phenetole. It enhances the rate of reduction of methyl ethyl ketone, benzaldehyde and certain of the nitranilines and nitrophenols.

4. Ortho substituted aromatic nitro compounds will reduce faster than the corresponding meta compounds which in turn will reduce faster than the para.

5. Nickel chloride is a poison for the reduction of nitrobenzene.

BROOKLYN, N. Y. RECEIVED OCTOBER 3, 1938

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reaction of Sulfur with Some of the Halogenated Derivatives of Diphenyl Sulfide

BY J. H. BILLMAN[1] AND GREGG DOUGHERTY

Krafft and Vorster[2] described the reaction which takes place when unsubstituted diphenyl sulfide is heated with sulfur at 260°. The following equation will summarize their results

$$C_6H_5SC_6H_5 + S \longrightarrow C_6H_5SSC_6H_5 \qquad (1)$$

An essential point is that the sulfur, entering the unsubstituted diphenyl sulfide molecule, takes up a position adjacent to the sulfur atom already present.

When halogen substitution products of diphenyl sulfide were heated with sulfur a marked reaction took place over the range 240–270°. The principal products were halogen substitution products of benzene, polymeric material of varying composition containing halogen and sulfur in addition to carbon and hydrogen. The sulfur was present as sulfide, disulfide and polysulfide linkages. Also a considerable quantity of unchanged halogenated diphenyl sulfide was always found among the products regardless of the reaction time. The compounds studied and the halogenated benzene derivatives formed were

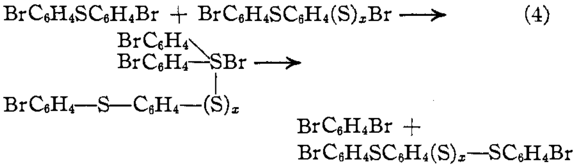
p,p'-Dibromodiphenyl sulfide ⟶ *p*-Dibromobenzene
p-Bromodiphenyl sulfide ⟶ *p*-Dibromobenzene and bromobenzene
p,p'-Dichlorodiphenyl sulfide ⟶ *p*-Dichlorobenzene
p-Chlorodiphenyl sulfide ⟶ Chlorobenzene
p,p'-Chlorobromodiphenyl sulfide ⟶ *p*-Dibromobenzene and *p*-chlorobromobenzene (2)

It was also found that the reaction could be extended to molecules of the type $X—C_6H_4—E—C_6H_4—X$ where X is halogen and E is an atom or group easily replaced by sulfur or converted to sulfur during the reaction. Thus dichlorodiphenyl oxide and dichlorodiphenyl sulfoxide, both known to satisfy the above conditions, gave positive results while dibromodiphenylamine and dichlorodiphenylmethane yielded no halogenated benzenes when heated with sulfur.

It is obvious that the reaction here must be far more complex than that given by Krafft and Vorster for the simple sulfide. A hypothesis which best accounts for all the products obtained is one which assumes that the reaction proceeds through the intermediate formation of a sulfonium compound, with subsequent splitting of that compound into simpler molecules. The most probable course involves first the addition of one or more atoms of sulfur to form an aryl sulfur halide

$$BrC_6H_4SC_6H_4Br + xS \longrightarrow BrC_6H_4SC_6H_4(S)_xBr \qquad (3)$$

This compound unlike an aryl halide is very reactive and at once forms a sulfonium salt with an adjacent sulfide molecule



(4)

Finally the complex breaks at the temperature of the reaction to give the dibromobenzene and an unsymmetrical polysulfide. There is an analogy to this method of sulfonium salt formation in the work of Scott and Klingen,[3] who obtained the diiodide of trimethylsulfonium iodide from sulfur and methyl iodide. Also the type of decomposition postulated, *i. e.*, the formation of a halide and a sulfide different from those used in forming the sulfonium complex, has been reported frequently in the literature. In order to test the proposed mechanism phenylsulfur chloride was mixed with dibromodiphenyl sulfide and heated over the temperature range ordinarily used.

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[1] From a thesis submitted by J. H. Billman in partial fulfillment of the requirement for the degree of Doctor of Philosophy at Princeton University.

[2] Krafft and Vorster, *Ber.*, **26**, 2813 (1893).

[3] Scott and Klingen, *Proc. Chem. Soc.*, 156 (1904).

p-Bromochlorobenzene was found among the products.

