

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

A NEW REDUCTION OF ARYL SULFONIC ACID SALTS AND DERIVATIVES. PHOSPHORUS PENTABROMIDE AS A REDUCING AGENT¹

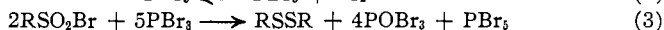
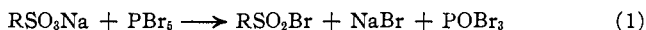
BY ARTHUR H. KOHLHASE²

RECEIVED JANUARY 15, 1932

PUBLISHED JUNE 6, 1932

By the action of a strong aqueous solution of bromine and potassium bromide upon the sodium salt of 2,4,6-tribromothiophenol,³ a new compound, tribromobenzenesulfonyl bromide, was obtained. We sought, for purposes of identification, to prepare this compound by heating potassium 2,4,6-tribromobenzenesulfonate with phosphorus pentabromide. However, the only product obtained was 2,4,6,2',4',6'-hexabromodiphenyl disulfide. This efficient reduction by pentavalent phosphorus was very puzzling, and led to the investigation described in this paper.

The following equations are now believed to represent the course of the reaction



The relative speeds of reactions (1) and (3) should be dependent on the nature of the aryl radical, R, and it was found that by varying R the reaction could be made to give almost exclusively the sulfonyl bromide, or varying proportions of the sulfonyl bromide and disulfide, or only the disulfide.

This mechanism would lead one to expect that the intermediate sulfonyl bromide would be reduced by phosphorus pentabromide and, more readily, by phosphorus tribromide. Furthermore, in those cases where no RSO_2Br could be found in the final reaction product it would be expected that the sulfonyl bromide would be rapidly reduced by phosphorus tribromide. As shown in Table I, the results fully confirmed this theory.

That *phosphorus pentabromide is essential for the first step* in the production of disulfides from sulfonic acid salts as indicated in reaction (1) was shown by heating some of the sodium sulfonate with phosphorus tribromide; neither the disulfide nor the sulfonyl bromide was formed in detectable amounts.

It is well known that phosphorus pentabromide dissociates very readily⁴

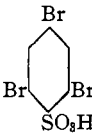
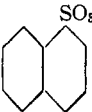
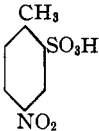
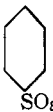

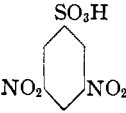
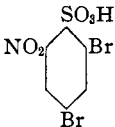
¹ This article is based upon Part I of a thesis presented by Arthur H. Kohlhasé to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1924. The work was carried out under the direction of the late Professor W. H. Hunter.—L. I. SMITH.

² Present address, 1114 North First St., Phoenix, Arizona.

³ Hunter and Kohlhasé, *THIS JOURNAL*, 54, 2425 (1932).

⁴ Kastle and Beatty, *Am. Chem. J.*, 21, 392-398 (1899).

TABLE I

Sulfonic acid	Derivative ^a	Reducing agent	Time of heating, min.	Products ^a	Yield, ^c %
	ASO ₃ Na ^e	PBr ₅ ^b	5-10	ASSA	86.5
	ASO ₃ Na	PBr ₅	5-10	ASSA	9-35.7
	ASO ₃ Na	PBr ₃	10	..	0
	ASO ₂ Br	PBr ₃	0	ASSA	91.5
	ASO ₂ Br	PBr ₅	25	ASSA	60.6
	ASO ₃ Na	PCl ₅	20	ASO ₂ Cl, ASSA	97 0
	ASO ₂ Br	PCl ₃	10	..	0
	ASO ₂ Cl	PBr ₃	25	ASSA	34
	BSO ₂ Cl	PBr ₃	25	..	0
	BSO ₂ Br	PBr ₃	15	BSSB BSH	28.7 19.5
	CSO ₂ Cl	PBr ₃	30	CSSC ^e	85.7
	DSO ₃ Na	PBr ₅	30	DSO ₂ Br DSSD	45 3
	DSO ₃ Na	PBr ₅ + PBr ₃	15	DSO ₂ Br DSSD	Ca. 20 Ca. 40
	ESO ₃ Na	PBr ₅	70	ESO ₂ Br, ESSE	Ca. 25 27.4
	ESO ₃ Na	PBr ₅ + PBr ₃	70	ESO ₂ Br, ESSE	0 57
	FSO ₃ Na (FSO ₃) ₂ Ba	PBr ₅ PCl ₅	40 40	.. FSO ₂ Cl	0 84
	FSO ₂ Cl	PBr ₃	40	FSSF ^e	Ca. 60
	FSO ₂ SC ₆ H ₅ ^e	PBr ₃	0	FSH ^e (FSSF) ^e	Ca. 85-95
	GSO ₃ Na	PBr ₅ at 100°	20	?	1-3
	GSO ₃ Na	PBr ₅ at 150°	60	(?) ^d	

^a The letters A, B, C, etc., used in these columns stand for the aryl radical of the parent sulfonic acids shown in the first column.

