

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE MECHANISM OF THE REDUCTION OF SULFONYL BROMIDES WITH PHOSPHORUS TRIBROMIDE¹

BY W. H. HUNTER AND B. E. SORENSON

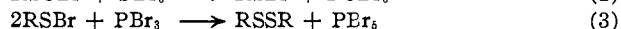
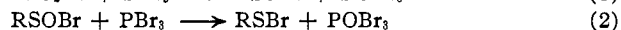
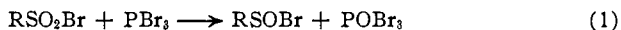
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Kohlhase² discovered that many aromatic sulfonyl bromides could be easily and conveniently reduced to disulfides by phosphorus tribromide. Hunter and Sorenson³ showed that the reaction could be applied with equal success to sulfonyl bromides of the aliphatic series. These earlier papers were concerned largely with the preparative aspects of the new reaction. Attention was logically next devoted to the mechanism of the change.

In order to elucidate the mechanism of the reaction, two methods of attack are possible: attempts could be made to isolate intermediate products of the reduction, or possible intermediate products could be synthesized by other means, and the action of phosphorus bromides upon these substances studied. Since the first procedure is attended with great difficulty and uncertainty under the conditions necessary for these reductions, we chose the latter method of attack.

For this purpose it was first assumed that the reaction took place in steps which might be represented as



Examples of each of these possible intermediate products were prepared and subjected to the action of phosphorus tribromide as described in this paper.

No sulfinyl bromides were described in the literature; therefore, *p*-toluene sulfinyl chloride⁴ was chosen for the first experiments. This sulfinyl chloride was reduced very readily by phosphorus tribromide, although it gave a slightly lower yield of *p*-toluene disulfide than *p*-toluene sulfonyl bromide which was also reduced as a control.⁵

¹ This article is an abstract of part of a thesis submitted by B. E. Sorenson to the Faculty of the Graduate School of the University of Minnesota, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

² Kohlhase, *THIS JOURNAL*, **54**, 2441 (1932).

³ Hunter and Sorenson, *ibid.*, **54**, 3364 (1932).

⁴ Hilditch and Smiles, *Ber.*, **41**, 4115 (1908).

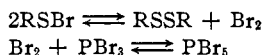
⁵ The comparison between the *p*-toluene sulfinyl chloride and the sulfonyl bromide was not entirely logical, but since previous work³ has shown that sulfonyl chlorides are not reduced by phosphorus tribromide whereas sulfonyl bromides are readily reduced, it seems probable that the sulfinyl bromide would be reduced at least as easily as the sulfinyl chloride.

Otto and Rössing⁶ also found that sodium benzene sulfinate was reduced to the disulfide by phosphorus trichloride according to the equation



If the first product of this reaction is the sulfinyl chloride it indicates that this is reduced by the phosphorus trichloride. Since sulfonyl bromides are not reduced by phosphorus trichloride,² this can be adduced as further evidence that sulfinyl bromides are more easily reduced than sulfonyl chlorides. This ease of reduction of the sulfinyl bromides very likely accounts for the fact that sulfinyl bromides do not appear as intermediate products.

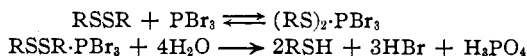
o-Nitrophenyl sulfur bromide⁷ was chosen for the next experiments as it was well known and quite stable. This sulfur bromide did not react rapidly with phosphorus tribromide. However, when it was allowed to stand for several days in dry ether with phosphorus tribromide it gave some *o*-nitrophenyl disulfide. Under similar conditions the sulfur bromide alone in dry ether also gave some *o*-nitrophenyl disulfide but not as much as when phosphorus tribromide was present. These phenomena may be explained by assuming that the sulfur bromide dissociates reversibly into bromine and the disulfide, and that phosphorus tribromide may upset the equilibrium by combining with the bromine thus liberated.



When *o*-nitrophenyl disulfide was treated with an excess of phosphorus pentabromide, *o*-nitrophenyl sulfur bromide was formed, thus proving that the above reaction is in fact reversible. An attempt was made to prepare tribromobenzene sulfur bromide from the disulfide and bromine according to the general method of Zincke and Farr⁷ but it could not be isolated. As soon as the solvent and excess bromine were removed the reaction was completely reversed to give back the disulfide.

o-Nitrophenylsulfonyl bromide was reduced by phosphorus tribromide at low temperatures. The products were the disulfide and the sulfur bromide when the reaction products were isolated in the absence of water. When the reaction mixture was dissolved in ether and hydrolyzed by adding water, *o*-nitrophenyl disulfide and *o*-nitrothiophenol were obtained.

