[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SPONTANEOUS DISSOCIATION OF TRIPHENYLMETHYL DISULFIDE WITH THE FORMATION OF TRIPHENYLMETHYL. THE POTASSIUM DERIVATIVE OF TRIPHENYL CARBINOL AND ITS USE AS A SYNTHETIC AGENT

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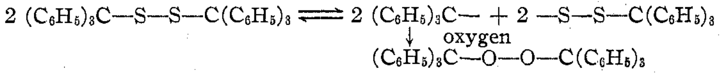
Received May 25, 1923

n-Pentamethylene-S-triarylmethyl-dithio-urethans dissociate spontaneously, in solution, with the formation of triarylmethyls; the latter were isolated in the form of their characteristic peroxides.[1]

It has now been found that triphenylmethyl disulfide also dissociates spontaneously, in solution, at ordinary temperature with the formation of triphenylmethyl; thus, when the colorless disulfide is dissolved in benzene the solution, colorless at first, soon assumes the deep yellow color which is characteristic for solutions of this radical. When air is passed into the solution, triphenylmethyl peroxide is precipitated. The rational explanation for the above phenomena is expressed as follows:[2]



$$2\,(C_6H_5)_3C{-}S{-}S{-}C(C_6H_5)_3 \rightleftharpoons 2\,\underset{\substack{\downarrow\ \text{oxygen}\\ (C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3}}{(C_6H_5)_3C{-}} + 2\,{-}S{-}S{-}C(C_6H_5)_3$$

A comparison of triphenylmethyl disulfide with triphenylmethyl peroxide, as regards dissociation, is interesting. Wieland[3] has shown that triphenylmethyl peroxide dissociates very readily when a xylene solution of the material is heated to the boiling point. The dissociation, in this instance, occurs not between the triphenylmethyl group and oxygen but through the severance of the bond between oxygen and oxygen.

It now seemed desirable to prepare the hitherto unknown thioperoxide, $(C_6H_5)_3C{-}S{-}O{-}C(C_6H_5)_3$, and study its behavior with regard to dissociation. It was thought that this substance might readily be prepared by reaction between triphenylmethyl sulfurchloride[4] and a metallic derivative of triphenyl carbinol. $(C_6H_5)_3C{-}S{-}Cl + M{-}O{-}C(C_6H_5)_3 = (C_6H_5)_3C{-}S{-}O{-}C(C_6H_5)_3 + MCl$.

Schlenk and Mair[5] have reported that the sodium derivative of triphenylcarbinol may be obtained by the action of metallic sodium upon a large excess of the molten carbinol at 185°. This method, however, is unsatisfactory since it is very difficult to free the hygroscopic sodium compound from the large amount of unchanged carbinol.

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[1] Blicke, THIS JOURNAL, **45**, 544 (1923).

[2] Judging from the yield of peroxide it seems that only one of the triphenylmethyl groups of the disulfide is obtained in the form of triphenylmethyl.

[3] Wieland, *Ber.*, **44**, 2550 (1911).

[4] Vorländer and Mittag, *ibid.*, **52**, 415 (1919).

[5] Schlenk and Mair, *ibid.*, **44**, 1076 (1910).

It was found that metallic potassium reacts readily with triphenyl carbinol when the latter is dissolved in boiling xylene. The potassium derivative which is formed is soluble in hot xylene but quite insoluble in the cold solvent and therefore crystallizes out of the latter quite pure.

$$2(C_6H_5)_3C—OH + 2K = 2(C_6H_5)_3C—OK + H_2.$$

Before undertaking a study of the reaction of the metallic compound with triphenylmethyl sulfurchloride it seemed desirable to study the reactions between the former substance and somewhat simpler compounds. Accordingly, the preparation of various triarylmethyl ethers and esters was attempted by treatment of the potassium compound with alkyl halides and acid chlorides, respectively. The potassium compound reacts readily with methyl iodide, and triphenylmethyl-methyl ether is formed in good yield: $(C_6H_5)_3C—OK + CH_3I = (C_6H_5)_3C—O—CH_3 + KI$. By the use of ethyl instead of methyl iodide little or none of the corresponding ethyl ether is formed, providing the reaction is carried out under the same conditions. In this instance, ethylene and triphenyl carbinol represent the reaction products: $(C_6H_5)_3C—OK + C_2H_5I = (C_6H_5)_3C—OH + C_2H_4 + KI$.

