

THE REACTION OF FREE RADICALS
WITH SILVER SALTS

A D i s s e r t a t i o n

Submitted in Partial Fulfillment of the Requirements
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By
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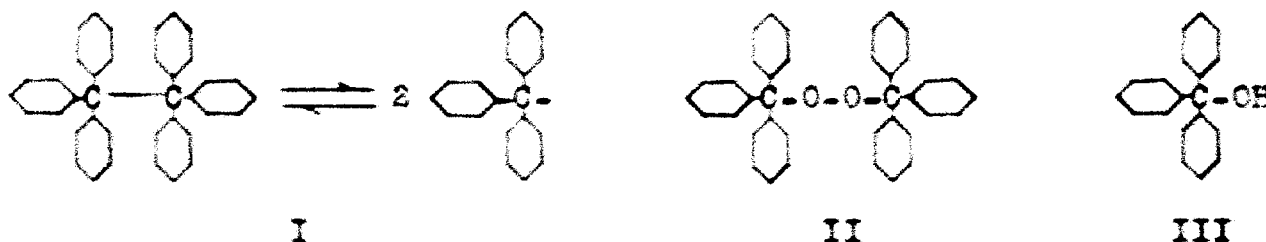
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INTRODUCTION

Metallic Properties of Triarylmethyls

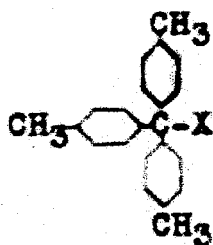
Shortly after the discovery of triphenylmethyl by Gomberg in 1900¹, Baeyer² drew attention to the formal relationship of free radicals to the elementary metals. Since triphenylmethyl (I) exists in the free state as do metal atoms, Baeyer reasoned that it is in reality a "compound metal." In support of his hypothesis he pointed out that triphenylmethyl, like sodium, forms a peroxide (II), and that triphenylcarbinol (III), like aluminum hydroxide, although itself not basic, forms salts with acids. From the modern point of view the analogy may be stated more precisely; both free radicals and metals possess unshared electrons.



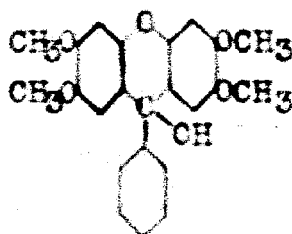
That triphenylmethyl and its salts are capable under the proper conditions of becoming good conductors is somewhat better evidence of a more than purely formal relationship. Gomberg³, and Walden⁴, early showed that triphenylmethyl, dissolved in liquid sulfur dioxide or in liquid hydrogen cyanide, is a good conductor. Recent investigation of the absorption spectrum of triphenylmethyl in the former solvent indicates that actually the triphenylmethyl cation is formed, presumably by transfer of the odd electron to

the solvent.⁵ The mechanism of conductivity by triphenylmethyl in this medium is therefore analogous to electrolytic conductivity by solutions of metals such as sodium dissolved in liquid ammonia.⁶ The triphenylmethyl halides, especially the bromide, also give appreciable conductivities in liquid sulfur dioxide, and even in cyanobenzene the conductivity of triphenylchloromethane is measurable.⁷ Diphenylbromomethane on the other hand shows no such tendency.

With certain substituted triarylcabinols, basicity is manifest even in non-polar solvents. Tousley and Gomberg⁸ demonstrated that the tri-p-tolylmethyl halides (IV) are conductors in cyanobenzene and Norris⁹ found that the electrolysis of an acetone solution of tri-p-tolylchloromethane leads to the production of a deep red color at the cathode, presumably because of the formation of the free radical, tri-p-tolylmethyl. Kehrmann¹⁰ has shown that certain of the xanthone derivatives exhibit enhanced basicity. For example, 2,3,6,7-tetramethoxy-9-phenylxanthanol (V) is strongly basic and its salts are water soluble. Kaufmann¹¹, and Lund¹², found the same properties in polymethoxytriphenylcarbinols, and there is evidence that salts of some of these carbinols are ionized even in the solid state.



IV



V



VI

In 1914 Cone¹³ observed that the chloride and sulfate of C-phenyl-N-phenylacridyl (VI) are soluble in and not hydrolyzed by water, and that aqueous solutions of these salts readily conduct a current. The electrolysis of either salt results in a good yield of the ethane at the cathode. Addition of zinc dust to an aqueous solution of the sulfate causes liberation of the free radical and the formation of zinc sulfate.^a

In the past fifteen years, Conant and his collaborators have prepared a large number of free radicals by a method which may be interpreted in terms of the metallic properties of free radical systems. In general, Conant found that triarylcabinols may be reduced to the corresponding free radicals by strong reducing agents depending upon the proper regulation of two conditions:^{14, 15}

(1) The carbinol must be dissolved in an acid medium, the strength of acid necessary being dependent upon the basicity of the carbinol and (2) A reducing agent of normal potential -0.20 volt (referred to hydrogen) or lower must be used for a rapid reduction. If the acidity of the carbinol solution is diminished the reductions become very slow; the same effect is noted if titanium trichloride ($E_0 = -0.04$ volt) is used in place of hypovanadous chloride or chromous chloride, unless the corresponding ethane is quite insoluble. Wanscheidt and Moldavski¹⁶ found however, that similar reductions of triarylcabinols ensue with stannous chloride ($E_0 = -0.13$ volt) in strongly acid solutions.

^aThe interpretation of these properties depends upon the constitution assigned to the acridyl derivatives. Many investigators claim that they form ammonium-like ions and not carbonium ions.

Conant interpreted these results from the electrochemical viewpoint. An acid medium is considered necessary to produce a polar "onium" ion. The reduction occurs therefore by interaction of the metal ion with the organic cation and is considered analogous to the reduction of stannous chloride to metallic tin by chromous chloride.²

He has, moreover, been able to show that a solution containing both a dissociable ethane and its halochromic salt gives rise to a characteristic and reproducible electrode potential.^{15, 17} The measured values agree quite closely with those calculated from the electrochemical equations. Such relations can of course be true only for strictly reversible processes, the process here concerned being:



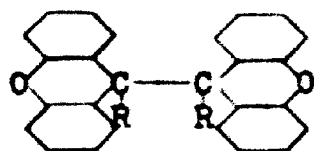
In further support of his viewpoint, Conant found that only those ethanes which dissociate appreciably in solution give reproducible electrode potentials; dixanthyl (VIIa) and tetraphenylethane (VIII), which exist entirely in the dimolecular form, may be prepared from the corresponding halochromic ions by reduction with hypovanadous chloride, but do not give characteristic potentials.¹⁵

The cation concentration of the system $R_3C \cdot$, R_3C^+ in Conant's experiments is governed by the equilibrium:



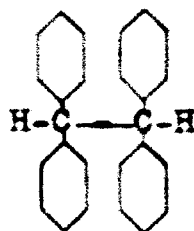
^aThis interpretation is subject to some criticism. Krauss¹⁸ was able to reduce such substances as triarylmethyl formates and triarylcarbinols in alcohol or in acetone solutions with aqueous or even with alcoholic solutions of titanium trichloride. Furthermore, he pointed out that benzophenone dichloride and benzhydrol which are known to be non-ionized are readily and quantitatively reduced by titanium trichloride to tetraphenylethylene and tetraphenylethane respectively.

In the pH range where hydrolysis is negligible the potential was found to be reproducible and independent of the particular value of the pH in that range. As the acidity decreases, however, the halochromic cation hydrolyzes to the non-polar carbinol and the potential becomes a linear function of pH. Obviously this decreased ion concentration results in a lower oxidation potential for the free radical system. Ostensibly this effect accounts for the impossibility of reducing the carbinols in neutral or weakly acid media.

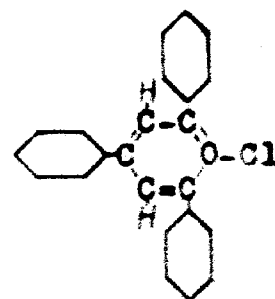


- a. R = H
b. R = Alkyl Group

VIIa, b



VIII



IX

In aqueous solutions Conant found that ferric chloride is reduced to the extent of 60-100% to ferrous chloride by the free radical formed from triphenylpyrylium chloride (IX).¹⁴ Other highly dissociated free radicals he found are also capable of rapidly reducing ferric chloride under the proper conditions, although the conditions and the extent of the reactions were not stated¹⁵.