Thionaphthol² was previously isolated in this type of reduction and was assumed to be formed in accordance with the equations

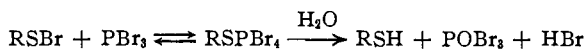


This mechanism was tested by mixing *o*-nitrophenyl disulfide and phosphorus tribromide, but no thiophenol resulted. The next postulate was

⁶ Otto and Rössing, *Ber.*, **24**, 3883 (1891).

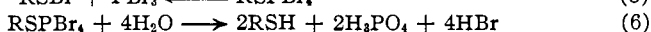
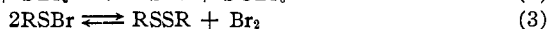
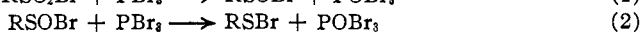
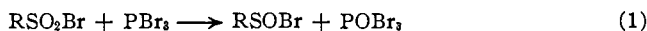
⁷ Zincke and Farr, *Ann.*, **391**, 67 (1912).

that the thiophenol resulted from the further reduction of the sulfur bromide when water was added to the ether solution. However, none of the reducing agents present in the reaction mixture, such as phosphorus acid and hydrobromic acid, reduced the sulfur bromide to the thiophenol in the presence of water and ether. However, pure *o*-nitrophenyl sulfur bromide and phosphorus tribromide in ether solution gave almost a quantitative yield of thiophenol when water was added. From this it was concluded that the thiophenol resulted from the hydrolysis of a molecular compound first formed from the sulfur bromide and phosphorus tribromide.



A freezing point method was devised to determine if evidence of the formation of a molecular compound could be obtained. Phosphorus tribromide or *o*-nitrophenyl sulfur bromide alone gave normal freezing point depressions in benzene. Likewise, the mixture gave a normal freezing point depression in benzene showing that no molecular compound was formed in this solvent. However, when a solution of the two in *benzene* was hydrolyzed (as was done with the ether solution) *o*-nitrophenyl disulfide was formed instead of the thiophenol obtained in ether. No direct proof of the presence of a molecular compound in the ether solution could be observed, but the different results obtained in ether and in benzene strengthened our opinion that some such explanation was probably correct.

On the basis of all the evidence we are able to postulate definitely that the steps in the reduction of sulfonyl bromides to disulfides are the following:



Experimental

Preparation of *p*-Toluenesulfinyl Chloride.—*p*-Toluenesulfinyl chloride was made by treating *p*-toluenesulfinic acid with an excess of thionyl chloride according to the method of Hilditch and Smiles.⁸ The material obtained was a liquid at room temperature. The above authors give the melting point as 54–58°.

Reaction between *p*-Toluenesulfinyl Chloride and Phosphorus Tribromide.—(a) Four grams (1 mole) of *p*-toluenesulfinyl chloride and 10 g. (1.5 moles) of phosphorus tribromide were mixed in a 50-cc. flask. The mixture became so hot that free bromine was given off and phosphorus pentabromide sublimed on the neck of the flask. When the reaction mixture became cool it was dissolved in 30 cc. of ether and water was added to hydrolyze the halides of phosphorus. The ether layer was separated, washed with sodium carbonate solution and dried. The ether was evaporated and the residual red oil allowed to solidify. This gave 1.5 g. (54% of the theoretical quantity) of crude *p*-

⁸ Ref. 4, p. 4114.

toluene disulfide. This was crystallized from alcohol and gave a colorless product of m. p. 44–45°. *p*-Toluene disulfide melts at 46°.⁹

Anal. Subs., 0.1190: BaSO₄ (Carius) 0.2308. Calcd. for C₁₄H₁₄S₂: S, 26.06. Found: S, 26.62.