^b This was a comparatively crude phosphorus pentabromide prepared in carbon bisulfide; all the remaining experiments were carried out with pure phosphorus bromides or chlorides prepared in carbon tetrachloride.

^c The yield depended to a large extent upon keeping the products thoroughly mixed and also on the rate of heating.

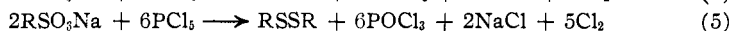
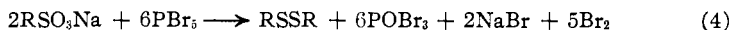
^d Reaction evidently occurred but the products could not be identified.

^e A new compound.

according to reaction (2) and that the pentachloride behaves similarly at somewhat higher temperatures. However, when sodium 2,4,6-tribromobenzenesulfonate was treated with phosphorus pentachloride, it gave a 97% yield of the sulfonyl chloride and no detectable quantity of hexabromodiphenyl disulfide.⁵

Even when the sulfonyl bromide was prepared and then heated with phosphorus trichloride, there was no reduction, in marked contrast to the action of the tribromide. As illustrated in Table I by the sulfonyl bromides and chlorides of tribromobenzene and naphthalene, the substitution of chlorine for bromine in the sulfonyl halide also results in an increased resistance to reduction by phosphorus tribromide.

Reactions (1) and (3) may be combined



By subtracting these two equations, taking account of the heats of formation of each substance,⁶ we obtain the interesting result that reaction (5) is the more exothermic, in the case of *all* sulfonic acids, by 34,000 cal. Yet reaction (5) does not take place at all while reaction (4) proceeds with varying ease, depending on the nature of R. Very similar results are obtained in the case of reaction (3) and its analog.

It is significant that, although the oxidations of the tribromide and trichloride of phosphorus occur with nearly the same heats of reaction, there is other evidence that the tribromide is oxidized far more *readily*.⁷

One disulfoxide (phenyl-3,5-dinitrobenzene thiosulfonate) was treated with phosphorus tribromide, and reacted with surprising ease to give 3,5-dinitrothiophenol. The 3,5-dinitrodiphenyl disulfide would have been expected but it has been shown⁸ that such unsymmetrical disulfides tend to rearrange to the symmetrical ones.

The production of 3,5-dinitrothiophenol instead of the corresponding disulfide was observed also in the case of α -naphthalenesulfonyl bromide. The final stage of the reduction is probably due to phosphorous acid. Some of these sulfonates have previously been treated with phosphorus pentabromide but the reductions here described were apparently not observed.⁹

This new method is very convenient for the preparation of disulfides which would otherwise be difficult to synthesize, even by the method of

⁵ Reinke, *Ann.*, **186**, 271 (1877); Knuth, *ibid.*, **186**, 284 (1877).

⁶ The data used were taken from Gmelin-Kraut, "Handbuch der anorg. Chemie," and are due to Thomsen, Berthelot and Ogier.

⁷ Demole, *Ber.*, **13**, 1980 (1880); *Jahresb.*, 384 (1880); Michaelis, *ibid.*, 280 (1870).

⁸ Lecher, *Ber.*, **53**, 591 (1920); Smiles and Gibson, *J. Chem. Soc.*, **125**, 176 (1924); but cf. also Smiles and McClelland, *ibid.*, **121**, 86 (1922).

⁹ Limpricht, *Ann.*, **278**, 246 (1894); Forsling, *Ber.*, **22**, 1402 (1899).

Leuckardt.¹⁰ These disulfides may in turn be converted to the corresponding thiophenols by reduction or by treatment with potassium sulfide.¹¹

Experimental Part

I. Preparation of Sodium 2,4,6-Tribromobenzenesulfonate, $C_6H_2Br_3SO_3Na \cdot 1.5H_2O$.—Redistilled 1,3,5-tribromobenzene (one degree boiling range) was sulfonated by the method of Bössmann.¹²

The sodium tribromobenzenesulfonate obtained was recrystallized from the minimum amount of boiling water. It formed pure white flakes, readily soluble in hot water, only slightly soluble in cold. The sodium salt has not been previously described.

