2. Of the dibasic acids, oxalic is unattacked, while succinic and glutaric yield anhydrides and malonic, suberic and sebacic acids form dichlorides.

3. Tartaric acid is unattacked.

4. Of the unsaturated dibasic acids employed, maleic forms an anhydride and fumaric acid is unchanged.

5. Of the benzoic acids, the three nitrobenzoic acids all form the acid chlorides. The *p*-nitrobenzoyl chloride is formed only with difficulty due to the presence of the negative nitro group in the para position. Acid chlorides of *m*-and *p*-aminobenzoic acid can be prepared by this method. The ortho acid does not form an acid chloride.

6. Only by the use of thionyl chloride can the acid chlorides of some of the aromatic hydroxy acids be prepared. *o*-Hydroxybenzoic acid forms an acid chloride while the para acid does not. *m*-Hydroxybenzoic acid and the cresotinic acids gave products which could not be identified as acid chlorides as stated by Meyer.

7. Of the phthalic acids, the ortho acid forms an anhydride, the meta acid a dichloride and the para acid is not attacked by thionyl chloride.

8. The action of thionyl chloride on other organic acids is being continued in this Laboratory.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

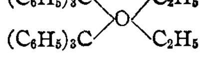
THE HEXAPHENYLETHANE ALKYL SULFIDE ADDITION COMPOUNDS[1]

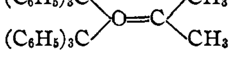
BY VICTOR C. ROGERS[2] AND GREGG DOUGHERTY

RECEIVED JUNE 27, 1927 PUBLISHED JANUARY 5, 1928

Introduction

Hexaphenylethane (triphenylmethyl) possesses the property of forming addition products with a great variety of organic substances.[3,4] The majority of these addition products have a composition corresponding to the ratio of one mole of hexaphenylethane to one mole of the substance added. In the case of the additions involving esters, ethers and ketones,[5] the oxonium theory is probably applicable, as follows





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[1] This article is based upon a thesis submitted by Victor C. Rogers to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] DuPont Fellow in Chemistry.

[3] Pfeiffer, "Organische Molekülverbindungen," F. Enke, Stuttgart, **1922**, p. 250.

[4] Schmidlin, "Das Triphenylmethyl," F. Enke, Stuttgart, **1914**, p. 75.

[5] (a) Gomberg, *Ber.*, **34**, 2730 (1901); (b) **38**, 2449 (1905).

However, the later discovery of addition products of hexaphenylethane with both olefin and saturated hydrocarbons,[6] in which the nature of the binding cannot be so explained, has led to some hesitation in suggesting structures for these complexes.

The alkyl sulfides are known to form a great number of complexes with both organic[7,8] and inorganic compounds.[9] The nature of some of these complexes has been interpreted by the use of the sulfonium theory, analogously to the conception of the oxygen linked complexes. One might expect then that hexaphenylethane with its remarkable additive tendency would form complexes with the alkyl sulfides. No mention of the formation of these substances is to be found in the literature, except for the statement by Schmidlin[10] that they have not been prepared. The preparation and a study of the properties of the methyl, ethyl and propyl sulfide addition products have been undertaken. The details of the preparation are found in the experimental part.

Properties of the Crystalline Addition Compounds

The crystals are colorless to light yellow in color. They are easily soluble in such solvents as benzene, ether, chloroform and the organic sulfides. The solutions are very sensitive to the action of the oxygen of the air; on standing in open vessels or when air or oxygen is passed through the solutions, the characteristic white peroxide is precipitated.[4]

We expected to find the sulfide addition compounds to be much more stable or inert than the analogous compounds involving oxygen linkage. Such is not the case. The strength of the bond between the sulfide and the hexaphenylethane appears to be of the same order as that in the complexes with ethers and esters. The sulfide is partially lost by washing the crystals with solvents of various kinds. The crystals also give up the alkyl sulfide when placed in a slow stream of carbon dioxide. This occurs to some extent even at room temperatures; a sample standing overnight lost about 20% of its sulfur content.

In the formation of the addition compounds of hexaphenylethane with esters, ketones, carbon disulfide, etc., Gomberg and Cone[11] found that although in general the ratio of the added substance to hexaphenylethane was one mole to one mole, varying results were obtained depending upon the temperature of preparation, nature of the solvent used to wash the crystals of the addition product and the amount of washing done. In the case of the ethyl sulfide addition product we obtained a consistently

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[6] Gomberg and Schoepfle, THIS JOURNAL, **37**, 2569 (1915).