Reaction between *p*-Toluenesulfonyl Bromide and Phosphorus Tribromide.—Three grams (1 mole) of *p*-toluenesulfonyl bromide¹⁰ was heated with 8.7 g. (2.5 moles) of phosphorus tribromide at 80–90° for twenty minutes. The *p*-toluene disulfide was isolated as in the previous experiment, and weighed 0.9 g. (56% of the theoretical). The recrystallized disulfide melted at 44–45°, and showed no depression when mixed with a sample prepared as in the previous experiment.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether.—One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 20 cc. of dry ether. To this 2.8 g. of phosphorus tribromide was added. The flask was stoppered and allowed to stand for five days. After several hours the solution became cloudy and in about eight hours a precipitate began to separate. This was filtered off after twenty-four hours and washed with benzene to remove a small amount of a green amorphous material. The disulfide weighed 0.05 g. (15%), m. p. 193–194°; mixed melting point with known *o*-nitrophenyl disulfide, 193–194.5°. The known disulfide melted at 195°. In a check experiment a yield of 5% of the disulfide was obtained.

The Action of Phosphorus Pentabromide on *o*-Nitrophenyl Disulfide in Dry Ether.—In a flask were placed 2 g. (1 mole) of *o*-nitrophenyl disulfide, 7 g. (3 moles) of phosphorus pentabromide and 50 cc. of dry ether. The *o*-nitrophenyl disulfide dissolved completely after about two hours. The ether solution was decanted from a small amount of a heavy red oil and evaporated at reduced pressure until a precipitate started to form. It was then treated with 50 cc. of ligroin and stirred until the precipitate was pale yellow. The solution was filtered and the precipitate washed several times with petroleum ether and dried. There resulted 1.2 g. (40%) of *o*-nitrophenyl sulfur bromide. The product melted at 78–81° after crystallization from benzene. Mixed with known *o*-nitrophenyl sulfur bromide it melted at 78–83°. The known product melted at 83–84°.

Attempt to Prepare Tribromophenyl Sulfur Bromide from Hexabromodiphenyl Disulfide and Bromine.—2.7 g. of hexabromodiphenyl disulfide was suspended in a mixture of 20 cc. of carbon tetrachloride and 4 cc. of bromine. The disulfide dissolved slowly and after twelve hours was all in solution. The carbon tetrachloride was evaporated in a vacuum desiccator. The solid which remained melted at 215–217°. The original disulfide melted at 215–217°; mixed m. p. 215–217°.

Preparation of *o*-Nitrophenylsulfonyl Bromide.—This compound was prepared by a modification of the process of Zincke and Farr⁷ for the preparation of sulfonyl chlorides.

Fifteen grams of *o*-nitrophenyl disulfide was suspended in 100 cc. of glacial acetic acid. To this was added 20 cc. of bromine dissolved in 100 cc. of glacial acetic acid. The mixture was heated at 50–60° until the disulfide dissolved. Water was added slowly until the total volume of the solution was about 500 cc. If the first addition of water caused a yellow bulky precipitate to form, it was necessary to heat the reaction mixture until this redissolved. The crude sulfonyl bromide which separated as a pink or colorless precipitate was filtered off, washed with water and dissolved in a small amount of ether without drying. The water was separated from the ether solution and after concentrating the ether to a volume of 35 cc. the sulfonyl bromide was precipitated by adding ligroin. The sulfonyl bromide was filtered off, washed once with ligroin and dried. The yield was 20 g. (79%); m. p. 62.5–63.5°. Recrystallized once from equal parts of benzene and benzine, a colorless product was obtained, m. p. 63–64° (uncorr.).

⁹ *J. prakt. Chem.*, [2] 41, 190 (1890).

¹⁰ Otto, *Ann.*, 142, 98 (1867).

Anal. Subs., 0.2488, 0.2215: AgBr (Carius), 0.1766, 0.1560. Calcd. for $C_6H_4O_2NBrS$: Br, 30.04. Found: Br, 30.24, 29.97.

For further identification, the sulfonyl bromide was converted to the sulfonamide by saturating a ligroin-benzene solution with dry ammonia. The amide melted at 190.5–191.5° after recrystallizing from water. *o*-Nitrophenylsulfonamide¹¹ melts at 190–191°.