Benzoyl chloride reacts immediately with the metallic carbinol derivative with the formation of triphenylmethyl benzoate.

When an equivalent amount of triphenylmethyl sulfurchloride, dissolved in benzene, was added to the potassium compound, heat was developed and a red-brown solution resulted. The only crystalline, organic products that could be isolated from the reaction mixture were triphenyl carbinol and triphenylmethyl peroxide. Since a considerable amount of potassium chloride was formed, it seems that triphenylmethyl thioperoxide must have been produced initially; the peroxide may have resulted from the interaction of the thioperoxide and unchanged potassium compound: $2(C_6H_5)_3C—S—O—C(C_6H_5)_3 + 4(C_6H_5)_3C—OK = 3(C_6H_5)_3C—O—O—C(C_6H_5)_3 + (C_6H_5)_3C—C(C_6H_5)_3 + 2K_2S$. This explanation of the formation of the peroxide receives support through the fact that triphenylmethyl sulfurchloride reacts with sodium methylate with the formation of triphenylmethyl-methyl thioperoxide;[6] when an excess of the alcoholate was used there resulted only a sulfur-free compound which the above-mentioned investigators suspected was triphenylmethyl peroxide. We have repeated this work and found that the sulfur-free substance was unquestionably peroxide. When the potassium compound of triphenyl carbinol was added to the triphenylmethyl sulfurchloride, in the attempt to avoid an excess of the former substance at any time during the reaction, peroxide was again obtained.

The potassium compound reacts with triphenylchloromethane and it was thought that the resulting product might be triphenylmethyl ether, formed in accordance with the equation, $(C_6H_5)_3C—OK + Cl—C(C_6H_5)_3 =$

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[6] Ref. 4, p. 416.

$(C_6H_5)_3C—O—C(C_6H_5)_3$ + KCl. However, in the examination of the reaction product no ether was found. From the mixture of products formed *p*-hydroxytriphenyl carbinol was isolated; the latter was probably present in the reaction mixture in the form of its anhydride, diphenyl-quinomethane. It is interesting to compare this result with that obtained by Gomberg[7] when he attempted to prepare triphenylmethyl ether by the action of silver oxide upon triphenylchloromethane in benzene solution. In this case, also, the desired ether was not obtained and diphenyl-quinomethane was isolated as a product of the reaction. If it is assumed that Gomberg obtained $(C_6H_5)_3C—O—Ag$ as the initial product in his experiment, the two reactions then become comparable.

In addition, it was found that the potassium compound of triphenyl carbinol reacts at once with iodine, phosphorus trichloride and other substances which contain reactive halogen.

Experimental Part

Triphenylmethyl Disulfide.—This compound was readily prepared from triphenyl thiocarbinol according to the method of Vorländer and Mittag;[8] the formation of the thiocarbinol, however, does not proceed smoothly. The investigators mentioned were the first to prepare triphenyl thiocarbinol; their method consists in treating triphenylchloromethane with sodium hydrogen sulfide, using ethyl alcohol as a solvent. Unfortunately, the method is not an entirely reliable one and occasionally fails to yield the desired product;[9] this is due to the fact that triphenylchloromethane reacts with the ethyl alcohol, used as a solvent, with the greatest ease to form triphenylmethyl ethyl ether. We have been able to prepare the thiocarbinol by the action of potassium hydrogen sulfide on triphenylchloromethane, using benzene as a solvent. The potassium hydrogen sulfide,[10] prepared from 6 g. of potassium, was added to 14 g. of triphenylchloromethane, dissolved in 80 cc. of dry benzene. After the mixture had been shaken for 1 week the reaction mixture was filtered and the solvent allowed to evaporate. The slightly gummy product thus obtained was converted directly into triphenylmethyl sulfurchloride and then into the disulfide. The yield of the sulfurchloride compound, based on triphenylchloromethane, never exceeded 50% of that calculated.

