2,2'-SULFONIDO-TRIPHENYLMETHYL.

By M. Gomberg and E. C. Britton.

The chlorides of aryl xanthenols, aryl thio-xanthenols and aryl acridols are prepared from their corresponding hydrogen chloride additive compounds,[1] in which however the acid is held with considerable tenacity.

$$\left(X\left\langle \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} \right\rangle C \left\langle \begin{matrix} C_6H_5 \\ Cl \end{matrix} \right. \right) \cdot HCl \xrightarrow{\text{heat}} \quad X\left\langle \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} \right\rangle C \left\langle \begin{matrix} C_6H_5 \\ Cl \end{matrix} \right. + HCl.$$

$$(X = O, S, \text{ or } NR)$$
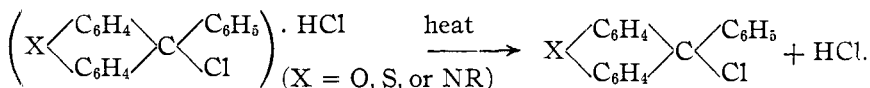
These normal chlorides are difficult to prepare in the pure state; the merest trace of moisture hydrolyzes them into carbinol and hydrochloric acid, the latter not escaping but being retained as the hydrochloride additive compound with the unhydrolyzed portion. In the process of the conversion of the carbinol chloride, contaminated in this manner, into the corresponding free radical the hydrogen chloride becomes liberated and tends to cause catalytic polymerization of the free radical. Herein may lie the reason why with this class of chlorides it has proved so difficult, and often wholly impossible, to isolate the free radical, notwithstanding the fact that the actual formation of the radical at the initial stage of the reaction could be demonstrated.

It seemed desirable to prepare a carbinol of bridged-ring type that would readily yield a stable chloride, one that would be devoid of the tendency to take on hydrogen chloride. Such a carbinol was found in 2,2'-sulfonido-triphenyl carbinol.[2]
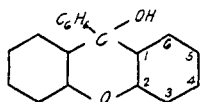

2,2'-Sulfonido-triphenyl Carbinol, (Formula II).—This was synthesized by the following set of reactions: thio-xanthone, prepared by the condensation of thiosalicylic acid and benzene in presence of sulfuric acid, was allowed to react with phenyl magnesium bromide, and the thio-xanthenol thus formed was oxidized to the sulfone.

(I).

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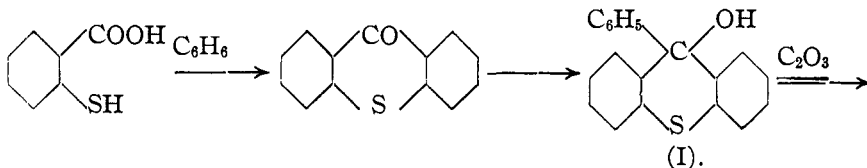
[1] Gomberg and Cone, *Ann.*, **370**, 142 (1909); **376**, 183 (1910).

[2] The nomenclature here adopted is analogous to that suggested for phenyl-xanthenol, namely, 2,2'oxido-triphenyl carbinol. Meyer and Jacobson's "Lehrbuch d. org. Chemie" Veit and Company, [II] **1914**, Part 3, p. 765.
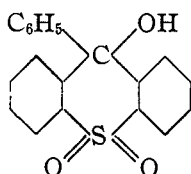
(II).

The thiosalicylic acid was prepared from anthranilic acid[3] with a yield of 80% to 90%. Thio-xanthone was prepared according to Smiles.[4] Fifty g. of thiosalicylic acid, 500 cc. of conc. sulfuric acid and 150 cc. of benzene were stirred for 10 hours; the reaction mixture was allowed to stand for 10 hours and finally heated for 1 hour on the water-bath. Water was then carefully poured over the surface of the acid and allowed to diffuse slowly, a procedure, we believe, first used by Graiebe. This gave a crystalline product which was easily filtered. The xanthone was purified by recrystallization from chloroform and then from acetic acid. Yield, 85%.

Phenyl thio-xanthenol (Formula I) was prepared from phenyl magnesium bromide and thio-xanthone,[5] and purified by recrystallization from petroleum ether, b. p. 100° to 110°. The yield of the pure product never fell below 90%.

For oxidation to the sulfone the following procedure was adopted. Twenty g. of phenyl-thio-xanthenol was dissolved in 140 cc. of hot glacial acetic acid, and 25.5 g. of chromic acid dissolved in 40 cc. of water was added at such a rate as to maintain the temperature above 100°. The reaction mixture was then heated for one hour on the water-bath; 50 cc. of hot water was added, and the solution was cooled. The precipitate was removed by filtration and was washed repeatedly with hot water to remove chromic acetate and chromic acid. For purification, the sulfonido compound was recrystallized from glacial acetic acid. Yield, 85%.

