

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

## REDUCTION OF ALIPHATIC SULFONIC ACID SALTS WITH PHOSPHORUS PENTABROMIDE AND PHOSPHORUS TRIBROMIDE<sup>1</sup>

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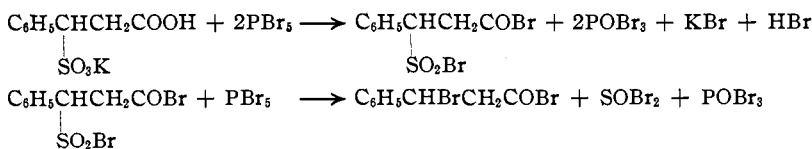
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In an attempt to prepare tribromobenzene sulfonyl bromide from the sodium salt of the sulfonic acid and phosphorus pentabromide, it was found that the reaction took a different course from that anticipated. Instead of the expected sulfonyl bromide, hexabromodiphenyl disulfide<sup>2</sup> was obtained. Further investigation showed that this reaction was quite general for salts of aromatic sulfonic acids.

The present work is an extension of this investigation to include the salts of the aliphatic sulfonic acids.

The sodium or potassium salts of methyl-, ethyl-, butyl-, isoamyl and benzylsulfonic acids, and the potassium salt of  $\beta$ -sulfo- $\beta$ -phenylpropionic acid were prepared and treated with phosphorus bromides. In general this was carried out as follows: one mole of the salt was treated with one mole of phosphorus pentabromide (to form the sulfonyl bromide) and the reaction mixture was then further treated with two and one-half moles of phosphorus tribromide to bring about the reduction. In some cases this procedure was varied by allowing phosphorus pentabromide alone to react upon the sulfonate, and in one case the sulfonyl bromide was isolated and treated with phosphorus tribromide.

All the salts mentioned gave the corresponding disulfides when treated with *mixed* phosphorus bromides, except  $\beta$ -potassium sulfo- $\beta$ -phenylpropionic acid, which gave  $\beta$ -bromo- $\beta$ -phenylpropionic acid by the replacement of the SO<sub>3</sub>K group by bromine as represented in the equations



This is similar to the action of phosphorus pentachloride on sulfonyl chlorides,<sup>3</sup> except that it takes place at a lower temperature.

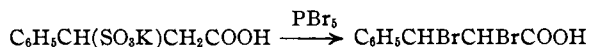
When phosphorus pentabromide was used alone, in sufficient quantities to cause reduction to occur, according to the reaction postulated in the

<sup>1</sup> The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by B. E. Sorenson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

<sup>2</sup> Kohlhase, THIS JOURNAL, 54, 2441 (1932).

<sup>3</sup> Carius, *Ann.*, 114, 142 (1860); Barbaglia and Kekulé, *Ber.*, 5, 876 (1872).

first paper of this series,<sup>2</sup> the product isolated was usually the disulfide, but in some cases the sulfonyl bromide or the alkyl bromide resulted. Substitution of hydrogen by bromine also took place in several cases. Thus,  $\beta$ -potassium sulfo- $\beta$ -phenylpropionic acid gave  $\alpha,\beta$ -dibromophenylpropionic acid.



The results are summarized in Table I.

TABLE I  
RESULTS OBTAINED BY REDUCING VARIOUS ALIPHATIC SULFONATES AND SULFONYL BROMIDES WITH PHOSPHORUS BROMIDES

Reactant	Reagent	Product	Yield, %
$\text{CH}_3\text{SO}_3\text{K}$	$\text{PBr}_5 + \text{PBr}_3$	$(\text{CH}_3)_2\text{S}_2$	26
$\text{C}_2\text{H}_5\text{SO}_3\text{K}$	$\text{PBr}_5 + \text{PBr}_3$	$(\text{C}_2\text{H}_5)_2\text{S}_2$	54
$\text{C}_2\text{H}_5\text{SO}_3\text{K}$	$\text{PBr}_5$	$\text{C}_2\text{H}_5\text{SO}_2\text{Br}$	41
<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_3\text{K}$	$\text{PBr}_5$ (1 mole)	<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_2\text{Br}$	66
<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_3\text{K}$	$\text{PBr}_5$ (3.5 moles)	$(n\text{-C}_4\text{H}_9)_2\text{S}_2$	49
<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_3\text{K}$	$\text{PBr}_5 + \text{PBr}_3$	$(n\text{-C}_4\text{H}_9)_2\text{S}_2$	52
<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_2\text{Br}$	$\text{PBr}_3$	$(n\text{-C}_4\text{H}_9)_2\text{S}_2$	63
<i>iso</i> - $\text{C}_5\text{H}_{11}\text{SO}_3\text{Na}$	$\text{PBr}_5 + \text{PBr}_3$	$(iso\text{-C}_5\text{H}_{11})_2\text{S}_2$	55
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na}$	$\text{PBr}_5 + \text{PBr}_3$	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}_2$	87
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na}$	$\text{PBr}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	70
$\text{C}_6\text{H}_5\text{CH}(\text{CO}_3\text{K})\text{CH}_2\text{COOH}$	$\text{PBr}_5 + \text{PBr}_3$	$\text{C}_6\text{H}_5\text{CHBrCH}_2\text{COOH}$	80
$\text{C}_6\text{H}_5\text{CH}(\text{SO}_3\text{K})\text{CH}_2\text{COOH}$	$\text{PBr}_5$	$\text{C}_6\text{H}_5\text{CHBrCHBrCOOH}$	62