Dissociation of the Disulfide.—A solution of 2.7 g. of the disulfide in 15 cc. of dry benzene immediately became deep yellow, the color of dissolved triphenylmethyl. A fairly rapid stream of dry air was passed through this solution and the escaping air was led into aqueous potassium hydroxide. The benzene solution soon became cloudy and after 1 hour quite a heavy precipitate had formed. After 8 hours the precipitated material was separated, washed with hot carbon disulfide and quickly recrystallized from toluene. The compound thus obtained melted at 185°; mixed with triphenylmethyl peroxide, prepared from triphenylchloromethane and molecular silver, the melting point of the mixture was found to be 185–186°. The yield of peroxide was 0.82 g. The alkaline solution was found to contain potassium sulfite, thus showing that sulfur dioxide had also been formed during the reaction.

In another experiment, 2.25 g. of the disulfide, dissolved in 10 cc. of benzene, was used. After air had been passed through the solution for 1 hour no peroxide appeared

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[7] Gomberg, THIS JOURNAL, **35**, 202 (1913).

[8] Vorländer and Mittag, *Ber.*, **46**, 3453 (1913).

[9] Mittag, *Dissertation*, Halle, **1915**.

[10] Bloxam, *J. Chem. Soc.*, **77**, 758 (1900).

but the latter soon settled out of the solution when the sides of the containing flask were rubbed with a stirring rod; yield of peroxide, after 12 hours, 0.70 g.

Potassium Derivative of Triphenyl Carbinol.—A mixture of 11.5 g. of pure, dry triphenyl carbinol and 100 cc. of xylene, which had previously been refluxed over metallic sodium and then distilled, was put into a 500cc. round-bottom, 3-neck flask. The latter was fitted with a reflux condenser, which was closed with a soda-lime tube, and an inlet tube. After the air in the flask had been displaced by dry nitrogen 1.5 g. of potassium was added; the mixture was then refluxed, enough heat being applied to keep the xylene boiling fairly vigorously. A continuous stream of nitrogen was passed through the flask. After 3 to 4 hours the potassium had practically all disappeared. As the clear, hot solution cooled, the potassium compound precipitated at once in the form of colorless, transparent crystals. After 12 hours the supernatant liquid was decanted and the crystalline material removed from the flask. During the latter operation the material was protected from atmospheric moisture by a stream of nitrogen; yield of crystals, about 10 g.

When the transparent crystals were heated to 220°, under 20 mm. pressure, an amount of xylene was evolved that corresponded to about 21% of the weight of the original material; calcd. loss for 1 molecular equivalent of xylene, 25%. The material, which did not melt during this process, was converted into an opaque, granular substance. For the purposes of synthesis it is not necessary to free the potassium compound from xylene.

When exposed to the air the crystalline product is quickly converted into a powder. Contact with moisture changes the material to triphenyl carbinol and potassium hydroxide; a weighed portion of the xylene-free compound was thrown into water, the resulting potassium hydroxide estimated and was found to be 93.4% of the calculated amount. The low result is due to the fact that a small amount of carbinol, which was used in slight excess in the preparation of the compound, always settles out of the xylene.

Reaction with Methyl Iodide.—A mixture of 10 g. of the potassium compound (the material containing xylene of crystallization was used in this and in all subsequent experiments), 12 g. of pure methyl iodide and 30 cc. of dry benzene was gently refluxed for 2 hours, then poured into an evaporating dish and, after the solvent had evaporated, the crystalline residue was washed with water until free from potassium iodide.[11] The dried material was boiled with 50 cc. of petroleum ether (80–100°) and then filtered. The first crop of crystals which appeared upon cooling proved to be carbinol, later the methyl-triphenylmethyl ether crystallized in pure condition. The substance melts at 83–4° as given in the literature.[12] Yield 6 g., or 82% of the calculated amount.

Reaction with Ethyl Iodide.—Ten g. of the potassium compound, 12 g. of ethyl iodide and 30 cc. benzene were refluxed for 2 hours in a 100cc. flask. The gas evolved during the reaction amounting to 480 cc. (N. T. P.) was collected over water, backward diffusion of moisture into the reaction flask being prevented by a calcium chloride tube, and proved to be ethylene by converting it into ethylene bromide and identification of the latter by its melting and boiling points. The amount of ethylene found corresponds to 78% of that calculated. 7.0 g. of triphenyl carbinol was obtained; calc., 6.9.

