

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

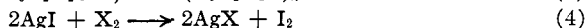
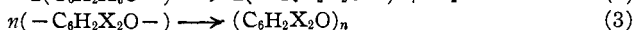
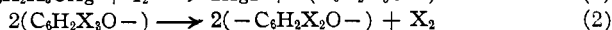
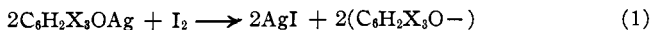
THE ACTION OF HALOGENS AND OF ALKYL HALIDES UPON THE SALTS OF TRIBROMOTHIOPHENOL¹

BY W. H. HUNTER AND ARTHUR H. KOHLHASE

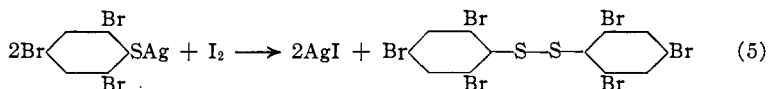
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The experiments described in this paper were undertaken in an attempt to substantiate the mechanism written by Hunter and others² for the decomposition of the silver salts of 2,4,6-trihalogenophenols in the presence of a trace of halogen, or simply on heating



In the hope that it might be possible to isolate either the thio analogs of some of the intermediates postulated in the above reactions or derivatives of these analogs, 2,4,6-tribromothiophenol was prepared and a study was made of its behavior under similar conditions. The first experiment, however, showed a marked difference in the behavior of the thiophenol as compared with the oxygen analog. On treatment of the dry silver salt, $\text{C}_6\text{H}_2\text{Br}_3\text{SAg}$, with one equivalent of iodine in dry benzene, no blue or any other color other than that of the iodine, appeared in the solution. There was an almost quantitative yield of 2,4,6,2',4',6'-hexabromodiphenyl disulfide, the reaction proceeding smoothly according to the equation



An amount of reddish, oily by-product, equal to 2 or 3% of the weight of disulfide, was formed. However, analysis showed it was not the analog of the polydibromophenylene oxides obtained from the corresponding phenols, being about 20% low in bromine and 60% low in sulfur.

Repetition of the experiment with one-tenth equivalent of iodine again gave an amount of disulfide equivalent to the iodine used and no other organic product. Boiling the silver salt in dry benzene produced no decomposition, while the addition of one equivalent of iodine to the boiling mixture again gave silver iodide and the hexabromodiphenyl disulfide.

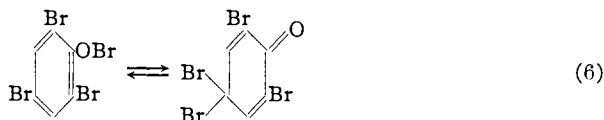
¹ The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Arthur H. Kohlhas, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in 1924. This paper was prepared by the junior author after the death of Dr. W. H. Hunter, which occurred on August 19, 1931.—L. I. SMITH.

² For leading references, see Hunter and Seyfried, *THIS JOURNAL*, **43**, 135 (1921).

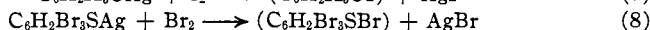
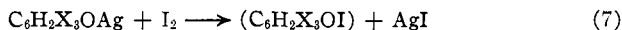
It was therefore expected that alkyl iodides would also fail to react in any other than a strictly normal fashion and such proved to be the case. Either cold or hot ethyl iodide or methyl iodide gave a smooth reaction leading to the ethyl or methyl thio ether in very nearly quantitative yield.

In the case of the trihalogenophenol silver salts, whatever the mechanism of the decomposition, the net result is the removal of a molecule of silver halide from the silver phenolate. This removal may, in fact, be brought about by heat alone. However, no such decomposition of the silver tribromothiophenolate could be produced by heating to various temperatures up to 180°. This greater stability of the silver thiophenolate toward heat might have been expected from a consideration of the relative stability of silver sulfide and oxide: the former melts at 842°; the oxide decomposes at 300–340°. Similar relations hold between some other pairs of compounds containing silver–sulfur and silver–oxygen unions.

Lauer³ has shown that the addition of bromine in sufficient concentration to tribromophenol or its salts results in the formation of tribromophenol bromide, in which he has demonstrated the following equilibrium to obtain



Also Zincke⁴ has prepared aryl sulfur halides (thiophenol halides) analogous to the compound at the left in reaction (6). It therefore seemed probable that in both the abnormal decomposition of the trihalogenated phenolates and the normal reactions of the tribromothiophenolates with halogens the first step is



followed by



In the absence of a large excess of halogen the products in (7) and (8) lose halogen, reaction (7) being followed by (2) and (3), and (8) being followed by (9), giving a disulfide which is stable.