[7] Oefele, *Ann.*, **132**, 82 (1864).

[8] Cahours, *Ann.*, **135**, 352 (1865).

[9] Ref. 3, p. 125.

[10] Ref. 4, p. 81.

[11] Gomberg and Cone, *Ber.*, **38**, 1333, 2447, 2451 (1905).

good ratio. With the methyl sulfide addition product greater irregularities of composition were encountered. However, there is no doubt that the figures (see experimental part) are of the magnitude demanded by the 1:1 ratio of the hexaphenylethane to the methyl sulfide. No satisfactory results were obtained with the crystals separating from the propyl sulfide. In this case careful drying resulted in a very low sulfur content, while less rigid drying gave a percentage somewhat above the theoretical value. It is interesting to note that the dipropyl ether compound with hexaphenylethane which Gomberg and Cone[12] prepared also gave no constant figure for the ether content.

Oxidation of the Alkyl Sulfide Addition Products

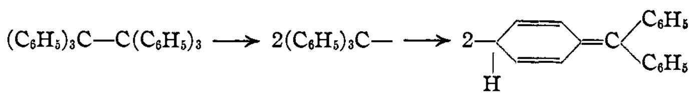
The absorption of oxygen by solutions of hexaphenylethane and related compounds has been shown by Gomberg and his co-workers[13] to be of the magnitude to warrant the equation

$$(C_6H_5)_3C—C(C_6H_5)_3 + O_2 \longrightarrow (C_6H_5)_3C—O—O—C(C_6H_5)_3$$

However, the reaction is clearly influenced by outside factors, for the yield of the triphenylmethyl peroxide may vary considerably according to the solvent used,[14] and also depending upon whether pure oxygen or air is used as the oxidizing agent.[15]

Now Moureu and Dufraisse[16] have pointed out the activity of sulfides, including the alkyl sulfides, in altering the rate of oxidation of auto-oxidizable substances, while Taylor[17] has pointed out the connection between catalysis of auto-oxidation and the property of addition complex formation.

It had been observed during the course of the work that the yellow color of the solutions of hexaphenylethane in pure alkyl sulfides was considerably deeper than when benzene or ether was used as the solvent. If the color is due to quinoxidation as proposed by Gomberg,[18] and Jacobson,[19] it would seem that the alkyl sulfides possess the property of shifting the equilibrium markedly toward the quinoid tautomer.



A test of this hypothesis could be made by studying the oxidation of hexaphenylethane in alkyl sulfide solutions, because it has been established

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[12] Gomberg and Cone, *Ber.*, **38**, 2449 (1905).

[13] Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, **1924**, p. 88.

[14] Gomberg and Sullivan, This Journal, **44**, 1817 (1922).

[15] Gomberg and Cone, *Ber.*, **37**, 3538 (1904).

[16] Moureu and Dufraisse, *Compt. rend.*, **178**, 1861 (1924).

[17] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

[18] (a) Gomberg, *Am. Chem. J.*, **25**, 334 (1901); (b) *Ber.*, 1824 (1902).

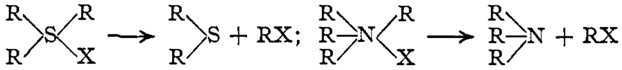
[19] Jacobson, *Ber.*, **38**, 196 (1905).

that the colored modification is rapidly transformed by air or oxygen into triphenylmethyl peroxide.[20]

Experiments were carried out to measure the rate of oxidation of hexaphenylethane in the presence of alkyl sulfides and also in the presence of other additive substances. The results as pictured by the curve in the experimental part show clearly that the presence of the alkyl sulfides has a marked accelerating effect. This may be explained by assuming that the sulfide increases the concentration of the quinoid or easily oxidized tautomer. Total absorption measurements showed this to be unaffected by the presence of the sulfides.