Anal. Calcd. for $C_6H_2Br_3SO_3Na \cdot 1.5H_2O$: H_2O , 6.08; SO_3 , 19.20; Br, 57.52. Found: H_2O , 6.09; SO_3 , 18.14; Br, 57.25, 57.96.

II. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus Pentabromide.—Two grams of the pure, anhydrous sodium salt was intimately mixed with 6.4 g. of phosphorus pentabromide and gently heated to 80–90° above a small flame with repeated remixing until the reaction started and rapidly spread throughout the mass; then about five minutes longer.

The reaction product was extracted twice with 20 cc. of dry, boiling benzene; these extracts were evaporated to a small volume and cooled. The yield of crystals was increased by diluting the oily mixture of benzene and phosphorus oxybromide with ether. The solvent was poured off and the crystals were washed with ether and then recrystallized from boiling benzene. Pale yellow rhombohedra separated, identical in form, color and solubility with 2,4,6,2',4',6-hexabromodiphenyl disulfide prepared by other methods;³ yield, 13–38%; m. p. 218–218.5°, mixed m. p. 218–218.5°; 40–60% of the original sodium salt was recovered. An 86.5% yield of the disulfide was obtained when crude phosphorus pentabromide was used.

Evaporation of the ether washings left a sirupy oil which proved to be phosphorus oxybromide. No tribromobenzenesulfonyl bromide could be found.

III. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus Tribromide.—Two grams of the anhydrous sodium salt, heated for ten minutes at 90° with 4.0 g. of phosphorus tribromide gave no disulfide, sulfonyl bromide or thiophenol. The mixture left after ether extraction was completely soluble in water. After neutralization and recrystallization 92% of the original sodium salt was recovered.

IV. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Tribromide.—Phosphorus tribromide was added in excess to 1.0 g. of the sulfonyl bromide. The temperature quickly rose to about 175° and the reaction was completed in about two seconds. Ether was added to the cooled mixture which was then carefully treated with 23 cc. of water. The disulfide was recrystallized from benzene; yield, 0.691 g. or 91.5%.

V. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Pentabromide.—An intimate mixture of the reactants was heated for twenty-five minutes at 85–90°. The cooled product was treated with ether and then excess water, causing the separation of disulfide. The ether layer was washed with water and evaporated, leaving the 2,4,6-tribromobenzenesulfonyl bromide; recovery, 17%. The hexabromodiphenyl disulfide was filtered from the water layer, washed with water and ether; yield, 60.6%.

VI. Reaction between Sodium 2,4,6-Tribromobenzenesulfonate and Phosphorus

¹⁰ Leuckardt, *J. prakt. Chem.*, [2] 41, 179–224 (1890).

¹¹ Otto and Rössing, *Ber.*, 19, 3129 (1886).

¹² Bössmann, *Ann.*, 191, 206 (1878).

Pentachloride.—The reaction was carried out as in II and III, with the addition of four drops of phosphorus oxybromide. No disulfide was formed; yield of sulfonyl chloride, 97%.

VII. Reaction between 2,4,6-Tribromobenzenesulfonyl Bromide and Phosphorus Trichloride.—This was carried out as in experiment IV. No reduction occurred.

VIII. Reaction between 2,4,6-Tribromobenzenesulfonyl Chloride and Phosphorus Tribromide.—The reactants when mixed became *colder*. After heating in a bath at 80–85° for twenty-five minutes, the product was isolated as in V; yield of disulfide, 34%. A large portion of the original sulfonyl chloride was recovered unchanged.

IX. Reaction between α -Naphthalenesulfonyl Chloride and Phosphorus Tribromide.—The mixture was treated as in experiment X, but the naphthalenesulfonyl chloride was unchanged.

X. Reaction between α -Naphthalenesulfonyl Bromide and Phosphorus Tribromide.—Two grams of the sulfonyl bromide was warmed at 70° for fifteen minutes with 3.0 g. of phosphorus tribromide; the cooled mixture was dissolved in 15 cc. of ether, filtered and treated dropwise with 5 cc. of water. The sirupy solution, which had begun to deposit crystals, was further diluted until a cloudiness just developed and then cooled to 0°. The crystals were washed with water and dried; yield, 28.7%; m. p. 86.3–88.5°; mixed m. p. 87–88.5°. The known disulfide alone melted at 88–89.5°. ¹³

The filtrate was diluted with excess water, the ether layer was separated and the water was extracted twice with ether. Evaporation of the ether extracts left an oil which was dissolved in ammonia water and oxidized in the air for twelve days, with occasional shaking. The white precipitate was recrystallized from alcohol; m. p. and mixed m. p. proved it to be α -naphthyl disulfide; yield, 19.5%.