Attempts to isolate the product in (8) resulted in failure, although good evidence for its formation was obtained: treatment of the sodium salt of the tribromothiophenol with a strong aqueous bromine–potassium bromide solution resulted in a fair yield of the sulfonyl bromide. The reaction is probably (8) followed by



³ Lauer, *THIS JOURNAL*, **48**, 442 (1926).

⁴ Zincke, *Ann.*, **391**, 55, 57 (1912).

The product obtained in (10) and the analogs of the product in (8) which Zincke⁴ has prepared, together with the equilibrium demonstrated to exist in (6), all support the existence of the products postulated in (7) and (8).

In equations (1) and (2) free radicals containing univalent oxygen are assumed as intermediates. Support for this assumption is found in the development of a marked color during the catalytic decompositions.²

In the course of the present work it was found that this color was instantly discharged by triphenylmethyl. Further evidence is found in the work of Goldschmidt and co-workers⁵ on free radicals containing oxygen. These substances very readily rearrange or decompose. The intermediates in (1) and (2) would be peroxides or, if dissociated, free radicals. Organic peroxides are rather rare and unstable.⁶ Some such decomposition as that shown in reactions (2) and (3) is therefore to be expected. In the case of sulfur compounds, on the contrary, the formation of disulfides appears to take place at every opportunity.

It is therefore to be expected that in the case of the thiophenols the reaction will stop with equations (8) and (9), the disulfide being perfectly stable.

Experimental Part

Preparation of 2,4,6-Tribromophenyl Ethylxanthate, $C_6H_2Br_3SCSOC_2H_5$.—The method is based on Leuckardt's general method for the preparation of thiophenols.⁷ The chief difficulty in this preparation is the slow diazotization, due to the insolubility of the tribromoaniline in acids.

Pure 2,4,6-tribromoaniline (38 g.) was dissolved in about 75 cc. of cold 95% sulfuric acid. The clear, gray-green solution was poured slowly with stirring into 800 cc. of ice water, precipitating the tribromoaniline in very finely divided condition. The mixture was neutralized, filtered and washed once with water.

The cake was digested in a 3-liter beaker with 200 cc. of concd. hydrochloric acid; 1400 cc. of cold water and 800 g. of ice were added. While maintaining the tribromoaniline in suspension with an efficient mechanical stirrer, about 15 cc. of a solution of 9.5 g. of sodium nitrite in 100 cc. of water was added and the remainder run in drop by drop over a period of about four hours, ice being added as needed to keep the temperature near 0°. After another hour the solution was fairly clear, 97–98% of the aniline having dissolved. About 10 cc. of a 20% solution of urea was then added to destroy excess nitrous acid.

A thin paste of sodium carbonate was added with stirring, as rapidly as the frothing would permit, until most of the free acid was neutralized, after which the neutralization was continued with a solution of sodium bicarbonate until the neutral point was almost, but not quite, reached. The reaction mixture should be faintly acid at the end.

The solution was then filtered through an ice-cold Buchner funnel into a flask containing ice. The filtrate, amounting now to about 2600 cc., was transferred to a broad

⁵ Goldschmidt and Vogel, *Ber.*, **64B**, 1744–1755 (1931).

⁶ Clover, *THIS JOURNAL*, **44**, 1107 (1922); cf. benzoyl hydrogen peroxide, *Ber.*, **33**, 858, 1575 (1900); Goldschmidt, *ibid.*, **55**, 3194 (1922).

⁷ Leuckardt, *J. prakt. Chem.*, [2] **41**, 179–224 (1890).

vessel; about 100 g. of ice and 100 cc. of ether were added and then a solution of 19 g. of potassium ethylxanthate in 75 cc. of water was poured in and the mixture stirred thoroughly for *not more than ten seconds*. A bright yellow oil separated, the color soon changing to orange and brown with the liberation of nitrogen.

The mixture was covered and allowed to remain *undisturbed* while slowly warming to room temperature. If disturbed while warming to room temperature, the oily material emits flashes of light and may even explode. After six hours it was warmed to 70° on a steam-bath. Most of the xanthic ester separated on the bottom as a viscous brown oil. After cooling the aqueous layer was decanted from the oil and extracted once with one-fifth volume of ether and discarded. The oil left adhering to the reaction vessel was dissolved in ether and the solution combined with the ether extract of the aqueous layer.