Hydrogen peroxide was tried as the oxidizing agent, but only a small quantity of the sulfone was produced, the chief product being a compound lower melting, presumably the sulfoxide, along with some benzophenone sulfone.

Another method for the preparation of the sulfone carbinol was devised, namely, the action of phenyl magnesium bromide on benzophenone sulfone. · The benzophenone sulfone was prepared by the oxidation of thio-xanthone in acetic acid solution with 30% hydrogen peroxide according to the method of Ullmann.[6] 0.1 mol of powdered benzophenone sulfone was slowly added to an ether-benzene solution of 0.1 mol of phenyl magnesium bromide, and the solution was heated under a reflux condenser for one hour. The magnesium-bromide addition compound was decomposed by ice in the usual manner, and since the sulfone carbinol is insoluble in both ether and water, it was removed by filtration after neutralization of the magnesium hydroxide with hydrochloric acid. This method gives a 90% yield of fairly pure product, but the benzophenone sulfone which does not enter into reaction is not easily separated from the carbinol. For this reason, the first method of preparation is preferable.

Analysis. Calc. for $C_{19}H_{14}O_3S$: C, 70.77; H, 4.09; S, 9.95. Found: C, 70.67; H, 4.50; S, 9.93.

The sulfonido-triphenyl carbinol crystallizes in the form of needles and melts without decomposition at 224° to 5°. The compound is only slightly soluble in the

[3] Friedlander, **9,** 542, Ger. pat. 205,450.

[4] Davis and Smiles, *J. Chem. Soc.,* **97,** 1296 (1910).

[5] Gomberg and Cone, *Ann.,* **376,** 203 (1910).

[6] Ullmann and Glenck, *Ber.,* **49,** 2487 (1916).

usual organic solvents at ordinary temperature, although it can be recrystallized from a mixture of equal parts of chloroform and absolute alcohol. The sulfonido-carbinol dissolves in conc. sulfuric acid producing a red-brown solution, and may be recovered unchanged upon addition of water.

2,2'-Sulfonido-triphenyl Methane, SO_2: $(C_6H_4)_2$: $CH(C_6H_5)$.—Reduction with stannous chloride and hydrochloric acid converts the chloride into the methane compound, the sulfone group remaining unaltered. Two g. of the sulfonido carbinol was dissolved in 25 cc. of glacial acetic acid and reduced with 3 g. of stannous chloride dissolved in 25 cc. of acetic and 3 cc. of hydrochloric acid. The mixture was heated for 1 hour on the water-bath, diluted with 10 cc. of hot water, and then allowed to crystallize. The sulfonido methane was recrystallized from glacial acetic acid and was obtained in the form of colorless needles, m. p. 193° to 194°. The yield of pure product was 1.7 g. No color is developed by treating the methane with conc. sulfuric acid; it is not acted upon by phosphorus pentachloride nor is it oxidized back to the carbinol by chromic acid in acetic acid solution.

Analysis. Calc. for $C_{19}H_{14}O_2S$: S, 10.47. Found: 10.49.

2,2'-Sulfonido-triphenyl Carbinol Chloride, SO_2:$(C_6H_4)_2$: $C(C_6H_5)Cl$.—The carbinol chloride cannot be obtained by treating the carbinol with hydrogen chloride in ether or benzene solution, nor by boiling with acetyl chloride, thionyl chloride, or phosphorus trichloride, whereas practically nearly all the triaryl carbinols are converted to the corresponding chlorides by such treatment. Twenty g. of the carbinol was intimately mixed with slightly more than the theoretical quantity of phosphorus pentachloride (1 g. in excess) and the mixture was heated in an oil-bath at 110° to 120°. When the evolution of hydrogen chloride had commenced, the flask was removed from the oil-bath until the evolution of the gas had practically ceased, and the mixture was further heated for ½ hour. The phosphorus oxychloride was then distilled and the excess of phosphorus pentachloride was volatilized under reduced pressure by means of a current of dry air. The residue was dissolved in 75 cc. of hot benzene, filtered from some red precipitate, and the carbinol chloride was precipitated by the addition of 80 cc. of dry ligroin. For purification, the chloride was recrystallized from high-boiling ligroin (100° to 10°), the accompanying red impurity being entirely insoluble in this solvent, while the chloride is soluble to the extent of about 2 g. in 100 cc. Yield of pure product, 80%.