Anal. Calcd. for $C_{20}H_{14}S_2$: S, 20.14. Found: S, 20.77.

XI. Reaction between 3-Nitro-6-methylbenzenesulfonyl Chloride and Phosphorus Tribromide.—Four grams of the sulfonyl chloride was heated with 14.4 g. of phosphorus tribromide at 75° for thirty minutes. The cooled mixture was dissolved in 15 cc. of ether. The clear solution was carefully treated with 8.5 cc. of water and cooled to 0°. The small needles, recrystallized from alcohol, melted at 147.3–148°; yield, 2.455 g. or 85.7%.

This disulfide is new. It crystallizes from alcohol in long, silky, white needles. It is soluble with difficulty in hot alcohol, more readily in hot glacial acetic acid, fairly soluble in ether, very soluble in benzene; it is insoluble in cold alkalies or dilute mineral acids. Analysis and its method of synthesis indicated it to be 3,3'-dinitro-6,6'-dimethyl diphenyl disulfide.

Anal. Calcd. for $C_{14}H_{12}O_4N_2S_2$: S, 19.07; N, 8.33; NO_2 , 27.35. Found: S, 19.20, 18.61; N, 8.74; NO_2 (English), ¹⁴ 26.84.

It is worthy of notice that, while the sulfonyl chloride group was reduced, the nitro group was unaffected.

XII. Reaction between Sodium Benzenesulfonate and Phosphorus Pentabromide.—The sodium benzenesulfonate contained 38.7% of sodium chloride; 3.60 g. (equivalent to 2.21 g. of pure sodium benzene sulfonate) was mixed with 30 g. of phosphorus pentabromide and heated at 85–90° for thirty minutes. The cooled mixture was digested twice with absolute ether; 40 cc. of 15% sodium hydroxide was added *slowly* to the ether and then sodium carbonate till nearly neutral. The ether layer was separated and the water layer was extracted twice with ether. The combined extracts were evaporated.

¹³ Schertel, *Ann.*, **132**, 91 (1864), gives m. p. 85°; Leuckardt, *J. prakt. Chem.*, [2] **41**, 217 (1890), gives m. p. 91°.

¹⁴ English, *J. Ind. Eng. Chem.*, **12**, 994 (1920).

The oily, semi-solid residue was digested with 10 cc. of hot, saturated ammonia water for fifteen minutes, diluted with water to 35 cc., heated to 80° and decanted, removing the sulfonyl bromide as the sulfonamide. A few drops of oil were left.

The sulfonamide solution was evaporated to 25 cc. and cooled, depositing 0.90 g., 47% of the sulfonamide.

The few drops of oil left after the extraction with ammonia water were extracted with ether; the ether was evaporated and the residue was boiled with 1.5 cc. of alcohol and decanted. A small amount of oil separated from the cooled alcohol. The alcohol was poured off and cooled in an ice-bath, depositing a few white needles. Recrystallized from 0.6 cc. of alcohol, these melted at 58–59°; mixed m. p. with known diphenyl disulfide, 58–60°; yield, 0.04 g. or 3%.

XIII. Reaction between Sodium Benzenesulfonate and Phosphorus Pentabromide and Tribromide.—The sodium benzenesulfonate, 3.60 g., containing 1.39 g. of sodium chloride, was heated with 20 g. of phosphorus pentabromide and 13.5 g. of the tribromide for fifteen minutes at 85–90°. The products were isolated substantially as in experiment XII: approximately 20 and 40% yields of the sulfonyl bromide and diphenyl disulfide, respectively; m. p. of disulfide 59.5–61.5°; mixed m. p. showed no depression.

Anal. Calcd. for $C_6H_5SSC_6H_5$: S, 29.38. Found: S, 29.99.