Solution of the oil in ether left a residue consisting of minute white crystals of di-tribromophenyl dithiolcarbonate, $(C_6H_2Br_3S)_2CO$. This red residue was saved as it also saponifies readily to the thiophenolate.

The combined ether solution of the oil was shaken thoroughly with 5% sodium hydroxide to remove any phenols, then with 5% sulfuric acid and then washed with water. The ether was evaporated and the residual oil was dried in a vacuum desiccator. The yield of oil was 40.6 g. or 81%. The yield of di-tribromophenyl dithiolcarbonate was about 10%, making a total yield of about 90% of products capable of saponification to the 2,4,6-tribromothiophenol.

The ester is a heavy, viscous, red-brown oil of characteristic, not unpleasant, odor; it is miscible with ether in all proportions, insoluble in water, forms about a 1% solution with cold alcohol and about 2% in hot alcohol. The solubility in methyl alcohol is considerably greater; benzene dissolves it readily. When boiled with alcoholic potassium hydroxide, it is saponified to the thiophenolate.

Analysis of the oil showed it was not very pure, probably containing decomposition products of the potassium xanthate.

Anal. Calcd. for $C_9H_7OBr_3S_2$: Br, 55.12; S, 14.74. Found: Br, 53.3; S, 17.5, 17.8.

Saponification of Tribromophenyl Ethylxanthate to 2,4,6-Tribromothiophenol, $(C_6H_2Br_3SH)$.—In a flask provided with a reflux condenser was placed 40.6 g. of the oily ester with 1500 cc. of methyl alcohol containing 12.6 g. of potassium hydroxide. The mixture was refluxed for about thirty minutes, until a 5-cc. sample added to water gave little or no precipitate. Too long boiling with excess alkali causes decomposition. About 80% of the methanol was then distilled off and 900 cc. of a 3% aqueous solution of sodium hydroxide was added. The mixture was warmed and stirred with a little animal charcoal and filtered. The clear, pale reddish-brown filtrate was acidified with 15% acetic acid, depositing 2,4,6-tribromothiophenol as a pale-yellow to pure white, flocculent precipitate. If not white, the precipitate was filtered off, redissolved in excess alkali, treated again with a little bone black and precipitated as before.

For the preparation of the pure thiophenol, free from disulfide, the acidification and washing of the precipitate must be carried out in an atmosphere of carbon dioxide.

The 2,4,6-tribromothiophenol crystallizes from hot alcohol as shiny, pale yellow, short needles, m. p. 115.5–115.9° corrected. It has the characteristic thiophenol odor although not nearly so pronounced or disagreeable as most of the thiophenols. It dissolves in the following solvents arranged in order of decreasing solubility: carbon disulfide, chloroform, ether, benzene, acetone, glacial acetic acid (some acetylation?), methyl alcohol, ethyl alcohol. Ethyl alcohol forms about 1% solution at 20°. It dissolves very readily in caustic alkalies. In solution or when wet it oxidizes readily, forming the disulfide.

This is the first member of the series of trihalogenated thiophenols to be prepared. Analyses by the Carius method required heating at 285–310° for five hours; derivatives were also refractory.

Anal. Calcd. for $C_6H_2Br_3SH$: Br, 69.12; S, 9.24. Found: Br, 69.15; S, 9.97, 9.80, 9.85.

Preparation of 2,4,6-Tribromophenyl Thiolacetate, $C_6H_2Br_3SCOCH_3$.—Boiling the free thiophenol in acetic anhydride for twenty minutes and pouring the solution into dilute sodium hydroxide left the acetyl derivative as a precipitate. This was filtered off, washed and recrystallized from hot alcohol. It forms long shiny, colorless needles melting at 102.1–102.7°, corrected. It is readily soluble in hot alcohol, glacial acetic acid, and benzene.

Di-2,4,6-tribromophenyl Dithiolcarbonate, $(C_6H_2Br_3S)_2CO$.—Solution of the crude, oily tribromophenyl ethylxanthate in ether (see preparation above) left this dithiolcarbonate as a mass of minute, white crystals, very slightly soluble in ether. These are saponifiable in the same way as the xanthic ester, although requiring about 50% more time. However, the saponification of this dithiolcarbonate yielded a tribromothiophenol which was more easily purified than that from the xanthate.⁸

From hot acetone the dithiolcarbonate crystallizes in long, white, silky needles, melting at 194.2–194.7° corrected. From benzene it forms shorter, thicker needles. It is very soluble in carbon bisulfide, chloroform or benzene, slightly soluble in ether and glacial acetic acid.