Analysis. Calc. for $C_{19}H_{13}O_2SCl$: C, 66.94; H, 3.84; S, 9.41; Cl, 10.41. Found: C, 66.65; H, 3.88; S, 9.42; Cl, 10.41.

The sulfonido-chloride melts without decomposition at 160° to 1°. It is readily soluble in benzene, chloroform, acetone, carbon tetrachloride, ethyl acetate, slightly soluble in ether, carbon disulfide, and practically insoluble in cold ligroin. It can be converted quantitatively into the carbinol by boiling with 80% acetic acid or diluted alcohol.

The Free Radical, 2,2' - Sulfonido - triphenylmethyl SO_2: (C_6H_4) :- $C(C_6H_5)$.—The carbinol chloride employed for the preparation of the free radical was the purest possible, checked by its melting point and analysis. After many trials the following procedure was adopted. Two g. of the sulfonido-chloromethane and 12 g. of molecular silver (100 mesh) were placed in a 75cc. bottle, and enough benzene was added almost to fill the bottle, which was then tightly stoppered. After 35 minutes of vigorous shaking, the benzene solution was filtered into the standard apparatus,[7]

[7] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1659 (1917).

and concentrated under reduced pressure at a temperature of 40°. Fifteen cc. of ether was then added to the sirupy residue in small portions, with shaking after each addition, and the free radical allowed to crystallize. After standing for 1 hour at 0°, the solvent was drawn off, the crystals were washed with ether and dried at a temperature of 40° for 1 hour. The yield of pure product was 1 to 1.3 g.

The free radical appears as a slightly yellow crystalline powder, which melts with decomposition at about 180°. It is soluble in all the usual organic solvents with the exception of ether, carbon disulfide, and ligroin, giving orange colored solutions, lighter in color than those of the radical phenyl-thio-xanthyl. When the free radical was recrystallized from carbon disulfide, the crystals formed did not lose all the carbon disulfide at any temperature below 80°, even under reduced pressure. Presumably a combination of free radical and solvent had occurred.
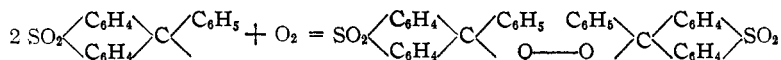
Calc. for $C_{19}H_{18}O_2S$: S, 10.50. Found: 10.57.

The procedure outlined above must be followed exactly in order to obtain a fair yield. If the weight of the silver is decreased, all of the carbinol chlorine will not be removed in a sufficiently short time, the same difficulty occurring if the silver is coarser than 100 mesh. If the time of·shaking is prolonged, the product will absorb less than the theoretical quantity of oxygen, indicating decomposition of free radical. Indeed, shaking for one day with the quantities indicated will give a product entirely incapable of absorbing oxygen. Further than this, the free radical even in the solid state cannot be heated above 40° for any length of time without suffering some change.

Oxygen Absorption and the Peroxide.—When a solution of the free radical is exposed to oxygen or air a crystalline peroxide is formed and the solution becomes decolorized. The yield of the peroxide is usually 80 to 85%, just as has been found to be the case with triphenylmethyl and a number of other free radicals. The peroxide is insoluble in nearly all the organic solvents except chloroform, in which it is readily soluble, and benzene, in which it is slightly soluble. It crystallizes in the form of colorless needles, which melt with decomposition at 238° to 9°. It may be converted into the carbinol by heating at 100° with conc. sulfuric acid, the yield of carbinol amounting to about 40%.

Calc. for $C_{38}H_{26}O_6S_2$: C, 70.97; H, 4.08; S, 9.99. Found: C, 70.22; H, 4.26; S, 9.99.

In the formation of the sulfonido-triphenylmethyl peroxide from a solution of free radical the theoretical amount of oxygen is absorbed, two mols of the radical uniting with one mol of oxygen.

$$2 \; SO_2 \underset{C_6H_4}{\overset{C_6H_4}{<}} C \underset{}{\overset{C_6H_5}{<}} + O_2 = SO_2 \underset{C_6H_4}{\overset{C_6H_4}{<}} C \underset{O \text{———} O}{\overset{C_6H_5 \quad C_6H_5}{<}} C \underset{C_6H_4}{\overset{C_6H_4}{>}} SO_2$$

Oxygen absorptions were taken on the free radical produced in solution directly from the chloride as well as upon the previously isolated crystalline compound. In the former instance, the chloride was dissolved in bromobenzene, shaken with silver for 35 minutes in a sealed tube, and the absorption then taken after breaking the tube in the absorption apparatus connected with the gas buret. In addition, the yield of the peroxide formed was determined in each experiment.