If this reverse reaction be likewise a manifestation of the metallic properties of free radicals, the rate of such a reaction should depend only upon the rate of dissociation of the ethane which produces the free radical. That this is probably the case is qualitatively demonstrated by a study of the reaction of a dilute aqueous solution of ferric chloride and potassium ferricyanide with chloroform solutions of a series of weakly dissociated dialkyldixanthyls (VIIb)¹⁹. The time required for the formation

of a visible precipitate of Prussian blue is roughly proportional to the rate of dissociation of the ethane as determined independently by the method of oxygen absorption. It was assumed that the Prussian blue is the result of oxidation of the free radical to the carbinol and reduction of the ferric chloride to ferrous chloride, followed by formation of the insoluble ferrous ferricyanide.

Several years after the work of Conant, Gomberg and Gamrath²⁰ found that triphenylmethyl is capable of reducing salts of a number of metals low in the electromotive series when these salts are dissolved in organic solvents instead of water, or even when merely suspended in the solvent. They found that ferric chloride is reduced to ferrous chloride, stannic chloride to stannous chloride, mercuric chloride to mercurous chloride, and also that silver, gold and platinum salts are reduced to the respective metals.

Although these reactions are of course interesting in view of their possible bearing on the question of the metallic properties of free radicals, another problem of more immediate concern to us was suggested. If the reductions of metallic salts proceed quantitatively, these reductions should prove useful as new methods for the estimation of dissociable ethanes, i.e. as criteria for the purity of these compounds.

Methods Used for the Determination of the Purity of Hexaarylethanes

Oxygen Absorption.— The most characteristic reaction of triarylmethyl radicals is the rapid absorption of oxygen with the formation of a peroxide:



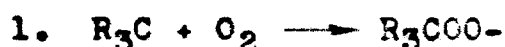
With triphenylmethyl and many others, the volume absorbed, under carefully regulated conditions, corresponds closely to that required by the equation. Because of this fact, the measurement of oxygen absorption has been accepted as a standard method of estimating the purity of these compounds.

There are however several serious objections to the method. It is well known that the yield of the peroxide proper, even if it is highly insoluble, is never greater than 90% of the theoretical²¹, and the yield depends not only upon the nature of the free radical but also upon the conditions of the reaction with oxygen. Triphenylmethyl, for example, gives 85% of the calculated amount of peroxide when oxidized in air, but in pure oxygen, only 65%²². Moreover the volume of oxygen absorbed is greater in pure oxygen²³, and the weight of the total oxidation products is in any case greater than that required by the equation²⁴. In some cases, of which triphenylmethyl and diphenyl-2-naphthylmethyl are examples, the amount of oxygen absorbed and the yield of peroxide depend also upon the solvent employed. In nitrobenzene, triphenylmethyl absorbs approximately 10% over the theoretical²². Diphenyl-2-naphthylmethyl gives a 72% yield of peroxide on oxidation in air of its ether solution; in benzene, under the same conditions, the yield is only 46%²⁵.

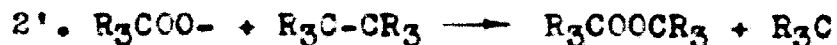
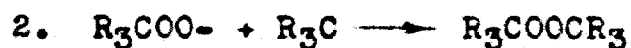
In most cases, high oxygen absorption is probably attributable to susceptibility of the intermediate $R_3COO\cdot$ radical (see equation 1 below) itself to further oxidation, or to side reactions induced by this active radical. In some others such as the dialkyl-dixanthyIs, extremely high values result due to further oxidation of the peroxide.¹⁹

Oxygen Absorption in the Presence of Pyrogallol.- Primarily to elucidate the kinetics of the reaction of triphenylmethyl with oxygen, Ziegler^{26, 27} has measured oxygen absorption using pyrogallol as an oxidation inhibitor. The initial step in the oxidation process is formulated as leading to the formation of the radical $R_3COO\cdot$; then, before chain reactions can set in, the radical is furnished hydrogen atoms by the loosely bound pyrogallol molecule and forms the unsymmetrical peroxide:

Primary reaction, whether pyrogallol be present or not



Without pyrogallol, all of the following secondary reactions may occur concurrently



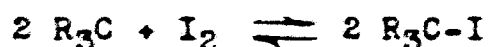
With pyrogallol, only the following secondary reaction takes place



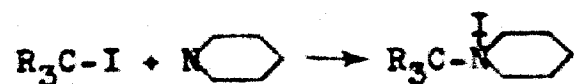
The quantitative aspect of the reaction in the presence of pyrogallol has not been extensively investigated, but Ziegler reported that in this case exactly one molecule of oxygen is absorbed per molecule of free radical²⁶. This conclusion is based on the value obtained with a triphenylmethyl solution whose concentration had been determined by titration with iodine. In an investigation of the reaction of pentaarylethanes with oxygen, Bachmann and Wiselogle²⁸ reported that these compounds at elevated temperatures, in the presence of pyrogallol, absorb exactly two molecules

of oxygen per molecule of ethane, whereas by the ordinary procedure from 1.1 to 1.2 molecules are absorbed. From these results, one would expect that measurement of the absorption of oxygen in the presence of pyrogallol offers an accurate method for determining the purity of free radicals, and the method should possess a definite advantage over the ordinary procedure in that double the volume of oxygen is absorbed by a given weight of free radical. As will be discussed later however, our experience with the method does not confirm this expectation.

Titration with Iodine.— Another characteristic reaction of triarylmethyl radicals derived from appreciably dissociated ethanes is the addition of iodine, resulting generally in equilibrium when 60-80% of the iodo compound has formed:



Obviously, because of the reversibility due to the instability of the iodo compounds, the reaction with iodine alone can under no circumstances be used as a method for the quantitative estimation of free radicals. Ziegler²⁹ has reported however that with excess of iodine in the presence of an organic base, suitably pyridine or quinoline, the free radicals react completely because of the formation of a stable quaternary iodo compound:

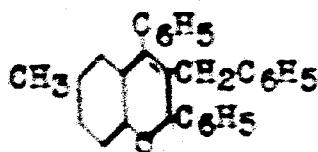


Under these conditions he has applied the reaction as a method of estimating hexaarylethane concentrations. A solution of the free radical in an organic solvent is added to an excess of iodine dissolved in chloroform containing 5% pyridine or quinoline, and,

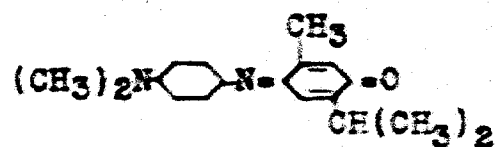
after standing sufficiently long to insure complete reaction, an excess of standard aqueous thiosulfate is added. The excess is then titrated with aqueous iodine.

The validity of the reaction as a basis for a quantitative method has not been definitely proved. With very small samples of the radical bis-(2,4-diphenyl-3-benzyl-6-methylchromenyl) (X) Ziegler³⁰ found 94% of the theoretical iodine absorption, the 6% deficiency being considered attributable to impurity of the sample. A great deal of work was done by him using aliquot portions of solutions of triphenylmethyl prepared in toluene from triphenylchloromethane and mercury and standardized, without isolating the crystalline ethane, by titration with iodine. No attempt was made however to compare the concentrations thus determined with the concentrations to be expected from the original amounts of triphenylchloromethane used for the preparation of triphenylmethyl solutions. In explanation, the vague statement is made that in transferring samples of free radical solutions a change in concentration occurs.²⁶ From this statement one is justified to infer that the iodine values found by him were somewhat lower than should be expected.

Only one experiment comparing this method with the usual oxygen absorption method was reported by Ziegler. Using an aliquot portion of a triphenylmethyl solution whose concentration was determined by iodine titration, he found that the volume of oxygen absorbed amounted to 134% of the calculated.²⁶

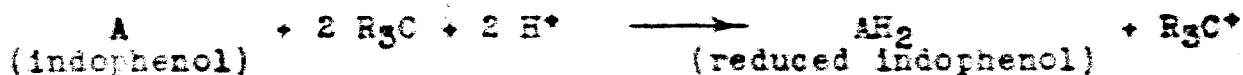


X



XI

Titration with Indothymol.— As a consequence of the low oxidation potential of free radicals as compared with the indophenol dyes, Conant¹⁷ found that quantitative estimation of free radicals is possible by titration in acid solution with indothymol (XI):



An excess of standard dye solution is added to the free radical in acetic acid and bromobenzene, then the excess dye is titrated with a standard solution of sodium thiosulfate. The latter reaction was shown to proceed quantitatively according to the equation:



This method likewise has been used only to a limited extent. In Conant's experiments, diphenyldioxanthyl showed the same purity by this method as by oxygen absorption. A typical titration is described however as one in which 2.329 mg. of ethane required 0.485 cc. of 0.00926 N $\text{Na}_2\text{S}_2\text{O}_3$.