Anal. Calcd. for $C_{12}H_4OBr_6S_2$: Br, 66.62; S, 8.91. Found: Br, 66.65, 66.84; S, 8.50, 8.91, 8.94. Molecular weight calcd., 655.6; found, 660.

Preparation of Silver Tribromothiophenolate, $(2,4,6)C_6H_2Br_3SAg$.—Recrystallized 2,4,6-tribromothiophenol was dissolved in an excess of halogen-free sodium hydroxide solution. The excess of alkali was nearly neutralized with 20% acetic acid, completing the neutralization with 4% acid until a slight permanent precipitate was obtained. The solution was stirred with animal charcoal and filtered. To the filtrate about 3 drops of 3% silver nitrate was then added to precipitate any halogen which might be present. The whole was shaken with bone black and again filtered. From this point the preparation was carried on in the dark-room.

To the clear filtrate a slight excess of dilute silver nitrate was added, precipitating the silver tribromothiophenolate as a white, gelatinous material. The silver salt was then washed repeatedly by digesting with water at 60° and filtering. This was repeated until the filtrate gave only a slight opalescence on adding dilute hydrochloric acid. The precipitate was finally drained on a fluted filter and allowed to dry in the air for thirty hours, carefully protected from dust. It was then dried in a vacuum desiccator over calcium chloride for a week.

This formed light-gray, very hard lumps which were crushed to a fine powder. The dried salt was kept in a desiccator in a dark-room, although it does not appear to be sensitive to light when dry. Heating to 80° in water causes considerable darkening. The product was not analyzed; however, the yields obtained in the following experiments indicated it to be quite pure.

Silver Tribromothiophenolate with One Equivalent of Iodine in Benzene.—Finely pulverized silver salt (7.4764 g.) was added to 2.091 g. of iodine in 50 cc. of dry benzene. The mixture was kept in a dark room for three days, with occasional shaking. The color of the iodine gradually disappeared. The solid was then filtered off and digested three times with warm benzene. The combined benzene filtrate and extracts were

⁸ Leuckardt had obtained the analog of this dithiolcarbonate in the course of his preparation of thio-*p*-cresol, *J. prakt. Chem.*, [2] 41, 189–191 (1890).

evaporated to about 4 cc. and cooled. Pale yellow crystals were deposited. The mother liquor was decanted and evaporated to dryness. This left 0.137 g. of a greenish-red oil. The crystalline product, which, as shown below, was 2,4,6,2',4',6'-hexabromodiphenyl disulfide, weighed 5.699 g., a yield of 92%.⁹ The oily product was equivalent to 2.4% of the theoretical yield of disulfide.

That the oily product was not polydibromophenylene sulfide (the thio analog of the polydibromophenylene oxides discussed in the theoretical part) was shown by analysis.

Anal. Calcd. for $(C_6H_2Br_2S)_n$: Br, 60.10; S, 12.05. Found: Br, 50.12; S, 4.77.

The hexabromodiphenyl disulfide, a new compound, was further purified by washing with a small amount of ether and recrystallizing from benzene. It forms pale yellow rhombohedra, melting at 221.8–222.7° corrected. It is quite soluble in hot benzene or toluene, slightly soluble cold, very soluble in hot bromoform, ethylene dibromide, carbon disulfide or chloroform, fairly soluble cold. Ethyl acetate, glacial acetic acid or alcohol dissolve it only slightly.

The disulfide may be reduced to the thiophenol by treating the cold benzene solution, containing a few per cent. of alcohol, with granular sodium, keeping the mixture cool to avoid too vigorous reduction and removal of bromine from the ring. The sodium 2,4,6-tribromothiophenolate may be extracted easily with water and precipitated by acid.

The same disulfide is easily obtained by atmospheric oxidation of the ammonium or sodium salt of the thiophenol, by the action of halogen on the free thiophenol or its salts, or by the reduction of the salts of tribromobenzenesulfonic acid with phosphorus pentabromide.

Anal. (Carius at 300°) calcd. for $(C_6H_2Br_3S)_2$: Br, 69.32; S, 9.78. Found: Br, 69.49, 69.52; S, 9.78. Molecular weight calcd.: 692; found (cryoscopic, ethylene dibromide), 614.