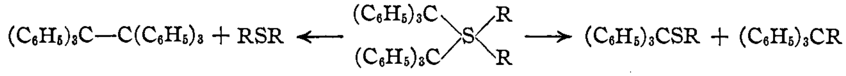
Thermal Decomposition of the Alkyl Sulfide Addition Products

When the alkyl sulfonium compounds and the quaternary ammonium compounds are heated, the following type of splitting occurs



$$\left.\begin{matrix}R\\R\end{matrix}\right\rangle S\left\langle\begin{matrix}R\\X\end{matrix}\right. \longrightarrow \left.\begin{matrix}R\\R\end{matrix}\right\rangle S + RX;\quad \left.\begin{matrix}R\\R\\R\end{matrix}\right\rangle N\left\langle\begin{matrix}R\\X\end{matrix}\right. \longrightarrow \left.\begin{matrix}R\\R\\R\end{matrix}\right\rangle N + RX$$

If the hexaphenylethane-alkyl sulfide complexes possess the sulfonium structure, an analogous splitting should occur and probably in two ways, as follows



$$(C_6H_5)_3C—C(C_6H_5)_3 + RSR \longleftarrow \left.\begin{matrix}(C_6H_5)_3C\\(C_6H_5)_3C\end{matrix}\right\rangle S\left\langle\begin{matrix}R\\R\end{matrix}\right. \longrightarrow (C_6H_5)_3CSR + (C_6H_5)_3CR$$

so that we should find among the decomposition products mixed sulfides containing the triphenylmethyl group, and hydrocarbons of the α, α, α-triphenyl paraffin type.

It has been noticed that when the addition compounds of hexaphenylethane are warmed, they lose to a greater or less extent the added substance. In some cases this loss is nearly quantitative, but in other cases the result is below that corresponding to the one mole to one mole addition ratio. Furthermore, it has been observed frequently that the material left after driving off the added substance had not entirely the properties of hexaphenylethane. In the case of the sulfide additions, a positive test for sulfur in the residue indicated a decomposition in addition to the simple dissociation of the addition compound.

Attempts were made to retard the dissociation by heating in sealed tubes. Although complex, the resulting mixture could be separated into two classes—complex hydrocarbons of low volatility, probably of the α, α, α,-triphenyl paraffin type, and compounds containing sulfur and triphenylmethyl groups, also of low volatility. These results are explained most simply by the assumption of a sulfonium structure for the addition compound and a splitting in such a way that the two triphenylmethyl groups are separated to take part in the formation of two new molecules

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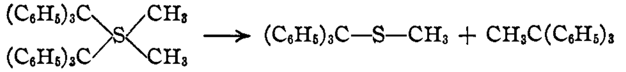
[20] Schmidlin, *Ber.*, 41, 2476 (1908).



$$\left((C_6H_5)_3C\right)_2S(CH_3)_2 \longrightarrow (C_6H_5)_3C{-}S{-}CH_3 + CH_3C(C_6H_5)_3$$

Experimental Part

Preparation of the Addition Compounds.—The hexaphenylethane was prepared by treatment of a solution of triphenylmethyl chloride with mercury.[21] It was found most convenient to prepare the addition compounds by using the respective sulfides as the solvent in which to prepare the hexaphenylethane. The preparation was carried out in a large deformed "U"-tube. The limbs of the "U" were sealed and near the bend was affixed a small side arm. Through this arm the reactants were introduced into the far limb of the vessel. Two and seven-tenths g. of triphenylmethyl chloride, 1.7 cc. of mercury and 8–10 cc. of carefully dried alkyl sulfide were used in each preparation. The vessel was then evacuated until quiet boiling of the solvent displaced most of the air present. The side arm was then sealed and the vessel agitated in such a manner that the mixture was always confined to one arm of the "U."

After agitating for two or three days the vessel was supported vertically and the mixture allowed to settle, after which the clear, deep yellow solution of hexaphenylethane was decanted carefully into the opposite arm of the "U." By warming the limb containing the solution and cooling the other most of the solvent was distilled away from the hexaphenylethane. Upon standing, colorless or pale yellow crystals separated. After crystallization the mother liquor was decanted back into the opposite limb and then by cooling the limb containing the crystals pure solvent was condensed upon the crystals for washing them. When the crystals were washed sufficiently they were dried by warming them gently or by cooling the opposite limb in a cooling mixture. In this manner the crystals were prepared, washed and dried in an atmosphere free from oxygen. When the operation was completed, the limb of the vessel was circled with a file scratch and broken off in an atmosphere of carbon dioxide. The above method yielded from one to two grams of solid product from each preparation.

Analysis.—Qualitative examination of the crystals showed no mercury, a trace of chlorine and a strong test for sulfur.

An attempt was first made to analyze the compounds after the method of Gomberg and Cone[12] by heating them in a stream of carbon dioxide to 60–80° until constant weight was attained. The loss of alkyl sulfide was always below the theoretical amount and the residue gave a test for sulfur, indicating that all of the sulfide was not lost in this way.