Purpose of This Investigation

In view of the apparent unreliability of the several methods for the determination of the purity of free radicals,

*Study of this method is still in progress.

it has appeared pertinent to investigate the possible applications of the reduction of metallic salts to this problem. We have therefore undertaken a detailed investigation of the reduction of silver salts by a variety of free radicals. In order to accomplish our aim it has been necessary to determine the factors which govern these reactions and the nature of the products formed, and to compare the results of our quantitative studies with the results obtained by several other methods.

DISCUSSION

The Reduction of Silver Salts by Triphenylmethyl

The abstraction of halogen from solutions of triarylchloromethanes or triarylbromomethanes in organic solvents by molecular silver (or mercury, zinc, or copper) represents one of the most convenient methods for the synthesis of triarylmethyl radicals:



Such a reaction may be regarded simply as the displacement of the "compound metal" from its halide by a true metal. That the halogen is quantitatively removed from the halomethane is readily demonstrable by determination of the silver chloride or bromide formed in the reaction. If, however, a solution of triphenylmethyl prepared in this manner is added to a suspension of a silver salt in an organic solvent, in many cases a rapid reduction to metallic silver results. These reactions may be followed qualitatively through the appearance of a dark grey or black deposit of metallic silver accompanied by the gradual disappearance in the solution of the characteristic yellow color of triphenylmethyl.

The reductions are governed primarily by the nature of the silver salt. Salts of organic acids, of which silver acetate, benzoate, phenylacetate, p-chlorobenzoate, and carbonate were chosen as typical examples, are slightly if at all soluble in organic solvents. Suspended in benzene and shaken with triphenylmethyl solutions, they are readily but not instantaneously reduced. The

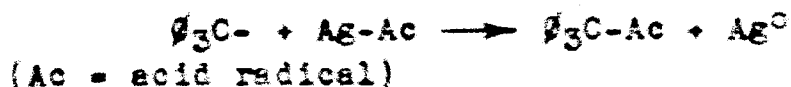
appearance of a deposit of metallic silver is visible within five minutes and the color of triphenylmethyl in all cases but silver carbonate disappears within a few hours. Salts of inorganic acids, also insoluble in organic solvents, such as silver nitrate, phosphate, and sulfate are likewise more or less rapidly reduced. The reduction of aqueous solutions of silver nitrate or silver perchlorate when shaken with a benzene solution of triphenylmethyl proceed at no appreciably greater rate, since here also heterogeneous reactions are involved. However, when a benzene or toluene solution of triphenylmethyl is mixed with a toluene solution of silver perchlorate (silver perchlorate is singularly soluble in this solvent), an immediate co-precipitation of metallic silver and the insoluble triphenylmethyl perchlorate occurs. Silver chloride, bromide, and cyanide are not reduced even on indefinite shaking with benzene solutions of triphenylmethyl, although if silver chloride is suspended in water or in pyridine, a slow reduction is noted after twenty-four hours.

These reductions may be explained on the basis of an electrochemical interpretation. Although silver perchlorate is highly polar in aqueous solution and only a weak electrolyte in solvents such as benzene or toluene, a measurable conductivity in these solvents indicates the presence of a small amount of silver ion³¹. If then the reduction reaction depends upon the presence of both the free radical and the metal ion in solution, the reaction with silver perchlorate in toluene should represent the ideal case. Reactions with other polar salts would be expected to be limited by the solubility of the salts in the solvents used. It

would also be expected that with insoluble salts which are predominately covalent, such as silver chloride, bromide, iodide, and cyanide, no reactions should occur. The reduction of silver chloride when suspended in water may be accounted for by assuming that the slight concentration of silver ion in water is sufficient for the reduction, and that this heterogeneous reaction is therefore roughly comparable to the reduction of polar silver salts in organic solvents when the salts are insoluble.

Formation of Triphenylmethyl Esters in the Reduction Process

Since the reaction of triphenylmethyl with silver salts results in the liberation of metallic silver, it may be expected that the triphenylmethyl group merely displaces the silver atom:



Such actually is the case. Benzene solutions of triphenylmethyl were shaken with excess of silver acetate, benzoate, phenylacetate, p-chlorobenzoate, carbonate, and perchlorate. On separation from the precipitate of metallic silver and excess silver salt, good yields of the esters were obtained. In all cases, except silver carbonate, all of the triphenylmethyl was used up in the reaction.

The identity of those esters not previously reported was established by comparison with authentic samples prepared according to a more conventional procedure³²:



Quantitative Estimations and the Purity of Triphenylmethyl

Analysis by the method of oxygen absorption of triphenylmethyl solutions prepared from triphenylchloromethane and mercury or molecular silver under widely variant conditions indicated that pure samples of triphenylmethyl solutions are readily prepared. From 97 to 101% of the theoretical absorption, calculated on the assumption of quantitative conversion of the chloromethane to free radical, was almost invariably obtained.

The silver salt reductions were studied quantitatively using aliquot portions of standard triphenylmethyl solutions prepared as indicated above since, from the results of oxygen absorptions, it appeared unnecessary to isolate the crystalline ethane in order to obtain pure samples. These solutions, approximately 0.2 N with respect to triphenylmethyl, were prepared directly in 100 cc. volumetric flasks. An apparatus was constructed by means of which accurately measured 10 cc. portions could be transferred without exposure to oxygen.

Quantitative studies of the reductions by triphenylmethyl were made with silver acetate, benzoate, phenylacetate, p-chlorobenzoate, nitrate, and perchlorate. Although solutions of triphenylmethyl prepared under identical conditions absorbed 97 to 101% of the calculated amounts of oxygen, only 85 to 90% of the expected amounts of metallic silver were liberated from excess of the various silver salts. The agreement between duplicate determinations with the same salt, and between values for different

silver salts, however, was very close.^s

That the discrepancy between the two methods--oxygen absorption and silver salt reduction--is not due to equilibrium reactions in the second method was established in the following manner. Carefully weighed samples of silver acetate and silver perchlorate were allowed to react with excess of pure crystalline hexaphenylethane. Under these conditions, reduction of the salts to metallic silver is complete, and it is evident then that we are not dealing with equilibrium reactions. Moreover, those esters which result from the action of triphenylmethyl on silver salts, do not react with molecular silver to form triphenylmethyl. After long shaking with molecular silver in benzene they are recovered unchanged and in excellent yields.

Analysis of triphenylmethyl solutions by iodine titration according to Ziegler's procedure²⁹, like the analysis by silver salt reduction, gave results which were 10 to 12% lower than expected on the basis of the original chloromethane or from the measurement of oxygen absorption. However, the values obtained by estimation of iodine absorption were the same as those found by estimation of the silver liberated from silver salts.

Any errors in the methods of analysis which might have been introduced due to impurity of triphenylmethyl solutions and differences in the experimental technique, were eliminated by

^sTwo exceptions were noted. Silver nitrate consistently gave 10% less silver than the other salts, possibly because of oxidation of triphenylmethyl by the initially liberated nitrate ion instead of by silver ion. Silver carbonate failed to react completely with triphenylmethyl.

analyzing freshly prepared samples of crystalline hexaphenylethane. The procedures were such that any discrepancies in the results should be due to differences inherent in the methods. Whereas these samples absorbed 101 to 103% of the calculated amounts of oxygen, only 88 to 90% of the calculated amounts of iodine were absorbed, and 88 to 90% of the expected metallic silver was liberated from silver perchlorate.

The discrepancy in these results is probably due to an inherent inaccuracy in the oxygen absorption method. For the reasons previously discussed (page 7), the analysis by oxygen absorption undoubtedly leads to high results. The values as determined by iodine absorption and by the liberation of silver are probably, within experimental error, correct, and are low only because of the impossibility of isolating entirely pure samples of hexaphenylethane. That oxygen absorption does give nearly the supposedly correct result may be attributed to the cancellation of two errors operating in opposite directions to the same, or to nearly the same, extent.