### Experimental Part

**Potassium Alkyl Sulfonates.**—These were made by oxidizing the corresponding alkyl thiocyanates with nitric acid (sp. gr. 1.42).<sup>4</sup> The reaction mixtures were neutralized with potassium carbonate and evaporated to dryness. The crude potassium alkyl sulfonates so obtained were purified by recrystallizing from 95% alcohol.

TABLE II  
PROPERTIES OF POTASSIUM ALKYL SULFONATES

Sulfonate	Yield, %	K	Calcd.	Analyses, %			Found	S
				S	K			
Methyl	90							
Ethyl	80							
<i>n</i> -Butyl	70	22.19		18.21	22.05	22.06	18.55	18.42
Isoamyl <sup>a</sup>	41	13.22 (Na)		18.41	13.19	13.10	18.78	18.90

<sup>a</sup> The sodium salt was made by oxidizing 50 g. of isoamyl disulfide with 20 cc. of nitric acid (sp. gr. 1.42).

**Alkyl Sulfonyl Bromides.**—One-tenth mole of potassium alkyl sulfonate and 0.35 mole of phosphorus pentabromide were heated for forty minutes at 70–80°, poured into 400 g. of crushed ice and stirred continuously until about 60 cc. of clear liquid remained undissolved. The lower layer was separated and shaken in a separatory funnel with 200 g. of ice for two minutes. The lower layer was separated, dried with calcium chloride and fractionated.

<sup>4</sup> Muspratt, *Ann.*, **65**, 261 (1848).

TABLE III  
 PROPERTIES OF ALKYL SULFONYL BROMIDES

Sulfonyl bromide	Yield, %	Boiling point, °C.	$d_4^{25}$	Analyses, %		S	Found, S	Br	M. p. of sulfonamide, °C.
				Calcd. S	Br				
Ethyl <sup>a</sup>	41	103–106 (40 mm.) <sup>b</sup>		18.50		20.44	20.30		57–58
<i>n</i> -Butyl	66	101–102 (11 mm.)	1.5109	15.94	39.75	15.58	15.51	40.03	39.93

<sup>a</sup> *J. prakt. Chem.*, [2] **26**, 384 (1880).

<sup>b</sup> Cherbuliez and Schnauder [*Helv. Chim. Acta*, **6**, 249 (1923)] give 80° (13 mm.).

**Alkyl Disulfides.**—One-third mole of finely ground potassium alkyl sulfonate was mixed with 0.33 mole of phosphorus pentabromide, after which the reaction flask was fitted with a calcium chloride tube and heated on a steam-bath for fifteen minutes. After cooling to 80°, 0.8 mole of phosphorus tribromide was added and the temperature maintained at 70–80° for forty minutes. The red reaction mixture was transferred to a 1-liter flask, cooled in an ice-bath and dissolved in 250 cc. of ether. The halides of phosphorus were hydrolyzed by adding water slowly until the ether formed a separate layer, and then the solution was steam distilled. The ether layer of the distillate was separated, washed once with water, then with 5% sodium carbonate solution and finally with water. After drying with calcium chloride, it was filtered and fractionated, using a Clarke flask with column attached.

 TABLE IV  
 PROPERTIES OF ALKYL DISULFIDES

Disulfide	Yield, %	Boiling point, °C.	$d_4^{20}$	Calcd.	Sulfur Found	Analyses	
						AgNO <sub>3</sub> double salt Ag, calcd.	Ag, found
Methyl	26	108–108.5 (748 mm.) <sup>a</sup>	1.0606 (16°)	68.08	68.54	68.43	40.87 40.69 40.84
Ethyl	54	151–152 (736 mm.) <sup>b</sup>	0.9981 (20°) <sup>b</sup>	52.47	52.96	52.89	38.95 37.01 36.88
<i>n</i> -Butyl <sup>c</sup>	52	227–229 (735 mm.)	.9327 (25°)	35.95	36.63	36.57	
Isoamyl	55	123.5–124 (12 mm.)	.9188 (18°) <sup>d</sup>	31.08	31.73	31.68	
Benzyl	87	(m. p. 70–71.5°) <sup>e</sup>		26.06	26.87	26.75	

<sup>a</sup> Pierre [*Ann.*, **80**, 128 (1830)] gives 112.1 (744 mm.). <sup>b</sup> Wasini [*Ber.*, **15**, 2882 (1882)] gives b. p. 152.8–153.4° (corr.);  $d_4^{20}$  0.9927. <sup>c</sup> Phosphorus pentabromide alone gave 49%, b. p. 224–233°. Phosphorus tribromide alone gave 63%. <sup>d</sup> Henry [*Jahresb.*, **48**, 699 (1847)] gives  $d_4^{18}$  0.918. <sup>e</sup> Hofmann [*Ber.*, **20**, 15 (1887)] gives 71–72°.