Determination of the sulfur content of the crystals was carried out by first heating in a Carius tube at 200° for eight hours with fuming nitric acid and a drop or two of bromine. This was followed by a fusion with a mixture of potassium hydroxide and sodium peroxide. The sulfur was then determined in the usual manner as barium sulfate.

The results were as follows:

Ethyl sulfide-hexaphenylethane: Calcd.: S, 5.56. Found: 5.48, 5.42, 5.43. Methyl sulfide-hexaphenylethane: Calcd.: S, 5.83. Found: 6.02, 5.31, 5.28, 4.98, 4.80, 4.83. Propyl sulfide-hexaphenylethane: Calcd.: S, 5.31. Found: 2.90, 2.78, 2.28, 1.30, 6.56, 6.33, 5.96, 7.37.

Oxidation Rate.—The alkyl sulfide-hexaphenylethane addition product was not isolated in the solid form for these experiments, but a solution resulting from the conversion of a definite amount of triphenylmethyl chloride in bromobenzene solution containing an equivalent of the additive substance was used. One-fourth of a gram of triphenylmethyl chloride, 0.5 cc. of mercury and 10 cc. of dry bromobenzene containing about four drops of the sulfide were sealed in an 11cc. thin-walled bulb which had been pre-

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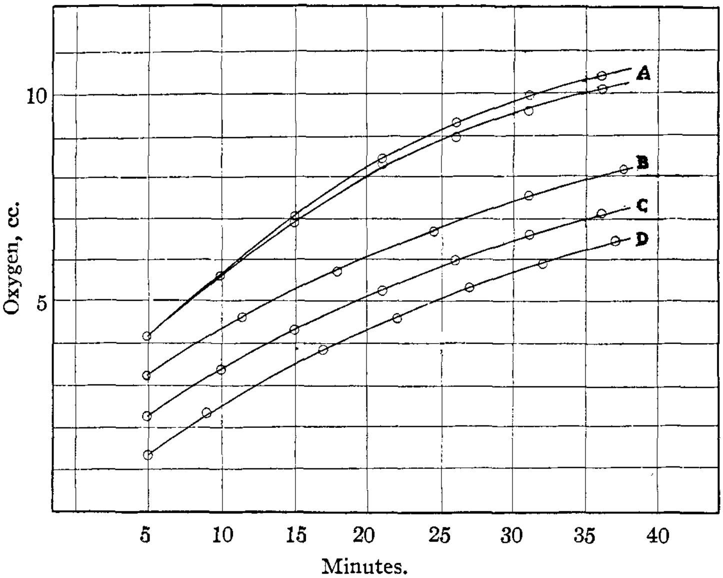
[21] Ref. 4, p. 30.

viously dried and swept out with nitrogen. This bulb was then agitated vigorously for eight hours, at which time all of the triphenylmethyl chloride had been converted to hexaphenylethane as shown by a total absorption. The bulb was then placed in a small vessel equipped with a manometer and a plunger for breaking the bulb. After the introduction of a few drops of bromobenzene the vessel was swept out with oxygen, closed and a few moments allowed for the saturation of the confined oxygen with bromobenzene vapor.

After recording the temperature, pressure and the position of the levels of the manometer tubes, the bulb containing the sample was completely crushed by striking the plunger in the vessel. As the oxygen in the vessel was absorbed, atmospheric pressure was maintained by continuous adjustment of the manometer levels. The position of the adjusted levels of the manometer was periodically recorded. The absorptions were carried out at 23.5°.



A, alkyl sulfide; B, acetone; C, carbon disulfide; D, bromobenzene.

Fig. 1.

The curves shown represent about two-thirds of the total absorption taking place over about forty minutes of time. The starting point of all of the curves is the same but the curves have been moved apart in order to emphasize the similarity of difference of slope. It is apparent from Curves II and III that the rate of oxidation is the same in the case of carbon disulfide and acetone and that it does not differ from the rate when bromobenzene alone is used. Curve I, on the other hand, representing the rate of oxidation in the presence of alkyl sulfides, has a much steeper slope than the other three, particularly during the first two-thirds of the reaction time.

Total Absorption.—Samples of hexaphenylethane in bromobenzene and in bromobenzene containing an equivalent amount of ethyl sulfide were prepared in the same manner as those used for the rate absorption measurements. These were placed in a glass-stoppered bottle which was connected to the mercury manometer of the previously used apparatus by means of a heavy-walled rubber tube. The bottle was shaken vigorously for five minutes. With the breaking of the sample tube the mercury rose immediately and at the end of five minutes the sample had absorbed from 11.2 to 11.3 cc. of oxygen, more than 10 cc. of this being absorbed in the first minute. At the end of the first minute the rate was very slow.