XIV. Reaction between Sodium *m*-Nitrobenzenesulfonate and Phosphorus Pentabromide.—The sulfonate used contained 4.2% sodium carbonate and 59.7% of sodium sulfate. This mixture, 4.5 g., was heated with 29 g. of phosphorus pentabromide at 85–100° for seventy minutes. Isolation of the products as in experiment XII gave about a 25% yield of the sulfonyl bromide (determined as the sulfonamide, m. p. 160.5–162.5°)¹⁵ and 0.30 g. or 27.4% yield of 3,3'-dinitrodiphenyl disulfide; m. p. 82–83°, recrystallized from ether.¹⁶

Anal. Calcd. for $C_6H_4NO_2SSC_6H_4NO_2$: S, 20.80. Found: S, 20.51, 21.44.

XV. Reaction between Sodium *m*-Nitrobenzenesulfonate and Phosphorus Pentabromide and Tribromide.—Four and five-tenths grams of the impure sodium salt (see XIV) was heated with 10 g. of phosphorus pentabromide and 14 g. of tribromide at 85–90° for seventy minutes. No sulfonyl bromide was found. The recrystallized disulfide melted at 81.2–82.2°; yield, 0.64 g. or 57.6%.

XVI. Reaction between 3,5-Dinitrobenzenesulfonyl Chloride and Phosphorus Tribromide.—Sodium 3,5-dinitrobenzenesulfonate could not be induced to react with phosphorus pentabromide. Accordingly, 2.00 g. of the sulfonyl chloride was heated with 2.5 cc. of phosphorus tribromide at 100–110° for forty minutes.

Treatment with ether and water, as in previous experiments, caused the separation of unchanged sulfonyl chloride. The filtrate was diluted with water until about to form two layers and cooled to 0°, giving 60% of the calculated quantity of 3,5,3',5'-tetranitrodiphenyl disulfide, a new substance.

Anal. Calcd. for $C_6H_3(NO_2)_2SSC_6H_3(NO_2)_2$: S, 16.10. Found: S, 15.99.

This disulfide crystallizes from benzene on careful dilution with ligroin or ether in small pale yellow crystals, m. p. 175–177.5°. It is about as soluble in cold as in hot solvents, quite soluble in chloroform, fairly soluble in glacial acetic acid, very slightly soluble in ether, ligroin, or alcohol. Heated well above the melting point, it puffs and chars.

Preparation of Phenyl 3,5-Dinitrobenzenethiosulfonate, and Unsymmetrical Disulfoxide.—One mole of 3,5-dinitrobenzenesulfonyl chloride dissolved in benzene was added slowly to a suspension of two moles of anhydrous sodium thiophenolate in benzene. The mixture was thoroughly digested and then stoppered tightly for one hour.

¹⁵ Limpricht, *Ann.*, 177, 71 (1875), gives m. p. 161°.

¹⁶ Cleve, *Ber.*, 20, 1534 (1887), gives m. p. 83°.

The solids were filtered off, washed with benzene, again suspended in benzene and treated with a benzene solution of bromine until the bromine color persisted. The solution was filtered and evaporated *in vacuo* at 105° to an oily residue which was then exposed on a watch glass, finally giving a partially crystalline mass consisting of two substances: A, exceedingly soluble (not identified but probably diphenyl disulfide), and B, slightly soluble in ether.

Substance A was separated by ether and B was recrystallized twice from benzene and once from alcohol. It was phenyl 3,5-dinitrobenzenethiosulfonate, a new compound. It crystallizes from alcohol as pale yellow needles, m. p. 139–141°. It is very soluble in benzene, fairly soluble in hot alcohol, slightly soluble in ether. The disulfoxide group is very readily reduced by phosphorus tribromide.

Anal. Calcd. for $C_6H_5(NO_2)_2SO_2SC_6H_5$: S, 18.84. Found: S, 19.43.

This disulfoxide gives sodium thiophenolate and sodium dinitrobenzenethiosulfonate when treated with sodium sulfide.¹⁷ The thiophenolate was identified as the disulfide, m. p. 59–60°, mixed m. p. 60.5–61.5°. This proved the presence of a C_6H_5S -group in the disulfoxide. The presence of a $C_6H_5(NO_2)_2SO_2$ -group was shown by experiment XVII.

XVII. Reaction between Phenyl 3,5-Dinitrobenzenethiosulfonate and Phosphorus Tribromide.—To 0.95 g. of phenyl 3,5-dinitrobenzenethiosulfonate was added 1 cc. of cold phosphorus tribromide. The temperature quickly rose to the boiling point and in about two seconds the reaction was over; 15 cc. of ether was added to the cooled mixture and then 40 cc. of water.