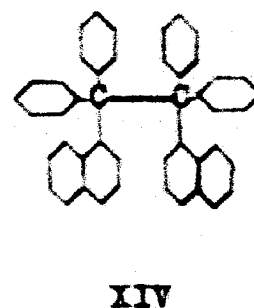
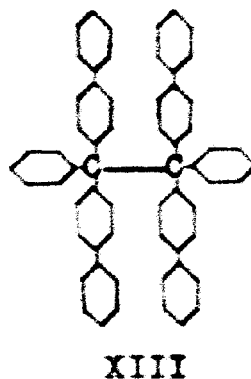
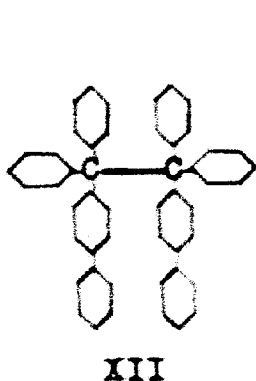
An attempt to utilize Ziegler's oxygen absorption method²⁶ in the presence of pyrogallol for the quantitative estimation of triphenylmethyl proved fruitless. The results of such analyses were invariably erroneous for reasons which are discussed in the experimental portion.

²⁶In a single case, 93.5% of the theoretical iodine was absorbed. Whether this was the result of an unusually pure sample, or of an error in the analyses, cannot definitely be stated.

Reduction of Silver Salts by Ethanes

More Highly Dissociated than Hexaphenylethane

Tetraphenyldibiphenylethane (XII), tetrabiphenyldiphenylethane (XIII), and tetraphenyldi-1-naphthylethane (XIV) were chosen as typical of the hexaarylethanes more highly dissociated than hexaphenylethane³³. Silver acetate and silver perchlorate were likewise chosen for typical examples of the two types of reduction to be expected, the acetate undergoing a relatively slow reaction due to its insolubility and the perchlorate dissolved in toluene undergoing rapid reduction.



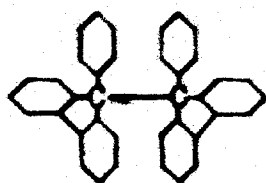
The reductions by these free radicals occur in a manner very similar to those found with triphenylmethyl. In each case silver perchlorate was immediately reduced and in addition to metallic silver, a precipitate having the color of the corresponding insoluble triarylmethyl perchlorate was formed. With silver acetate decolorization of the solutions, accompanied by liberation of silver was complete within one to two hours.

Comparative quantitative determinations of the reactions of diphenylbiphenylmethyl (XII) and diphenyl-1-naphthylmethyl (XIV) solutions with oxygen, iodine, silver perchlorate, and silver

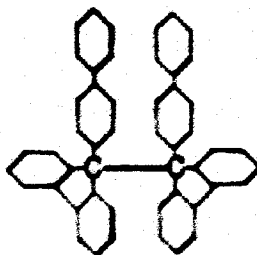
acetate were also made. With both free radicals, separate samples prepared under identical conditions absorbed nearly the calculated amounts of oxygen (96 to 97%), but only 85% of the calculated amount of free radical was found by the other methods. The agreement between analyses by iodine titration and by silver liberation however, was again very close. Evidently here again, as with triphenylmethyl, a discrepancy of 10 to 12% between oxygen absorption and the two other methods is encountered.

The Reduction of Silver Salts by Slightly Dissociated Ethanes

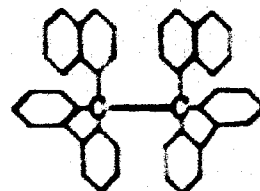
The reactions with a number of slightly dissociated ethanes appeared of interest in order to determine qualitatively to what extent the reduction of silver salts depends upon the presence in solution of an appreciable concentration of free radical. It was also hoped that slightly dissociated ethanes might be obtained in a greater purity because of their greater stability toward oxygen. Diphenyldifluoryl (XV) and dibiphenyldifluoryl (XVI) appeared to be ideal for these purposes. Measurements of the molecular weights by Schlenk³⁴ indicate that both compounds exist entirely in the bimolecular form, i.e., as ethanes. On the basis of their behavior toward iodine, and from the intensities of the colors produced by the heated solutions, he concluded that the biphenyl derivative, in contrast to expectation from the relation of triphenylmethyl to diphenylbiphenylmethyl, is more stable than the phenyl derivative. No attempt to relate di-1-naphthyldifluoryl (XVII) to the other members of this series has been made.



XV



XVI



XVII

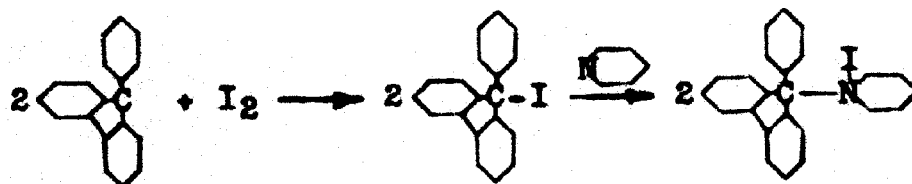
When crystalline diphenyldifluoryl is treated with a 0.1 N solution of silver perchlorate in toluene, a slow reduction to metallic silver occurs. The first visible sign of reduction is the development of a pale yellow color in the solution in thirty minutes followed within six hours by the production of a deep red solution and an appreciable precipitate of silver. Crystalline dibiphenyldifluoryl on the other hand produces a definite precipitate of silver in thirty minutes and a much more deeply colored solution. From these differences in the rate of reduction of silver perchlorate, it would be concluded that the dibiphenyl derivative dissociates more rapidly than the diphenyl derivative. From the two structures, despite Schlenk's conclusions, this is the order which is to be expected. Neither of these ethanes is apparently sufficiently dissociated at room temperature to reduce silver acetate. However, when dibiphenyldifluoryl was shaken at 60° with silver acetate a very slow reduction to metallic silver occurred.

Due to instability of 1-naphthylfluoryl (page 30) only the reaction of this compound with silver perchlorate was tested. An almost instantaneous precipitation of silver resulted. This rapid reaction, together with the rapid rate of oxygen absorption

by 1-naphthylfluoryl¹⁶, indicates qualitatively that the dissociation of this compound is of the same order of magnitude as the dissociation of hexaphenylethane.

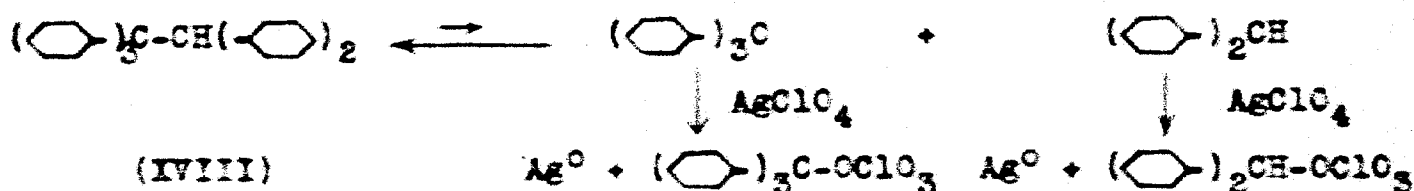
For the quantitative estimation of the silver liberated from silver perchlorate the reactions with diphenyldifluoryl were allowed to proceed for three to five days, and sufficient silver to account for 93% of the ethane was liberated. However, when excess of the ethane was allowed to react with silver perchlorate, approximately 5% of the silver was not reduced. This failure to reduce silver perchlorate completely may indicate that the reaction in this length of time is incomplete, or conceivably that equilibrium is attained at this point. With dibiphenyldifluoryl, quantitative reduction of silver perchlorate by excess of the ethane resulted in three days, but with excess silver perchlorate here again only 88% of the calculated amounts of silver were liberated.

Both ethanes (XV and XVI) in the presence of pyridine slowly absorb iodine at room temperature. With the diphenyl derivative, however, no starch endpoint could be obtained. In the titration, instead of the formation of a blue color, near or at the endpoint a dirty yellow turbidity was observed. Excess iodine did not cause a blue endpoint but only increased this turbidity. The difficulty is caused by the pyridinium iodide formed in the reaction:

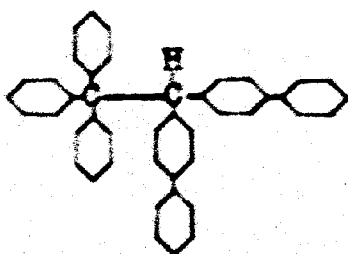


In a blank experiment under the conditions of the titration, it alone caused the same endpoint characteristics. The iodine titration of biphenylfluoryl was conducted without difficulty, but the value, 88% agreed within experimental error with the silver titration.