If the suggested interpretation of the reaction is correct it is obvious that the process need not stop at the stage indicated in equation 4. Further sulfonium salt formation with subsequent splitting can take place on the polysulfide first formed as well as on dibromodiphenyl sulfide. The tendency, therefore, would be toward the formation of complex polymeric, probably resinous or plastic, material, with the approximate structure

$$BrC_6H_4[S(S)_x—C_6H_4]_ySC_6H_4Br \qquad (5)$$

The major portion of the reaction products did, in fact, consist of a resinous substance, rather inert, very slightly soluble in organic solvents and little amenable to investigation. Reduction gave rise to mercaptyl compounds, which would not have been the case if only monosulfide linkages had been present. Further, hydrogen sulfide was evolved when an excess of sulfur ($x > 1$) was used in the initial reaction thus pointing, under those conditions, to the formation of polysulfide linkages containing more than two sulfur atoms. Although attempts to isolate any mercaptans of high molecular weight were unsuccessful, it is apparent that reduction of the suggested structure, 5, should always result in the formation of some *p*-bromothiophenol. This was isolated and identified.

It seems probable that the explanation offered for this reaction is a likely one in the many other cases in which sulfur reacts with organic compounds to give complex resinous material. It happens in this instance that one of the products, a halogenated benzene, resulting from decomposition of the intermediate sulfonium compound, is rather inert to sulfur and so is obtained easily and unchanged. This simplifies the whole process somewhat. With most other compounds, for example, phenols and aromatic amines, all the scission products of any intermediate sulfonium compound would themselves react with sulfur and so tend to obscure the fundamental mechanism of the reaction.

Experimental

Ten grams of *p,p'*-dibromodiphenyl sulfide was mixed thoroughly with varying quantities of sulfur, and 0.93–4.56 g. placed in a 250-cc. distilling flask equipped with a thermometer reaching to the bottom of the flask. The side-tube of the flask was attached to a train consisting of an empty ice–salt cooled U-tube, an absorption vessel containing silver nitrate solution and a buret arranged to collect any exit gases over mercury. The flask was placed in a Wood's metal bath and in the average run the contents were heated to 250–260° for three hours. Volatile material consisted only of a few drops of sulfur bromide, and no permanent gases were evolved.

The reaction mass in the flask was steam distilled for four hours and the white crystalline material which distilled over was collected on a filter, dried and identified as *p*-dibromobenzene by means of its melting point, 89°, and the mixed melting point with that compound.

The residue at the end of the steam distillation was light brown in color and had the consistency of putty. It was thoroughly mixed, warmed and washed with sodium sulfide solution to remove unreacted sulfur. The material remaining was washed with water, dried and extracted with boiling alcohol. The alcohol solution on evaporation left a residue of the starting material, *p,p'*-dibromodiphenyl sulfide.

The alcohol insoluble material was reduced with zinc and hydrochloric acid. Hydrogen sulfide was evolved at this point varying greatly in amount and varying roughly proportionally to the quantity of sulfur used in the original reaction. The reduction products were steam distilled and in the distillate was a white solid with a mercaptan odor. It had a m. p. of 75° which corresponds to that of *p*-bromothiophenol. The dinitrobenzene derivative prepared according to Bost[4] from 2,4-dinitrochlorobenzene had a m. p. of 142°, corrected, which is the same value as that given by the above worker. The non-volatile reduction products were partially soluble in alcohol and this soluble portion gave the characteristic yellow color test for the mercaptyl group when treated with an alcoholic solution of lead acetate. No individual mercaptans, however, could be isolated or identified.

Runs made with other halogenated aryl sulfides, and compounds not containing sulfur, were carried out in the same manner except that in most cases the reduction step was omitted. As might be expected, the yields of the halogenated benzene derivatives varied greatly with quantity of sulfur used, temperature and time of heating. This is shown in the table.

10 g. compound	Grams, S	Temp., °C.	Time, hrs.	Grams product
p,p'-$BrC_6H_4SC_6H_4Br$	0.931	245	1.5	0.99 *p*-$C_6H_4Br_2$
p,p'-$BrC_6H_4SC_6H_4Br$	4.65	240–245	3.0	1.29 *p*-$C_6H_4Br_2$
p,p'-$BrC_6H_4SC_6H_4Br$	4.65	254–256	3.5	1.39 *p*-$C_6H_4Br_2$
p,p'-$BrC_6H_4SC_6H_4Br$	4.65	261–263	3.0	1.93 *p*-$C_6H_4Br_2$
p-$BrC_6H_4SC_6H_5$	3.02	252–254	4	0.54 C_6H_5Br .01 *p*-$C_6H_4Br_2$
p-$ClC_6H_4SC_6H_5$	1.45	260–270	3	.40 C_6H_5-Cl
p,p'-$ClC_6H_4SC_6H_4Cl$	4.53	263–265	3	1.42 *p*-$C_6H_4Cl_2$
	1.23	250–270	8	2.64 *p*-$C_6H_4Cl_2$
p,p'-$ClC_6H_4SC_6H_4Br$	1.07	260–270	3	2.21 *p*-C_6H_4ClBr *p*-$C_6H_4Br_2$
p,p'-$ClC_6H_4SOC_6H_4Cl$	1.28	250–270	1.5	1.16 *p*-$C_6H_4Cl_2$
p,p'-$BrC_6H_4OC_6H_4Br$	2.00	250–270	1.5	0.75 *p*-$C_6H_4Br_2$

The various aryl sulfides, dichlorodiphenylmethane and dibromodiphenylamine used in this work were prepared by methods easily accessible in the literature. The 4,4'-dibromodiphenyl ether was obtained from the Eastman Kodak Company.