Reaction with Benzoyl Chloride.—A mixture of 8 g. of the potassium compound, 3.8 g. of carefully purified benzoyl chloride and 30 cc. of benzene reacted immediately with considerable evolution of heat, moisture having been carefully excluded. After

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[11] A trace of unchanged potassium often remains mixed with the potassium compound. It is advisable, therefore, to treat the reaction mixture as described above; during the evaporation of the solvent the atmospheric moisture reacts with the potassium and the solid residue may then safely be treated with water.

[12] Hemilian, *Ber.*, **7,** 1208 (1874). Straus and Hüssy, *ibid.*, **42,** 2176 (1909).

24 hours the reaction mixture was poured into an evaporating dish, the solvent was removed and the organic matter was extracted with hot benzene. The benzene solution was concentrated under reduced pressure; triphenylmethyl benzoate separated from the cold, concd. solution in good yield. The compound was further purified by recrystallization from a mixture of chloroform and petroleum ether. The ester melts at 165–166°.

For the purpose of comparison the ester was prepared by another method: 4 g. of triphenylchloromethane, 6.5 g. of silver benzoate and 50 cc. of benzene were heated to 60°, for 4 hours, in a bath. After the benzene had been removed from the reaction mixture by evaporation, the organic material was recrystallized twice from benzene. The ester, prepared by this method, melted at 165–166°.

One g. of the ester was hydrolyzed quantitatively by boiling for 1 hour with 30 cc. of water containing a few drops of sulfuric acid.

Reaction with Triphenylmethyl Sulfurchloride.—A mixture of 8 g. of the potassium compound, suspended in 30 cc. of benzene, with an equivalent amount of triphenylmethyl sulfurchloride dissolved in the same solvent, became warm, and after standing for 24 hours protected from moisture the clear, red-brown solution was poured into an evaporating dish. The presence of a gelatinous, transparent precipitate, presumably colloidal potassium chloride, which was obtained in all of the reactions, made filtration of the reaction mixture impossible. After spontaneous evaporation of the benzene the residue was treated with dry ether; from the latter triphenyl carbinol was obtained. The ether-insoluble residue was washed with water to remove potassium chloride, dried, and then dissolved in a small amount of boiling toluene. As the solution cooled, triphenylmethyl peroxide was obtained.

Reaction with Triphenylchloromethane.—Equivalent amounts of triphenylchloromethane and the potassium derivative of the carbinol, suspended in benzene, were shaken in a sealed tube. After 4 hours the mixture was deep red and after 4 days the contents of the tube consisted of a heavy gelatinous precipitate and an orange-colored liquid. Absolute ether was added and the mixture was filtered; the filtrate was then heated under diminished pressure until the solvent was removed. The residue, which consisted of crystals and an orange-colored oil, was dissolved in acetone and, after the addition of 5% sodium hydroxide solution, was heated on a steam-bath until all of the acetone had evaporated. After filtration from alkali-insoluble material the filtrate was concentrated to a small volume; flaky crystals, possessing a pearly luster, were formed as the solution stood. This material was the sodium salt of *p*-hydroxytriphenyl carbinol. It was converted into both the colorless benzenoid and the yellow quinonoid forms of the hydroxycarbinol.[13] When the yellow form of the carbinol was heated at 110° for several hours the brown-yellow fuchsone resulted; after several recrystallizations from benzene and petroleum ether this melted[14] at 166–167°.

Summary

1. Triphenylmethyl disulfide dissociates spontaneously, in solution, at ordinary temperature with the formation of triphenylmethyl; the latter was isolated in the form of its peroxide.

2. The potassium derivative of triphenyl carbinol was prepared. It reacts with alkyl halides to form ethers and with acid chlorides to form esters. In some instances, however, the potassium compound reacts abnormally.

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[13] Gomberg, THIS JOURNAL, **35**, 1037 (1913).

[14] Bistrzycki and Herbst, *Ber.*, **36**, 2335 (1903).