2,4,6- $C_6H_2Br_3S$ Ag with One-Tenth Equivalent of Iodine.—This experiment was carried out in the same way as the preceding one except that the reaction was completed in about thirty minutes, excess silver salt being present. The characteristic rhombohedron crystals of hexabromodiphenyl disulfide, identified by their melting point, were obtained; there was no oily or other by-product.

$C_6H_2Br_3S$ Ag with One Equivalent of Iodine in Boiling Benzene.—The reaction was complete in thirty minutes. The product was hexabromodiphenyl disulfide and a trace of an oily by-product.

$C_6H_2Br_3S$ Ag with Cold Ethyl Iodide.—To 1.994 g. of the dry, finely pulverized silver salt was added 15–20 cc. of dry, colorless ethyl iodide and the mixture kept in a darkened place for two days, when the reaction appeared to be complete. The silver iodide was filtered off and washed with ethyl iodide. Evaporation of the ethyl iodide left a viscous, light yellow oil which was freed of solvent by warming under vacuum and then drying in a desiccator.

The calculated yield was 1.649 g.; the actual yield was 1.655 g. or 100.3%. Analysis indicated the product to be pure ethyl tribromophenyl thio ether, $C_6H_2Br_3SC_2H_5$.

Anal. Calcd. for $C_8H_7Br_3S$: Br, 63.95; S, 8.55. Found: Br, 64.39, 64.02; S, 8.88, 9.04.

$C_6H_2Br_3S$ Ag with Boiling Ethyl Iodide.—The same product was obtained as with cold ethyl iodide and in the same purity.

Anal. Calcd. for $C_8H_7Br_3S$: Br, 63.95; S, 8.55. Found: Br, 64.25; S, 8.86.

⁹ This is not the same as the "hexabromodiphenyl disulfide" prepared by Taboury, *Bull. soc. chim.*, [4] 1, 741 (1907).

$C_6H_2Br_3S$ Ag at 110° with Ethyl Iodide.—About 2.0 g. of the silver salt was heated to 110° in an oil-bath and boiling ethyl iodide added; the silver salt was heated again up to 110° and another portion of hot ethyl iodide was added. The mixture was extracted with benzene and also chloroform but the only product obtained was the same light yellow, viscous oil produced with cold or hot ethyl iodide.

$C_6H_2Br_3S$ Ag with Cold Methyl Iodide.—An excess of redistilled and dried methyl iodide was added to the finely pulverized, dry silver salt and the mixture allowed to stand in a darkened place for three days. The excess methyl iodide was filtered off and the solids washed with pure benzene. Evaporation of the combined extracts left long, colorless needles, plus about 1 or 2% of reddish oil which was not further investigated. The solid was recrystallized from hot alcohol or acetone and analyzed. It was methyl tribromophenyl thio ether (2,4,6-tribromothioanisole), $C_6H_2Br_3SCH_3$, crystallizing in long, flat, glistening, colorless needles, melting at $59.6-60.5^\circ$, very soluble in carbon bisulfide, acetone, chloroform, fairly soluble in glacial acetic acid, slightly soluble in ether or alcohol.

Anal. Calcd. for $C_7H_5Br_3S$: Br, 66.43; S, 8.88. Found: Br, 66.59; S, 9.12.

Effect of Heat upon $C_6H_2Br_3S$ Ag.—The dry salt heated in a test-tube immersed in an oil-bath at various temperatures from 120 to 180° for one hour suffered no detectable decomposition, as shown by extraction of the salt with chloroform, benzene, ether or carbon disulfide. The salt after these treatments was finally treated with iodine in benzene and gave the usual yield of hexabromodiphenyl disulfide in good purity.

2,4,6- $C_6H_2Br_3S$ Na with Bromine in Aqueous Potassium Bromide. Preparation of $C_6H_2Br_3SO_2Br$.—2,4,6-Tribromothiophenol (11.5 g.) was dissolved in a small excess of sodium hydroxide, the excess alkali nearly neutralized and then the mixture diluted to 150 cc., after which it was filtered in a very thin stream, with stirring, into a solution of 25 g. of bromine and about 20 g. of potassium bromide in 45 cc. of water. A reddish oil separated and solidified in a few minutes. The red-brown solid was washed with water several times by decantation and dried in the air.

The dried solid was extracted with ether several times. The insoluble portion was recrystallized from benzene and shown to be the 2,4,6,2',4',6'-hexabromodiphenyl disulfide obtained in the preceding experiments; yield about 45%.