Wt. of sample.		Oxygen.		Peroxide.	
Chloride.	Free Rad.	Cc	% of calc.	G.	% of calc.
0.5000	....	16.2	99.0	0.3700	79.0
0.5000	....	16.0	97.0	0.3500	74.5
0.5000	....	16.0	97.0	0.3645	77.5
....	0.4525[a]	15.3	92.0	0.3522	74.0
....	0.7110	26.1	100.0	0.5920	79.0
....	0.8567	30.0	96.5	0.7390	80.7

[a] Absorption taken in benzene.

Iodine Absorption.—By adding a standard benzene solution of iodine to a benzene solution of the free radical, a titration may be accomplished, although the end point is rather indistinct, being observed in a brown solution. Two samples, 1.1000 and 0.7568 g. absorbed 0.412 and 0.298 g. of iodine, equivalent to−90.0 and 99.0%, respectively.

No attempts were made to isolate the unstable iodide. When the solution of the iodide is allowed to stand in air, iodine is liberated and large amounts of peroxide are formed.

Molecular Weight Determination.—Similar apparatus and manipulation were employed by us in the determination of the molecular weight of the free radical as previously described.[8] The samples used for the molecular weight determinations were all carefully dried under reduced pressure in an atmosphere of carbon dioxide at the temperature of boiling ether, and were in an inert atmosphere except during the short period of weighing. The determinations were carried out in an atmosphere of hydrogen to prevent oxidation of the free radical. Every sample to be used was analyzed as to its purity, and none was used which did not indicate an absorption of oxygen above 95% of that calculated. But two solvents were used, namely benzene and p-bromotoluene, giving temperatures of 5.4° and 27° respectively. The molecular depression constant for benzene was taken as 50 and for p-bromotoluene as 82.

At the completion of each molecular-weight determination the solution was exposed to air and the amount of peroxide formed showed that the radical had undergone practically no change in the process of the molecular-weight determination.

The results given in the following table indicate that there is little change in the molecular weight with increase in temperature from 6° to 27°, but there

[8] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1662 (1917).

Solvent.	Wt. of solvent. G.	Wt. of free radical. G.	Concentration. %.	Depression of f. p.	Mol. wt.
Benzene	17.42	0.1733	0.98	0.106	469.3
	...	0.3335	1.88	0.194	493.4
	...	0.5120	2.85	0.279	526.7
	17.14	0.1900	1.10	0.126	450.1
	...	0.3446	1.97	0.212	474.2
	...	0.5231	2.96	0.305	500.3
	17.20	0.2140	1.23	0.130	478.5
	...	0.3210	1.83	0.188	496.3
	...	0.4242	2.41	0.247	520.3
p-Bromotoluene	19.61	0.2612	1.31	0.257	424.9
	...	0.4563	2.27	0.388	491.8
	...	0.6309	3.12	0.528	499.6
	19.82	0.1800	0.90	0.167	446.0
	...	0.3427	1.70	0.292	485.6
	...	0.4453	2.20	0.366	503.3

is a remarkable change with increasing concentrations, the latter change however being somewhat irregular, and the results are possibly not so accurate as might be wished. The free radical, in solution, is evidently monomolecular to the extent of 30 to 38%, and dimolecular to 62 to 70%.

Summary.

1. 2,2'-Sulfonido-triphenyl carbinol and the corresponding chloride were prepared. It was found that this chloride, unlike the chlorides of aryl thio-xanthenols, does not make additive colored compounds with hydrogen chloride.

2. The free radical, 2,2'-sulfonido-triphenylmethyl, was prepared. Its oxygen absorption, the degree of combination with iodine, and extent to which it exists as monomolecular have been determined.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO.]

THE FRIEDEL AND CRAFTS' REACTION. BROMOPHTHALIC ANHYDRIDES, BENZENE AND ALUMINUM CHLORIDE.

BY H. N. STEPHENS.

Rubidge and Qua[1] have studied the reaction between phthalic anhydride, benzene and aluminum chloride and have-shown the conditions which will give a good yield of o-benzoyl-benzoic acid, and also the conditions which will give no acid and a 35% yield of diphenylphthalide. Lawrance,[2] who used the nitrophthalic anhydrides and the acetylamino-phthalic anhydrides in this reaction, points out that from each substituted phthalic anhydride there are possible two acid products and two derivatives of diphenyl-phthalide.

[1] Rubidge and Qua, THIS JOURNAL, 36, 732 (1914).

[2] Lawrance, ibid., 42, 1871 (1920).