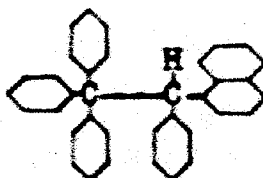
Pentaphenylethane (IVIII) is the most stable polyarylethane which will cause reduction of silver perchlorate at room temperature. On the assumption that the reactions involved are the following:



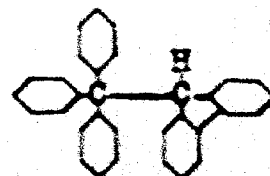
43% of the calculated silver was liberated by shaking pentaphenylethane with a 0.1 N toluene solution of silver perchlorate for four months. The first visible reduction in this case occurs only after ten to twelve days, whereas with 1,1,1-triphenyl-2,2-dibiphenylethane (XIX) and 1,1,1,2-tetraphenyl-2-(1-naphthyl)ethane (XX) metallic silver is formed in two to three days. On the other hand, 1,1,1-triphenyl-2-biphenyleneethane (XXI) was not reduced in six months. These differences in the rates of reduction are again in the order expected on the basis of the structural differences of the ethanes.



XIX



XX



XXI

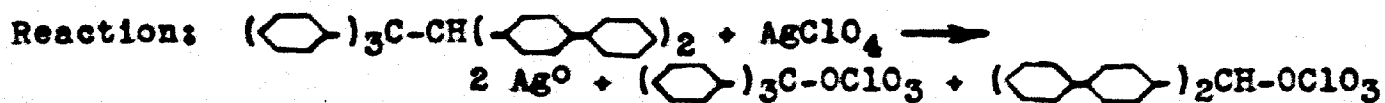
The extreme sensitivity of silver perchlorate to slight concentrations of free radicals was also evidenced in another way. In the table below are given the temperatures at which visible color is obtained with pentaarylethanes in ethyl benzoate alone³⁵, and the temperatures at which a turbidity due to reduction of 0.1 N silver perchlorate in toluene by the same ethanes, is visible.

<u>Ethane</u>	<u>Turbidity</u>	<u>Color</u>
Pentaphenyl	94°	105°
Triphenyldibiphenyl	84°	93°
Tetraphenyl-1-naphthyl	73°	85°

Concentration of ethane: 0.02 M
Rate of heating: 2°/minute

Obviously the reduction reaction affords a more sensitive test for the presence of free radicals than the production of color by the ethanes in the absence of the silver salt.

Various attempts were made to detect differences in the yields of silver at elevated temperatures as engendered by differences in the dissociation tendencies of various pentaarylethanes. This is possible, however, only if the stabilities are rather widely variant. For example, whereas pentaphenylethane and triphenyldibiphenylethane (XIX) in toluene both yield approximately 70% of the calculated silver at the boiling point (110°) in ten minutes, no reduction by triphenylbiphenyleneethane (XXI) occurred at that temperature even after five hours. The principal difficulty preventing quantitative comparisons at elevated temperatures is that at these temperatures there is decomposition which in some way causes re-solution of metallic silver originally liberated by the desired reaction. The following example is typical:



<u>Time of Heating at 110°</u>	<u>Yield of Silver</u>
10 minutes	65.1%
30 "	71.0%
60 "	78.0%
90 "	56.6%
180 "	32.3%

This decomposition is apparently quite complicated. Even though heating at the boiling point for short periods gave relatively high yields of metallic silver, none of the expected organic products could be crystallized from the reaction mixtures.

An attempt was also made to determine the extent of reaction of pentaphenylethane with iodine in the presence of pyridine at higher temperatures. Complete reaction would of course corroborate the previously intimated assumption that the reaction of iodine with free radicals, in the presence of pyridine is quantitative. However, like phenylfluorylpyridinium iodide, diphenylmethylpyridinium iodide formed in the reaction prevents the formation of the starch-iodine endpoint. With very small samples this interference is avoided, and as high as 95% of the calculated absorption was found. The accuracy of the analysis under these conditions is however not great enough to permit definite conclusions as to the quantitative nature of the reaction.

Mechanism of the Reaction in the Reduction of Silver Salts by Dissociable Ethanes

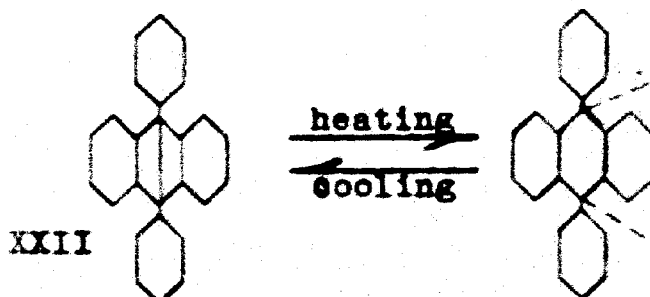
It should be expected, a priori, that the reduction of silver salts by dissociable ethanes proceeds only through interaction of the silver salt with the free radicals resulting from

dissociation of the ethane and not by direct reaction of undissociated ethane with the silver salt. If such be the case, the reduction proper would be expected to occur instantaneously, and hence the overall rate of reaction would be governed by the rate of dissociation of the ethane which gives rise to the free radical. Our results with slightly dissociated ethanes indicate qualitatively that this hypothesis is probably correct.

A critical test of the hypothesis depends, of course, upon a study of the kinetics of the reaction of these compounds with silver perchlorate solution. Thus far, no ethane investigated has proven entirely suitable for this purpose, and we are unable then to state definitely whether these reactions involve reduction of silver by free radicals alone, or whether also the less likely possibility of a direct reduction by undissociated ethane occurs concurrently.

The Reduction of Silver Salts by Biradicals

Ingold and Marshall³⁶ have reported that 9-10-diphenylanthracene (XXII) in boiling xylene develops, reversibly, a color which they attribute to the formation of the biradical:



It will be recalled that pentaarylethanes rapidly reduce silver perchlorate in toluene solution 10° below the temperatures at which a visible color due to free radicals is produced. Therefore, it was expected that at the boiling point of xylene (140°), Ingold's

compound should cause a rapid reduction of silver perchlorate to metallic silver. No such reaction ensued, and after five hours heating at the boiling point, the original hydrocarbon was recovered. That reduction of silver perchlorate by free radicals, if such be present, can take place at such elevated temperatures was proved by heating triphenylbiphenyleneethane (XXI) with silver perchlorate in *p*-dichlorobenzene. Rapid reduction occurred at about 165°. This compound in ethyl benzoate gives a visible color at 170°35.

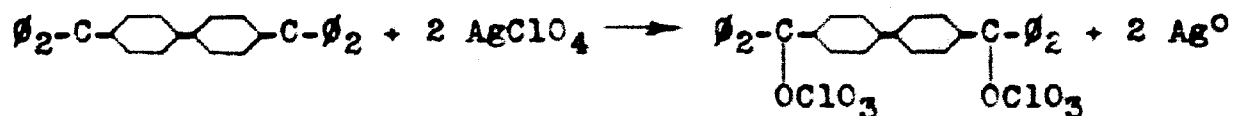
Tschitschibabin's hydrocarbon, *p,p'*-biphenylene-bis-(diphenylmethyl) (XXIII) is another interesting example. Although the compound in solution is extremely sensitive to oxygen, Müller and Müller-Rodloff³⁷, from measurement of the paramagnetic susceptibility, concluded that nonetheless, it is not a biradical. They admit the possibility of an equilibrium



with not more than one percent of the biradical in order to account for the sensitivity of the compound toward oxygen. Hückel³⁸, on the basis of quantum theory considerations, has concurred with the viewpoint that this compound should be diamagnetic, and hence not a biradical, in contrast to the corresponding *m,m'*-derivative, which he regards as paramagnetic.

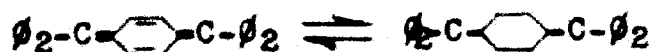
In view of this information, it was somewhat surprising to find that the absorption of iodine and the reduction of silver perchlorate by this hydrocarbon are quantitative, and nearly instantaneously complete. On addition of the intensely purple

solution of the hydrocarbon to a solution of silver perchlorate in toluene the purple color disappears at once and an immediate coprecipitation of metallic silver and the deep red perchlorate of the biradical results:



Because of the intense color of the hydrocarbon it was also possible to note that complete decolorization by iodine solution in the presence of pyridine is accomplished almost instantaneously at room temperature. In a qualitative experiment with silver acetate, the color of the hydrocarbon completely disappeared in thirty minutes. It will be remembered that such reactions were noted only with those hexaarylethanes which are appreciably dissociated at room temperature. It is of interest that in this case too, the quantitative estimation by means of iodine and silver perchlorate agree within experimental error.