For three samples in bromobenzene only the absorption was: (a) 11.2, (b) 11.2, (c) 11.3; theoretical, 11.8. For three samples in bromobenzene containing ethyl sulfide: (a) 11.2, (b) 11.3, (c) 11.3.

Thermal Decomposition of the Addition Product.—A sample of hexaphenylethane dissolved in a large excess of methyl sulfide was heated in a sealed tube at 150° for eight hours. The resulting mixture was still yellow in color. Enough benzene was added to attain solution. Air was passed through the solution in order to convert any unchanged hexaphenylethane to the difficultly soluble peroxide. The small amount of solid resulting was separated by filtration. The filtrate was then evaporated and the solid residue was separated into several parts by fractional crystallization with petroleum ether and alcohol as solvents.

All of these fractions were solids or thick oils. Some contained sulfur and others did not. No attempt was made to carry out ultimate analyses since difficulties of purification and the probable slight variation in the composition of the hydrocarbons of high molecular weight made it extremely doubtful whether information could be obtained in this way. The fractions containing no sulfur showed, however, the general characteristics of hydrocarbons of the triphenyl paraffin class. They were extremely soluble in benzene, petroleum ether, chloroform, carbon tetrachloride, ether and acetone. They were slightly soluble in alcohol and could be recrystallized from this solvent. Concentrated solutions in benzene and petroleum ether showed a strong tendency to supercool and set to a hard, glassy mass without crystallizing. The solids were neither colored nor dissolved by concentrated cold sulfuric acid. Warm acid (80–90°) brought about partial solution and a slight coloring, but dilution of the mixture with water precipitated the substance unchanged.

The sulfur-containing solids were non-volatile and practically odorless; consequently the sulfur could not be present as originally in the molecule of the comparatively low-boiling alkyl sulfide. Attempts to recrystallize some of the sulfur-containing portions resulted in the appearance of the insoluble triphenylmethyl peroxide. This behavior is characteristic of sulfides and disulfides[22] containing triphenylmethyl groups. Also char-

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[22] Blicke, This Journal, 45, 1965 (1923).

acteristic is the ready solubility and yellow to brown coloration in cold sulfuric acid. When the sulfuric acid solutions were warmed, alkyl mercaptans were evolved. The resulting solution when cooled, diluted and made alkaline yielded a solid precipitate which proved to be triphenylcarbinol.

$$(C_6H_5)_3C—S—R + H_2O\ (H_2SO_4) \longrightarrow (C_6H_5)_3C—OH + H—S—R$$

It seems certain, after consideration of the evidence, that our sulfur-containing products were of the triphenylmethyl alkyl sulfide class.[23]

The authors wish to express their appreciation for the suggestions offered by Professor L. W. Jones during the course of the investigation and also for the aid of the duPont Fellowship held by one of us during the latter part of the work.

Summary

1. Addition products of methyl, ethyl and propyl sulfides with hexaphenylethane have been prepared.

2. It has been found that the alkyl sulfides accelerate the rate of oxidation of hexaphenylethane in bromobenzene solution. This is apparently not so with carefully purified carbon disulfide and acetone, which also yield addition products with hexaphenylethane.

3. Observations have been made concerning the probable course of the thermal decomposition of the hexaphenylethane methyl sulfide addition product.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

CONDENSATION PRODUCTS OF BENZALACETOPHENONE AND SOME OF ITS DERIVATIVES[1]

BY L. CHAS. RAIFORD AND H. L. DAVIS

RECEIVED JUNE 30, 1927 PUBLISHED JANUARY 5, 1928

Fischer and Knoevenagel[2] found that phenylhydrazine and acrolein react to give 1-phenylpyrazoline instead of the expected hydrazone. Much later Auwers and Müller[3] argued that this product is formed through the rearrangement of an unstable hydrazone, and noted that in those

$$C_6H_5—NH—N{=}C(H)—CH{=}CH_2 \longrightarrow C_6H_5—N—N{=}C(H)—CH_2—CH_2 \text{ (ring)}$$

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[23] Ref. 4, p. 124.

[1] From a portion of the thesis submitted to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy by H. L. Davis, August, 1925.

[2] Fischer and Knoevenagel, *Ann.*, **239**, 194 (1887).

[3] Auwers and Müller, *Ber.*, **41**, 4230 (1908).