The ether extracts were evaporated to dryness, the residues redissolved in the minimum amount of cold ether and filtered from the small amount of disulfide. From three crops of crystals was isolated 7.55 g. or nearly 50% yield of the sulfonyl bromide,¹⁾ $C_6H_2Br_3SO_2Br$. Recrystallized from ether, m. p. $74.5-75.7^\circ$. It is exceedingly soluble in ether, benzene or chloroform. It forms the ethyl ester on boiling with alcohol. It is rapidly hydrolyzed to the sulfonate by warm alkali; it reacts violently with phosphorus tribromide, being almost instantly reduced to hexabromodiphenyl disulfide. Boiling with dilute acid for one hour hydrolyzed the product to hydrobromic acid, sulfuric acid and 1,3,5-tribromobenzene.

Anal. Calcd. for $C_6H_2Br_3SO_2Br$: Br, 69.85; S, 7.00. Found: Br, 69.70, 70.10; S, 6.86, 6.83.

2,4,6- $C_6H_2Br_3S$ Na with Liquid Bromine.—Treatment of about a gram of the sodium salt with liquid bromine gave rise to a rather violent reaction yielding a sticky red mass. This was extracted with chloroform but nothing was identified in the chloroform extract except the disulfide.

$C_6H_2Br_3SH$ with Bromine in Benzene.—To 20 cc. of dry benzene containing 1.2

¹⁰ Michaelis and Ruhl prepared $C_6H_5SO_2Cl$ by analogous methods, *Ber.*, **23**, 475 (1890). This sulfonyl bromide is new although Reinke prepared the analogous sulfonyl chloride, $C_6H_2Br_3SO_2Cl$, *Ann.*, **186**, 277 (1877).

g. of the free thiophenol was added 0.3 cc. of bromine in 10 cc. of benzene and the mixture then allowed to stand for forty-eight hours. Evaporation of the benzene left yellowish granules and a little red oil. On exposure to the air the oil largely solidified. Although the product had first shown definite indications of the presence of considerable amounts of some other products, the procedure resulted in the ultimate identification of about 97% of the product as hexabromodiphenyl disulfide.

Product Formed by Bromine with Thiophenol in Glacial Acetic Acid.—Thiophenol (5.7 g.) was dissolved in 50 cc. of glacial acetic acid. To this was added 11.4 cc. of bromine and it was then allowed to stand for several hours, part of the time in sunlight. The solution was then cooled in an ice-bath, the solid filtered off, washed five times with cold acetic acid and then five times with water. After drying, the solid was recrystallized from alcohol; m. p. 91–93°. The melting point, crystalline form and analysis correspond to the 4,4'-dibromodiphenyl disulfide of Hübner and Alsberg.¹¹

Anal. Calcd. for $(C_6H_4BrS)_2$: Br, 42.50. Found: Br, 42.87.

Summary

1. The salts of 2,4,6-tribromothiophenol, as well as the free thiophenol, react in a perfectly normal manner with halogens and alkyl halides to give the disulfide or thio ethers in nearly quantitative yield. The products contain nothing analogous to the amorphous polydihalogenophenylene oxides obtained from the trihalogenated phenols and phenolates.

2. The first stage in the reaction of both phenolates and thiophenolates is probably the formation of metal halide plus an unstable product containing halogen directly attached to oxygen or sulfur.

3. The first known member of the series of trihalogenated thiophenols has been prepared. From this eight derivatives have been prepared and characterized.

¹¹ Hübner and Alsberg, *Ann.*, **156**, 328 (1870).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

KETENES FROM ACYLPHTHALIMIDES AND OTHER SUBSTITUTED AMIDES

BY CHARLES D. HURD AND MALCOLM F. DULL

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Acetylcarbazole is known¹ to regenerate carbazole on heating above its melting point. Propionylcarbazole,² *n*-nonoylcarbazole³ and palmitylcarbazole show a similar instability on fusion. Although carbazole was identified in all cases, no attention was directed to the fate of the acyl radicals.

If the elements of carbazole, $(C_6H_4)_2NH$, are subtracted from those of acetylcarbazole, $(C_6H_4)_2NCOCH_3$, the elements of ketene remain. Whereas

¹ Graebe and Glaser, *Ann.*, **163**, 351 (1872).

² Oddo, *Mem. accad. Lincei*, [v] **14**, 510 (1923).

³ Copisarow, *J. Chem. Soc.*, **113**, 816 (1918).