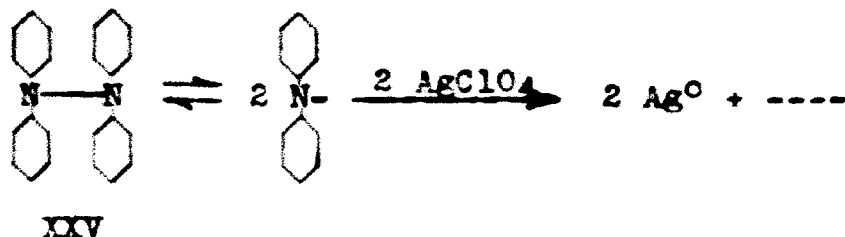
In contrast, *p*-phenylene-bis-(diphenylmethyl) (XXIV) reacts only very slowly with silver perchlorate or with iodine. After five days shaking, only 30% of the calculated silver was liberated, and similarly with iodine in the presence of pyridine, approximately 60% of the calculated iodine was absorbed. The tendency of this compound toward radical formation may be considered therefore as intermediate between that of pentaphenylethane and that of diphenyldifluoryl.



XXIV

The Reduction of Silver Perchlorate by Tetraphenylhydrazine

In an attempt to determine whether silver perchlorate is reduced by elements, other than carbon, in an abnormal valence state, the effect of tetraphenylhydrazine (XXV)³⁹ was tested. A reduction to metallic silver to the extent of 60% of the calculated was obtained, assuming the reaction:

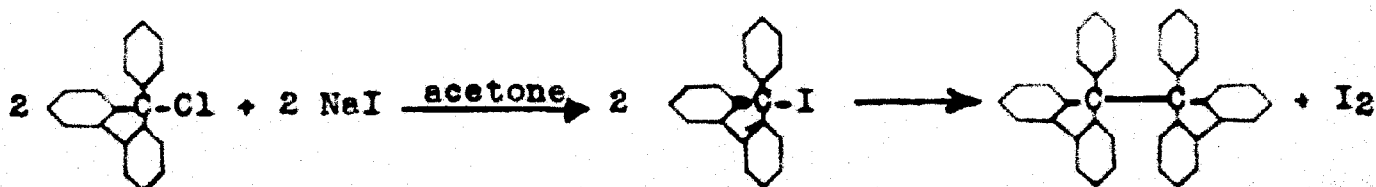


However, no further investigation of this apparently complicated reaction was made.

The Synthesis of Slightly Dissociated Ethanes

In most cases, the syntheses of the ethanes used in these experiments have been adequately described in the literature. Both of the previously reported methods for the preparation of diphenyl- and dibiphenyldifluoryl however^{34, 40} involve rather laborious procedures and result in low yields. We have therefore extended a previously unreported method for the preparation of diphenyldifluoryl to the preparation of several other ethanes.

In connection with another problem, Gomberg and Clarkson⁴¹ found that the action of sodium iodide on 9-phenyl-9-chlorofluorene leads not to 9-phenyl-9-iodofluorene, but to the formation of the ethane, 9,9'-diphenyldifluoryl:



We have found this method to be of general applicability in the preparation of slightly dissociated ethanes. The reaction becomes feasible in these cases because of the stability of the ethanes as compared to the lability of the corresponding iodo compounds.

When 9-(1-naphthyl)-9-chlorofluorene was treated with sodium iodide in acetone, a product which absorbed only 50% of the calculated amount of oxygen was obtained. Wanscheidt and Moldavskii¹⁶ have prepared a similarly impure ethane by the action of stannous chloride on the corresponding carbinol, or by the action of metals on the corresponding halomethanes, and we have now shown that this impurity is the result of a relatively rapid spontaneous decomposition of the free radical, 1-naphthylfluoryl. Unlike most triarylmethyls, which on polymerization decompose to a dimer, this free radical polymerized to a product or products of molecular weight higher than that calculated for a dimer.

The sodium iodide method cannot be applied to the preparation of hexaphenylethane because of the relatively slight dissociation of triphenyliodomethane into triphenylmethyl and iodine.

EXPERIMENTAL

Preparation of Starting Materials

Triarylmethyl Halides

Triphenylchloromethane was prepared from benzene and carbon tetrachloride⁴² and by the action of acetyl chloride on triphenylcarbinol³². It was recrystallized from benzene and petroleum ether, then dried and stored in a vacuum desiccator containing phosphorus pentoxide, soda-lime, and paraffin. Analysis indicated 99.4 to 100% of the calculated amounts of chlorine.

Diphenylbiphenylchloromethane.- 4-Phenylbenzophenone was prepared from biphenyl and benzoyl chloride⁴³. The crude ketone was best purified by vacuum distillation, the fraction boiling at 225-235°/3 mm. being collected. On recrystallization from acetone, an 84% yield of the pure ketone was obtained. Diphenylbiphenylcarbinol was prepared from the ketone and phenylmagnesium bromide⁴⁴. The chloride was obtained by the action of acetyl chloride on the carbinol. Recrystallization of the crude product from benzene and petroleum ether gave a 90% yield of pure chloromethane⁴⁴. Analysis indicated 99.2% of the calculated chlorine.

Phenyldibiphenylchloromethane.- 4,4'-Diphenylbenzophenone was prepared from oxalyl chloride and biphenyl according to the directions of Bachmann⁴⁵. Excess biphenyl was most readily removed by fractional vacuum distillation. The fraction boiling at 295-310°/2 mm. consisted of the nearly pure ketone which was purified by Soxhlet extraction with toluene. The yield was 78%. The

carbinol was prepared by addition of the finely powdered ketone to a slight excess of phenylmagnesium bromide in ether-benzene. As previously found in this laboratory²⁸, and contrary to other reports, the addition occurs without necessity of replacing the ether-benzene by xylene⁴⁴, and no difficulty was experienced in crystallizing the reaction product from benzene and petroleum ether⁴⁶. The yield was 96%. The chloride was prepared from acetyl chloride and the carbinol, a drop of pyridine being added to the reaction mixture before addition of petroleum ether to destroy the deep red color which formed. The recrystallized product was obtained in 89% yield and melted at 134-5°. Analysis indicated 99.6% of the calculated chlorine.

Diphenyl-1-naphthylchloromethane.- Eastman's diphenyl-1-naphthylcarbinol was recrystallized from benzene and petroleum ether and converted to the chloromethane by means of acetyl chloride⁴⁷. Analysis indicated 97.3% purity.

9-Phenyl-9-chlorofluorene.- 9-Phenylfluorenol was prepared in 91% yield from fluorenone and phenylmagnesium bromide⁴⁸. The compound, recrystallized from benzene and petroleum ether, melted at 109-10°. The chloride was prepared from the carbinol and acetyl chloride. It was recrystallized from petroleum ether and obtained in 82% yield; m.p. 80-1°⁴⁹.

9-Biphenyl-9-chlorofluorene.- As found in this laboratory by Schoepfle⁵⁰, and contrary to previous reports by Schlenk^{34b}, 9-biphenylfluorenol was readily prepared from fluorenone and biphenylmagnesium bromide. The yield was 74% of the calculated, based on fluorenone. The chloride, prepared from the

carbinol and acetyl chloride, was recrystallized from benzene and petroleum ether; yield, 95%; m.p. 138-9°^{34b}.