**Preparation of *n*-Butyl Disulfide by a Known Method.**—Since *n*-butyl disulfide was not described in the literature, it was made by refluxing an alcoholic solution of sodium disulfide with *n*-butyl chloride. The alcohol and excess butyl chloride were distilled off at atmospheric pressure and enough water added to dissolve the sodium chloride. The oily upper layer was separated, dried and fractionated at reduced pressure. *n*-Butyl disulfide was water white and had the following properties: b. p. 93–94° (7 mm.) or 226–229° (740 mm.),  $d_4^{25}$  0.9329.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>S<sub>2</sub>: S, 35.95. Found: S, 36.64, 36.50.

*n*-Butyl trisulfide, the by-product, was pale yellow and had the following properties: b. p. 119–121° (6 mm.) and  $d_4^{25}$  1.0117.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>S<sub>3</sub>: S, 45.73. Found: S, 46.50, 46.62.

**Preparation of Benzyl Bromide from Sodium Benzyl Sulfonate.**—Benzyl bromide was obtained in 70% yield when fifteen grams of sodium benzyl sulfonate and 93 g. of phosphorus pentabromide were heated at 85–90° for fifteen minutes. The mixture,

which fused and gave off hydrogen bromide, was dissolved in 100 cc. of ether, and water was added until the ether layer separated. The ether solution was separated, washed once with water and dried with calcium chloride. After evaporating the ether, the residual liquid was fractionated at 18 mm., and redistilled at atmospheric pressure; b. p. 195–197° (740 mm.).

*Anal.* Calcd. for  $C_7H_7Br$ : Br, 46.73. Found: Br, 48.64, 48.33.

**Preparation of  $\beta$ -Bromo- $\beta$ -phenylpropionic Acid.**—Eighteen grams of  $\beta$ -potassium sulfo- $\beta$ -phenylpropionic acid (made from cinnamic acid and potassium sulfite by the method of Valet [*Ann.*, 154, 63 (1870)] and purified by washing with benzene and recrystallizing from alcohol), 58 g. of phosphorus pentabromide and 45 g. of phosphorus tribromide were heated at 85–90° with occasional shaking until the phosphorus pentabromide was dissolved. The reaction mixture was cooled and dissolved in 125 cc. of ether. The ether solution was treated with water to hydrolyze the phosphorus bromides, dried, filtered and evaporated to dryness. This gave 12 g. (80%) of crude gray  $\beta$ -bromo- $\beta$ -phenylpropionic acid, which was crystallized twice from benzene to give a colorless material, m. p. 135–137°. An authentic sample of  $\beta$ -bromo- $\beta$ -phenylpropionic acid melted at 137°; mixed m. p. 135.5–137°.<sup>5</sup>

**Preparation of  $\alpha,\beta$ -Dibromo- $\beta$ -phenylpropionic Acid.**—Nineteen grams of  $\beta$ -potassium sulfo- $\beta$ -phenylpropionic acid and 125 g. of phosphorus pentabromide were mixed and heated at 100° until the evolution of hydrogen bromide ceased (about one hour). The reaction product was isolated in the same way as the  $\beta$ -bromo- $\beta$ -phenylpropionic acid. The crude product was crystallized once from benzene, giving 13.2 g. (62%) of  $\alpha,\beta$ -dibromo- $\beta$ -phenylpropionic acid, m. p. 188–195° (with decomposition). It was recrystallized and melted at 197° (when heated rapidly near the melting point).<sup>6</sup>

*Anal.* Calcd. for  $C_9H_9O_2Br_2$ : Br, 51.94. Found: Br, 51.60, 51.80.

### Summary

1. Several salts of aliphatic sulfonic acids were reduced to the corresponding disulfides with a mixture of phosphorus pentabromide and phosphorus tribromide.
2. Phosphorus pentabromide alone gave the same disulfides in some cases. In other cases the sulfonic acid group was replaced by bromine.
3. The sulfonyl bromide group is more easily replaced by bromine (by means of phosphorus pentabromide) when attached to an aliphatic radical than when attached to an aromatic nucleus.
4. The presence of a phenyl radical on the carbon holding the sulfonyl bromide group facilitates the replacement of the latter by bromine.

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<sup>5</sup> Bodwig, *Ber.*, 12, 538 (1874).

<sup>6</sup> Sudborough and Thompson [*J. Chem. Soc.*, 83, 670 (1903)] give the melting point as 197° (when heated rapidly).