine described above, the formation of *trans*-stilbene, not the expected *cis*-stilbene, was observed. Considering that thiophenol is a powerful catalyst for the *cis*-*trans* isomerization of doulbe bonds, the above result may be explained in terms of the isomerization of the primary product, *cis*-stilbene, to the *trans* isomeride in the presence of *p*-thiocresol, formed as another main product.

In the literature, the reduction efficiency of sulfonylhydrazines has been reported to be rather poor; for instance, the amount of the alkene reduced was 0.2—0.3 mole per mole of sulfonylhydrazine.[15] On the contrary, the efficiency of the sulfinate esters or other sulfur compounds described in this paper in the reduction of cyclohexene is very good. This may be attributable to the presence of a large excess of hydrazine, in which the rate of the decay of diimide to nitrogen and hydrogen or to nitrogen and hydrazine[14] could be retarded.

Experimental

Materials.—Anhydrous hydrazine was prepared by boiling hydrazine hydrate with sodium hydroxide and barium oxide successively.

The Reaction between Ethyl *p*-Bromobenzenesulfinate and Hydrazine.—When 1.0 g. of the ester and 0.7 ml. of hydrazine were mixed at room temperature, the reaction proceeded very slowly at first, but after some time the exothermal reaction, accompanied by the evolution of gas, was started; the total gas volume was 150 ml. (1.6 mole). Upon the dilution of the reaction mixture with water, di-*p*-bromophenyl disulfide was obtained in a nearly quantitative yield.

The Reaction of *p*-Toluenesulfinyl Chloride with Hydrazine.—To a mixture of 4 g. of hydrazine and 1 ml. of anhydrous pyridine, cooled in a dry ice-acetone bath, 7 g. of sulfinyl chloride was added slowly; a very vigorous reaction, accompanied by the evolution of gas, occurred to give a solid mass, from which 2.5 g. of di-*p*-tolyl disulfide and 1 g. of *p*-toluenesulfinic acid were then isolated.

The Reaction of *p*-Tolyl *p*-Toluenethiolsulfonate with Hydrazine.—When 0.7 ml. of hydrazine was added, drop by drop, to 2 g. of the thiolsulfonate, a vigorous reaction started, and about 20 mole% of gas was evolved. After an hour, the mixture was diluted with water to leave 1 g. of di-*p*-tolyl disulfide.

The Reduction of Cyclohexene with Methyl *p*-Toluenesulfinate and Hydrazine.—A mixture of 2.0 g. of the methyl ester, 5.0 g. of cyclohexene, and 1.0 g. of hydrazine in 40 ml. of anhydrous methanol was warmed on a water bath for one hour. The reaction mixture was then diluted with water, and the organic layer was separated, dried, and analyzed by gas liquid chromatography (a 1 m. tricresyl phosphate column at 82°C), and found to contain 1.83% of cyclohexane. A similar reaction of 5.0 g. of ethyl *p*-toluenesulfinate, 5.0 g. of cyclohexene, and 5.0 g. of hydrazine in 40 ml. of ethanol at 70—80°C gave 750 ml. of gas in 8 hr. Analysis by gas chromatography revealed the formation of 1.48 mole of cyclohexane per mole of the sulfinate ester. The extraction of the water layer with methylene chloride gave 3.0 g. of di-*p*-tolyl disulfide.

The Reduction with Di-*p*-tolyl Disulfide.—A mixture of 3.0 g. of the disulfide, 5.0 g. of hydrazine, and 5.0 g. of cyclohexene in 40 ml. of ethanol was warmed at 65°C for 11 hr.; 180 ml. of gas was thus evolved. By treatment similar to that of the above reaction, the formation of 75 mole% cyclohexane (based on the disulfide) was indicated.

The Reduction of Tolan.—A solution of 585 mg. of tolan, 2 g. of hydrazine, and 480 mg. of ethyl *p*-toluenesulfinate in 15 ml. of absolute ethanol was refluxed for 5 hr. The reaction mixture was then diluted with water, extracted with *n*-hexane, and fractionated by elution chromatography over alumina with petroleum ether. Bibenzyl, di-*p*-tolyl disulfide, and *trans*-stilbene were eluted in this order. Since the separation of bibenzyl from the disulfide was incomplete, the yield of these compounds was estimated by infrared spectroscopy and found to be 401 mg. of bibenzyl and 127 mg. of the disulfide, whereas the yield of *trans*-stilbene was 113 mg. No *cis*-stilbene was detected.