9-(1-naphthyl)-9-chlorofluorene and 9-(1-naphthyl)-9-bromofluorene.- 9-(1-naphthyl)-fluorenol was prepared by the method of Ullmann and Wursterberger⁵¹. This carbinol, recrystallized from benzene and petroleum ether, melted at 155-6°. The previously reported melting point is 151.5°. The chloride was prepared from the carbinol and acetyl chloride. The recrystallized product was obtained in 82% yield, m.p. 149-50°¹⁶. The bromide was prepared from the carbinol and acetyl bromide. Recrystallized from benzene and petroleum ether, it retained a slight yellow color; yield, 92%; m.p. 194-5°¹⁶.

p-Phenylene-bis-(diphenylchloromethane).- p-Phenylene-bis-(diphenylcarbinol) was prepared from dimethyl terphthalate and phenylmagnesium bromide following the directions of Ullmann and Schlaepfer⁵². The chloride was prepared by dissolving 10 gms. of the carbinol in 50 cc. of hot benzene, and adding slowly to this solution 10 cc. of acetyl chloride. The mixture was refluxed for one hour, during which time the colorless chloride precipitated. After cooling the mixture, the crystals were filtered and thoroughly washed with benzene; yield, 94%; m.p. 246-7°⁵².

p,p'-Biphenylene-bis-(diphenylchloromethane).- p,p'-Dibenzoylbiphenyl was prepared according to the directions of Schlenk⁵³, except that purification by recrystallization from nitrobenzene was avoided. The crude product was instead distilled at 2 mm. pressure and recrystallized from o-dichlorobenzene. The yield of purified product was 64%. The carbinol was prepared in 95% yield according

to Schlenk's directions.

A mixture of 12 gms. of p,p'-biphenylene-bis-(diphenylcarbinol), 15 cc. of acetyl chloride and 50 cc. of dry benzene was refluxed for one and one-half hours. The chloride which precipitated on addition of 50 cc. of petroleum ether was recrystallized from benzene and petroleum ether. The yield of recrystallized product was 85%, m.p., 218-222.5°⁵⁴. Chloride analysis indicated a purity of 99.5%.

Pentaarylethanes

Pentaarylethanes were prepared by the reaction of triphenylmethyl sodium with the corresponding diarylbromomethanes²⁸. In each case the ethane was recrystallized from benzene and alcohol and dried in vacuum at 80-100° to completely remove solvent of crystallization. The melting points in nitrogen checked those given in the literature⁵⁵.

Silver Salts

Except for silver phenylacetate and silver-p-chlorobenzoate, the salts used in these experiments were the available C.P. materials. Silver phenylacetate and p-chlorobenzoate were prepared by adding a slight excess of silver nitrate solution to a solution of the corresponding acid containing 5% less than the theoretical amount of sodium carbonate. The salt which precipitated on cooling was recrystallized from hot water.

The salts of organic acids were dried in a vacuum desiccator over phosphorus pentoxide; the inorganic salts were dried in the oven at 110° for two hours. Hydrated silver perchlorate was dried for at least three hours immediately before use. One-tenth

normal solutions of silver perchlorate in toluene, if carefully protected from light remained colorless for four to six weeks; after that period a slight darkening occurred and on longer standing a black precipitate formed.

Analysis of the organic salts and of silver perchlorate indicated in every case a purity of 99.6-100%.

Solvents and Metals

Commercial bromobenzene was purified and dried by redistillation, the first 10% being discarded. Reagent quality thiophene-free benzene was dried over sodium wire and used without further purification. Commercial toluene was purified by redistillation and drying over sodium wire.

The mercury used was the redistilled product, dried at 110° for two hours. Molecular silver was prepared according to the directions of Gomberg⁵⁶, except that final drying over phosphorus pentoxide in a vacuum for two weeks was found sufficient to remove the last traces of moisture. A sample heated at 250° in a stream of dry nitrogen for twenty hours showed no loss in weight.

Estimation of Oxygen Absorption

The apparatus for the measurement of oxygen absorption by triarylmethyl radicals was of the standard type described by Gomberg and Schoepfle⁵⁷. The retaining liquid used in the gas buret was in each case the same as the solvent for the triarylmethyl. With benzene and toluene the correction for the vapor pressure of the solvent was applied; no correction was deemed necessary for the vapor pressure of bromobenzene.

Samples for the direct determination of oxygen absorption were prepared by carefully weighing into a constricted test tube, 1.0 to 1.3 gms. of the pure triarylchloromethane and an equal weight of molecular silver or a double weight of pure mercury. After replacing the air in the tube by nitrogen, the tube was filled to the constriction with solvent and sealed off in a small flame. It was then wrapped in black cloth and placed on the shaking machine.

With triphenylmethyl solutions prepared in bromobenzene, experience showed that if the apparatus was filled with pure oxygen and the absorption allowed to proceed until no further contraction could be noted, the process required from one and one-half to two hours. The absorptions of oxygen corresponded to 105-110% of the calculated amounts, on the assumption that conversion of the chloromethane to free radical had occurred quantitatively. If, however, the absorption was run in air, the oxidation was complete in four to five minutes, and with the purest samples led to only slightly high results. A standard procedure of shaking the free radical solution in an atmosphere of air for five minutes was thereafter adopted.

Samples of triarylmethyl radicals prepared in bromobenzene from mercury or molecular silver and shaken for at least two days absorbed, under these conditions, from 97 to 101% of the calculated amounts of oxygen. Although solutions prepared from mercury contained traces of halogen, it could not be shown that this halogen was derived from unreacted triarylchloromethane. With benzene or toluene as the solvent, our experience indicated that the most reliable results were obtained with solutions prepared with mercury. Using this metal, 96-100% of the calculated

absorption resulted.

Estimation of Triarylmethyls by Iodine Absorption
and by Silver Liberation

Preparation of Triarylmethyl Solutions.- Solutions of triarylmethyl radicals to be used in these analyses were prepared directly in 100 ml. volumetric flasks, the stoppers of which were excellently ground and sealed with a special grease⁵⁸. Five to six gms. of the pure triarylchloromethane was carefully weighed into the flask which was then filled to the mark with the desired solvent. The air space was thoroughly flushed with nitrogen, 2 cc. of mercury and a little lead powder was added, and the flask quickly stoppered. When molecular silver was to be used for abstracting the halogen, the chloromethane and double its weight of silver (weighed to .01 gm.) were placed in the flask. The flask was then evacuated and filled with nitrogen several times before filling to the mark with solvent. Since the formation of silver chloride produced no detectable change the volume of the solution was found by subtracting from 100 ml. the volume originally occupied by molecular silver. The stoppered flasks were wrapped in black cloth and placed on the shaking machine.

Apparatus.- The apparatus used for transferring these solutions in the absence of oxygen is shown in Diagram I. The entire system was evacuated and filled with pure dry nitrogen, the process being repeated several times. After quickly replacing an empty flask at A by the volumetric flask containing the stock solution of free radical and after flushing the small gas space through the stopcock C, the flask was raised so that the tip of