The water layer was neutralized with sodium carbonate, then 4 cc. of ammonia water was added and the mixture was allowed to oxidize in the air. The brown, tarry precipitate formed during the first twenty-four hours was discarded. The succeeding precipitate was filtered after one week and recrystallized from benzene and ligroin. It was shown to be 3,5,3',5'-tetranitrodiphenyl disulfide (see experiment XVI), m. p. 175–177.5°; yield, 85–95%.

Preparation of 2,4-Dibromo-6-nitrobenzenesulfonic Acid.—Blanksma's preparation of the corresponding disulfide by the use of sodium disulfide¹⁸ suggested that this sulfonic acid might be prepared by the interaction of sodium sulfite and 1,2-dinitro-3,5-dibromobenzene.¹⁹

Ten grams of dinitrodibromobenzene was dissolved in 100 cc. of hot 95% alcohol. To this was added 4.63 g. (20% excess) of sodium sulfite dissolved in 90 cc. of water and 50 cc. of alcohol. The mixture was refluxed for three and one-half hours, after which the alcohol was distilled off.

One cc. of 98% sulfuric acid was added and a rapid current of air was passed through the solution at 80° for ten minutes to expel sulfur dioxide and oxides of nitrogen. The cooled solution was extracted twice with ether and then neutralized with sodium carbonate and evaporated to dryness. The residue was extracted three times with 95% alcohol. The combined alcohol extracts were evaporated to 8 cc. and diluted with 35 cc. of ether. The sodium salt of the sulfonic acid separated and was filtered off and washed with ether; yield, 7.0 g. A second crop was isolated from the filtrate and washings; total yield, 8 g. or 70%.

Summary

1. Aryl sulfonic acid salts, when heated with phosphorus pentabromide, are converted to the corresponding aryl sulfonyl bromides and diaryl disulfides.

¹⁷ Otto, *Ber.*, 15, 131 (1882); 19, 1239 (1886); 24, 713 (1891).

¹⁸ Blanksma, *Rec. trav. chim.*, 27, 46 (1908).

¹⁹ Cf. Willgerodt, *J. prakt. Chem.*, [2] 32, 117 (1885).

2. The relative yields of sulfonyl bromide and di-aryl disulfide depend upon the nature of the aryl radical; in some cases the disulfide is the only product; in other cases it is formed in very small amounts.

3. In these reactions the sulfonyl bromide is formed first. It is subsequently reduced by the phosphorus tribromide, simultaneously formed by the dissociation of phosphorus pentabromide. The sulfonic acid salts are unaffected by phosphorus tribromide alone.

4. Aryl sulfonyl bromides are readily reduced by phosphorus tribromide; sulfonyl chlorides are reduced with much greater difficulty by the same reagent. Neither the sulfonyl chlorides nor bromides are reduced by phosphorus trichloride.

5. By the use of the bromides of phosphorus certain disulfides, otherwise difficult or impossible to prepare, are readily obtained.

6. One disulfoxide was investigated. It was reduced with extraordinary ease by phosphorus tribromide.

7. In some cases where the reaction products, containing excess phosphorus tribromide, were decomposed with water and ether, the sulfonyl compounds were reduced to the thiophenols.

8. Addition of bromine to an apparently incompletely reacted mixture in the course of an Otto synthesis of a sulfinate gave a new mixed disulfoxide.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE MACKAY CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA]

ESSENTIAL OIL IN DESERT PLANTS. II. EXAMINATION OF THE OIL OF *CHRYSOTHAMNUS NAUSEOSUS*

By MAXWELL ADAMS AND LEWIS KEHOE

RECEIVED JANUARY 18, 1932

PUBLISHED JUNE 6, 1932

In a former article by one of us¹ attention has been called to the occurrence and physical properties of the essential oil of *Chrysothamnus Nauseosus*. Coulter and Nelson² list eighteen species and four additional varieties of *Chrysothamnus* growing in the arid plateau region of the United States. This entire group of shrubs is known to the western stock men as "Fall Rabbit Brush." Some attention was called to this plant by the work of Hall,³ who found considerable quantities of rubber in the stems of this shrub. In our former work we collected small samples of oil from carefully selected plants of the following varieties of *Chrysothamnus*: *nauseosus*,

¹ Adams, THIS JOURNAL, 49, 2895 (1927).

² Coulter and Nelson, "Manual of Botany of the Central Rocky Mountain Region," page 494.

³ Harvey M. Hall and Thos. H. Goodspeed, University of California publications in Botany.