The Action of Phosphorus Tribromide on *o*-Nitrophenylsulfonyl Bromide.—Three grams (1 mole) of *o*-nitrophenylsulfonyl bromide was placed in a 100-cc. flask fitted with a dropping funnel. The flask was cooled in an ice-bath and 7.6 g. (2.5 moles) of phosphorus tribromide was added slowly through the dropping funnel. The reaction mixture was then agitated with 20 cc. of ligroin until only a flocculent yellow precipitate and a small amount of tarry material on the bottom of the flask remained undissolved. The crude yellow *o*-nitrophenyl sulfur bromide was filtered and the tar extracted with hot benzene. The crude sulfur bromide was crystallized from benzene and gave 1.1 g., m. p. 79–82°; mixed m. p. with known *o*-nitrophenyl sulfur bromide (m. p. 83–84°) was 80–83°.

Anal. Subs., 0.1242, 0.1214: AgBr (Carius), 0.0985, 0.0963. Calcd. for $C_6H_4O_2NBrS$: Br, 34.14. Found: Br, 33.68, 33.75.

The residue which did not dissolve in the benzene in the second crystallization was extracted with the benzene used to extract the original residue in the flask. The solution was filtered and evaporated to a volume of 4 cc. The precipitate which formed on cooling was filtered, washed with dilute sodium hydroxide solution and dried. There was obtained 0.3 g. of crude *o*-nitrophenyl disulfide. It was recrystallized from benzene and melted at 192.5–193.5°. *o*-Nitrophenyl disulfide¹² melts at 195°. Mixed with known disulfide it melted at 193–194°.

If instead of isolating the reaction products as described above, the reaction mixture was dissolved in ether and hydrolyzed by adding water slowly, the products were *o*-nitrothiophenol and *o*-nitrophenyl disulfide. These were separated by extracting with normal sodium hydroxide solution. After filtration the thiophenol was precipitated by adding dilute hydrochloric acid. The crude disulfide was purified by recrystallizing from benzene. The *o*-nitrophenyl disulfide melted at 194–195°. The *o*-nitrothiophenol melted at 54–55°. Mixed with known *o*-nitrothiophenol (m. p. 56–56.5°) it melted at 54–55°.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Disulfide in Ether.—One gram of *o*-nitrophenyl disulfide was suspended in 15 cc. of ether. To this was added 3 cc. of phosphorus tribromide. The phosphorus tribromide was hydrolyzed by adding water slowly without cooling. When 15 cc. of water had been added the mixture was allowed to stand at room temperature until the ether evaporated. The precipitate which resulted was filtered off, washed with water and dried. This gave 0.95 g. of *o*-nitrophenyl disulfide, m. p. 194–195°. The original disulfide melted at the same temperature.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether and in Benzene.—(a) **In ether:** 0.5 g. of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. The solution was diluted with 10 cc. of ether; 10 cc. of water was added to the ether solution drop by drop without cooling, and the mixture was allowed to stand until the ether layer evaporated. The crystals which formed were filtered, washed with cold water and dried. This gave 0.3 g. (93%) of crude *o*-nitrothiophenol; m. p. 49–51°. It was dissolved in normal sodium hydroxide solution,

¹¹ Ekbohm, *Ber.*, **35**, 657 (1902).

¹² Wohlfahrt, *J. prakt. Chem.*, **66**, 553 (1902).

reprecipitated with hydrochloric acid, filtered, washed with water and dried. The purified thiophenol melted at 56–56.5°. *o*-Nitrothiophenol¹³ melts at 56°.

Anal. Subs. 0.1415: BaSO₄, 0.2070. Calcd. for C₆H₄O₂NS: S, 20.20. Found: S, 20.09.

(*b*) **In Benzene:** One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. To this 10 cc. of benzene was added. The reaction mixture was hydrolyzed as in part (*a*). The crystals formed were stirred with sodium hydroxide solution, filtered, washed with water and dried. This gave 0.25 g. (92% of theoretical) of *o*-nitrophenyl disulfide; m. p. 192–194°; no depression when mixed with known *o*-nitrophenyldisulfide (m. p. 195°). The sodium hydroxide filtrate was acidified with hydrochloric acid but no *o*-nitrothiophenol separated.

Determination of Freezing Points

***o*-Nitrophenyl Sulfur Bromide in Benzene.**—Sample 0.4995; benzene 17.40; depression 0.600°. Calcd. for C₆H₄O₂NBrS: mol. wt. 234. Found: 239.

Phosphorus Tribromide and *o*-Nitrophenyl Sulfur Bromide in Benzene.—The experiment was carried out in the same way as molecular weight determinations by the cryoscopic method. The phosphorus tribromide was added to the benzene first and the freezing point depression noted. An equivalent weight of *o*-nitrophenyl sulfur bromide was added to this in three portions and the freezing point observed after each addition.