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[4] Bost and Turner, This Journal, **54**, 1985 (1932); **55**, 4956 (1933).

Summary

1. A study of the reaction of sulfur on various halogenated derivatives of diphenyl sulfide was made. It was found that the reactions were quite different from those involving unsubstituted aryl sulfides. The products were halogenated benzenes and complex sulfides and polysulfides.

2. It was found that a halogen substituted aryl sulfoxide or a halogen substituted aryl ether gave products similar to those in 1 due to a preliminary reduction to the sulfides.

3. A mechanism has been proposed to account for the course of the reaction.

4. Experiments, using halogen substitution products of diphenylamine and diphenylmethane, showed that these compounds, when acted upon by sulfur, do not yield halogenated benzenes.

PRINCETON, N. J. RECEIVED OCTOBER 28, 1938

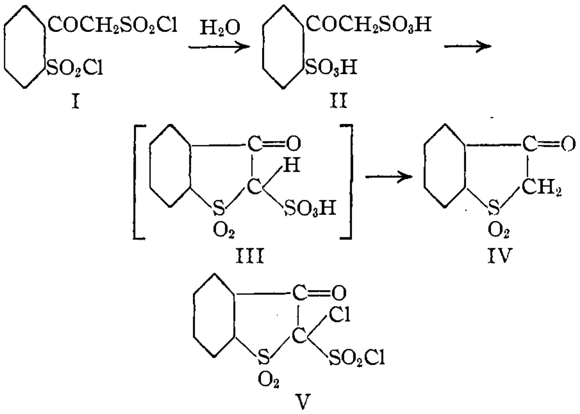
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Chlorosulfonic Acid with Acetophenone. New Synthesis of a Cyclic Ketosulfone

BY ARTHUR W. WESTON AND C. M. SUTER

It was reported by Riesz and Frankfurter[1] that the action of chlorosulfonic acid upon acetophenone yields a disulfonyl chloride. Since the dithiol obtained by reduction of this, unlike o-thiolacetophenone,[2] did not oxidize in alkaline solution to a thioindigo dye, they concluded that the sulfonyl groups must occupy the 3,4- or 3,5-positions. Further, sulfonation of acetophenone-4-sulfonic acid gave a disulfonyl chloride differing from the compound obtained directly from acetophenone and still not containing an ortho sulfonyl group. The product from acetophenone was therefore assigned the 3,5-structure.

It has now been found that this assignment is in error. The disulfonyl chloride does not give the haloform reaction. When it is hydrolyzed and the resulting potassium sulfonate fused with alkali the sole product identified is salicylic acid. Titration of the solution obtained by hydrolysis of the disulfonyl chloride with boiling water requires four equivalents of alkali. When the hydrolysis solution is evaporated to dryness without neutralization, sulfuric acid and a crystalline solid only slightly soluble in water are produced. This solid when hydrolyzed with strong alkali gives *o*-methanesulfonylbenzoic acid[3] and therefore must be 3(2)-thianaphthenone-1-dioxide[3,4] (IV), a conclusion confirmed by its physical properties. The reactions are indicated by the accompanying equations.



That the disulfonyl chloride did not correspond to structure V was shown by its lack of oxidizing action toward aqueous potassium iodide. Although there seems to be no exactly parallel case known, the loss of sulfuric acid from the intermediate III is accounted for by the accumulation of activating groups.

The question arises as to the mechanism by which I is formed. Feist[5] has assumed that in the preparation of 2-carbethoxy-3(2)-thionaphthenone-1-dioxide by the action of fuming sulfuric acid upon ethyl benzoylacetate the first step is ortho sulfonation followed by ring closure. Krekeler[6] has shown that acetophenone may be monosulfonated by pyrosulfuric acid but the position assumed by the substituent was not determined. Repetition of Krekeler's experiment and fusion of the resulting barium sulfonates with potassium hydroxide gave a mixture in which

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[1] Riesz and Frankfurter, *Monatsh.*, **50**, 68 (1928).

[2] Farbw. vorm. Meister Lucius and Brüning, German Patent 198,509, *Chem. Zentr.*, **79**, I, 2118 (1908).

[3] Arndt, Kirsch and Nachtwey, *Ber.*, **59B**, 1079 (1929).

[4] Lanfry, *Compt. rend.*, **155**, 1518 (1912).

[5] Feist, *Ber.*, **58B**, 2311 (1925).

[6] Krekeler, *ibid.*, **19**, 678, 2626 (1886).