Substance added	Freezing point, °C.
Pure benzene	4.920
0.5920 g. phosphorus tribromide	4.306
0.1280 g. <i>o</i> -nitrophenyl sulfur bromide	4.147
0.3840 g. <i>o</i> -nitrophenyl sulfur bromide	3.835
0.5120 g. <i>o</i> -nitrophenyl sulfur bromide	3.688
Depression due to phosphorus tribromide 0.614°	
Depression due to <i>o</i> -nitrophenyl sulfur bromide 0.618°	

Calcd. mol. wt. of PBr₃: 271. Found: 277. Calcd. mol. wt. of C₆H₄O₂NBrS: 234. Found: 233.

Summary

1. *p*-Toluene-sulfinyl chloride was reduced readily to *p*-toluene disulfide by phosphorus tribromide.
2. *o*-Nitrophenyl sulfur bromide was slowly reduced by phosphorus tribromide to give the corresponding disulfide in poor yield. The presence of phosphorus tribromide increased the yield of disulfide.
3. Phosphorus pentabromide reacted with *o*-nitrophenyl disulfide to give *o*-nitrophenyl sulfur bromide.
4. *o*-Nitrophenyl sulfonyl bromide was reduced to *o*-nitrophenyl sulfur bromide by phosphorus tribromide.
5. The action of water on an ether solution of *o*-nitrophenyl sulfur bromide and phosphorus bromide gave *o*-nitrothiophenol.
6. It is therefore postulated that the course of the reduction of a sulfonyl bromide by phosphorus tribromide is as follows: sulfonyl bromide → sulfinyl bromide → sulfur bromide ⇌ disulfide + Br₂. Sulfur

¹³ Mayer, *Ber.*, **42**, 3059 (1909).

bromide + PBr_3 (in ether) \longrightarrow addition compound \longrightarrow thiophenol (on hydrolysis).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION No. 209 FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE HYDROLYSIS OF LIGNIN WITH 12% HYDROCHLORIC ACID

BY MAX PHILLIPS AND M. J. GOSS

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Hägglund and Björkman¹ and later Hägglund and Rosenqvist² distilled lignin (isolated by the fuming hydrochloric acid method) with 12% hydrochloric acid and obtained a distillate which gave a precipitate with phloroglucinol, barbituric acid and with thiobarbituric acid. The substance present in the distillate was not definitely identified, but was shown to be neither furfural, methylfurfural nor hydroxymethylfurfural.

Freudenberg and Harder³ distilled lignin (isolated from wood by a method similar to that used by Urban⁴) with 12% hydrochloric acid and identified the volatile hydrolytic product as formaldehyde. In a subsequent paper, Freudenberg, Harder and Markert⁵ advanced the hypothesis that the formaldehyde arises from a methylene dioxide group ($-\text{O}-\text{CH}_2-\text{O}-$) present in the lignin molecule, as compounds containing the methylene dioxide group are known to yield formaldehyde when they are distilled with hydrochloric acid. However, this interpretation of the reaction involved has been questioned by Fuchs and Horn.⁶ They distilled with hydrochloric acid lignin, acetylated lignin and two oxidized acetylated lignin preparations and found that lignin itself gave a greater yield of formaldehyde-barbituric acid condensation product than the other three modified lignin preparations.

The present investigation was undertaken for the purpose of determining (1) whether lignin isolated from materials other than wood gives formaldehyde when distilled with 12% hydrochloric acid, and (2) whether the method employed for the isolation of the lignin has any effect on the formaldehyde-yielding component presumably present in lignin.

Experimental

The lignin used in these experiments was isolated from three different sources by the following different methods. The lignin was isolated from corn cobs by the alco-

¹ Hägglund and Björkman, *Biochem. Z.*, **147**, 74 (1924).

² Hägglund and Rosenqvist, *ibid.*, **179**, 376 (1926).

³ Freudenberg and Harder, *Ber.*, **60**, 581 (1927).

⁴ Urban, *Cellulosechem.*, **7**, 73 (1926).

⁵ Freudenberg, Harder and Markert, *Ber.*, **61**, 1760 (1928).

⁶ Fuchs and Horn, *Ber.*, **62**, 2647 (1929).