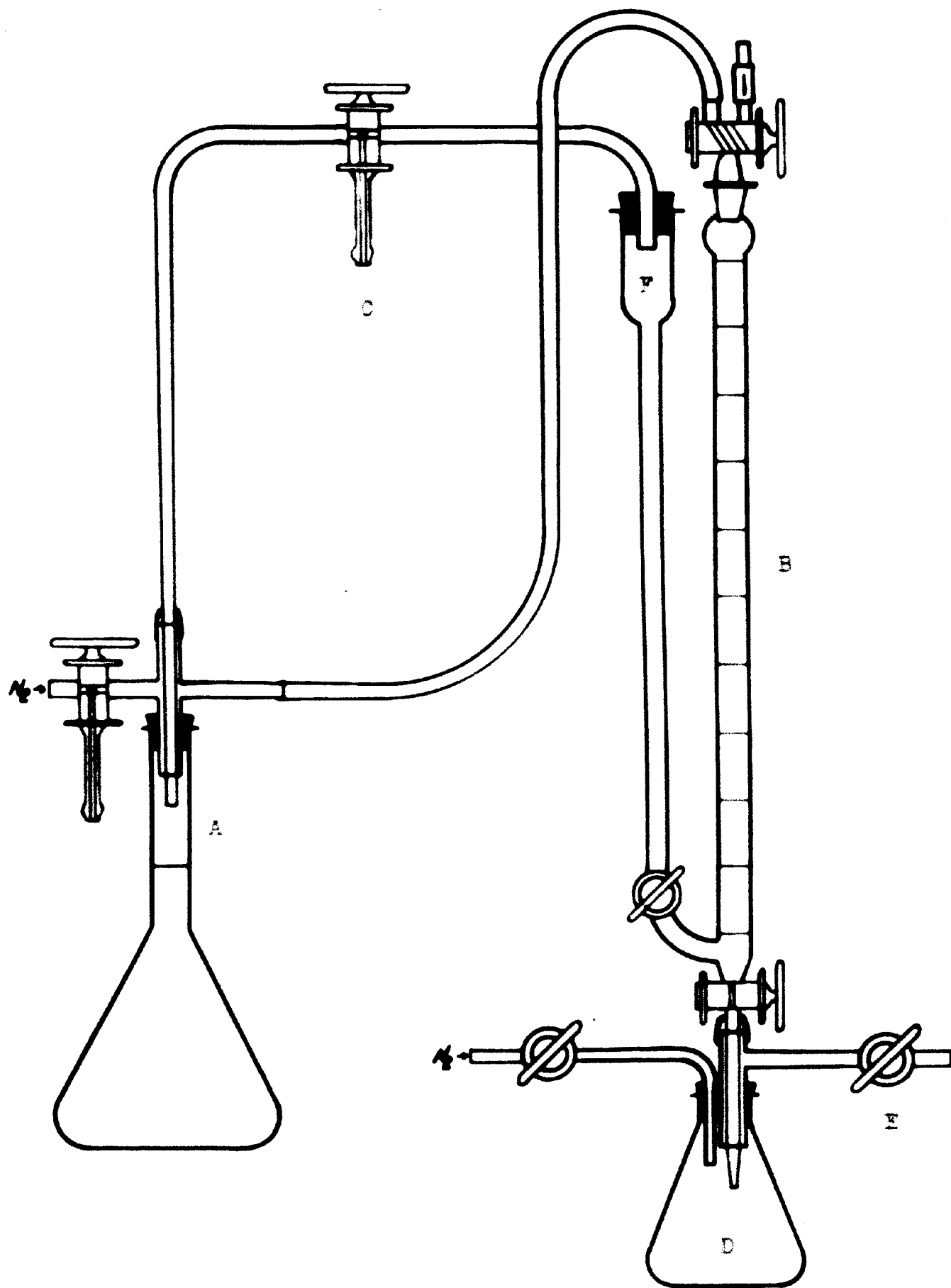


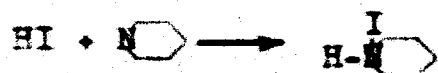
DIAGRAM I

the siphon tube was just above the precipitate of metal and metal halide. The solution was then forced under positive pressure through a hardened filter paper at F and into the buret B. The 50 cc. glass stoppered Erlenmeyer flask D was replaced by another containing the desired reagent, and after flushing this flask with a stream of nitrogen for fifteen to twenty minutes, it was protected from air by closing the stopcock E. A measured volume of free radical solution was then introduced. Before removing and quickly stoppering the Erlenmeyer flask, the buret was filled for the next sample.

In those cases where oxygen absorptions were measured on these solutions, the sample was passed into a constricted test tube which had been previously filled with nitrogen. The tube was then sealed in a small flame.

The entire buret arrangement was enclosed in a framework covered with black cloth in order to minimize decomposition by light.

Estimation of Iodine Absorbed.— The method was essentially that described by Ziegler²⁹. One-tenth normal solutions of iodine were prepared in a mixture of 950 cc. of *o*-dichlorobenzene and 50 cc. of pyridine. Bromobenzene or chloroform served equally well as the solvent. In order to prevent precipitation of the tri-arylmethylpyridinium iodide, it was convenient to have present, 5% of absolute alcohol. The reactions then become:



The procedure was as follows: 25 cc. of the above standard iodine solution was pipetted into a 50 cc. glass stoppered Erlenmeyer flask. If alcohol was to be used, 1 cc. was added at

this stage. A measured volume of free radical solution was then added by means of the apparatus described above. After allowing the reaction mixture to stand at least thirty minutes, the solution was transferred to a 125 cc. flask and 25 cc. of $\text{Na}_2\text{S}_2\text{O}_3$ solution slightly stronger than 0.1 N was added by means of a pipet. The mixture was shaken until the iodine color disappeared, then diluted to 100 cc. and the excess of thiosulfate titrated with 0.1 N aqueous iodine solution. The difference between the volume required for such a sample and that required for a blank run in the same manner, corresponds to the volume of aqueous iodine solution required by the free radical.

Estimation of Silver Liberated.- In a 50 cc. glass stoppered Erlenmeyer flask, a 50% excess of the silver salt was suspended in 25 cc. of benzene or toluene. In the case of silver perchlorate, 25 cc. of a 0.1 N solution in toluene was used. By means of the apparatus described, 10 cc. of the stock solution of free radical was then added. All reaction mixtures except those involving silver perchlorate were shaken over night before analyzing for metallic silver liberated. With silver perchlorate the analyses could be made safely after shaking for thirty minutes.

The metallic silver which formed in the reaction mixtures was separated by decantation, passing the supernatant liquid through a fine Jena funnel to prevent loss of the finely divided black or grey powder. It was freed from the triarylmethyl ester and excess silver salt by successive washing with acetone, 3% ammonium hydroxide, and finally with water. Separate experiments showed that ammonium hydroxide of this concentration rapidly

dissolved the silver salts used, but even on long standing with molecular silver no detectable amount of the metal was dissolved. The metallic silver was then dissolved in hot 7% nitric acid and titrated with 0.1 N KCNS.

The results of these experiments are shown in the following tables.

TABLE I

Estimation of Triphenylmethyl by the Method of Iodine Absorption
and by the Method of Silver Liberation

Exp. No.	Iodine Absorption			Silver Liberation		
	Calc. ϕ_{3C} in sample, g.	N/10 iodine absorbed cc.	ϕ_{3C} found, % of calc.	Silver salt used	Calc. ϕ_{3C} in sample, g.	Ag liber- ated in terms of N/10 Ag, cc.
1	0.460 0.458	16.40 16.58	86.8 88.1	Acetate Acetate Benzoate Benzoate Carbonate	0.459 0.461 0.460 0.457 0.458 0.459	16.48 16.33 16.43 16.53 17.60 11.78
2	0.474 0.478	16.59 16.89	85.2 86.0	Acetate Acetate Benzoate	0.478 0.482 0.480 0.484	16.59 16.71 16.53 17.38
3	0.450 0.467	16.46 16.91	88.9 88.2	Acetate Acetate Perchlorate Perchlorate Perchlorate Nitrate	0.474 0.475 0.476 0.476 0.476 0.471 0.468	17.60 17.31 17.80 17.84 17.59 15.09 14.84
4	0.504 0.500	17.16 17.41	82.9 84.8	Perchlorate Perchlorate Nitrate	0.500 0.501 0.500 0.502	16.93 16.86 14.97 14.68
5	0.499 0.423 0.402	17.33 14.20 13.73	84.5 82.3 83.2	Perchlorate Perchlorate Perchlorate in water	0.464 0.500 0.500 0.490	15.91 17.22 15.09
6	0.498 0.546	17.64 19.60	86.3 87.3	Phenyl- acetate Phenyl- acetate p-Chloro- benzoate p-Chloro- benzoate	0.546 0.538 0.542 0.541	18.55 18.33 18.43 18.41
						87.4 86.2 87.0 88.0 40.4 61.9 84.4 84.4 83.9 87.4 90.4 88.6 91.2 91.3 90.0 77.9 79.0 82.4 81.9 72.8 71.2 83.5 83.8 74.9 82.6 82.8 82.7 82.7

Exp. No.

- Stock solution: 4.628 gms. of ϕ_{3C} in 100 cc. of benzene, prepared by shaking ϕ_{3CCl} with mercury for ten days.
- Stock solution: 4.870 gms. of ϕ_{3C} in 100 cc. of benzene, prepared by shaking ϕ_{3CCl} with mercury for two days.
- Stock solution: 4.786 gms. of ϕ_{3C} in 100 cc. of toluene, prepared by shaking ϕ_{3CCl} with molecular silver for five days.
- Stock solution: 5.047 gms. of ϕ_{3C} in 100 cc. of benzene, prepared by shaking ϕ_{3CCl} with mercury for one day.
- Stock solution: 5.051 gms. of ϕ_{3C} in 100 cc. of toluene, prepared by shaking ϕ_{3CCl} with mercury for three days.
- Stock solution: 5.523 gms. of ϕ_{3C} in 100 cc. of benzene, prepared by shaking ϕ_{3CCl} with mercury for ten days.

TABLE II

Estimation of Triarylmethyls by the Methods of Oxygen Absorption,Iodine Absorption, and Silver Liberation

Triarylmethyl	Iodine Absorption				Silver Liberation				Oxygen Absorption†		
	Calc.		N/10		Silver salt used	Calc.		Silver liberated in terms of N/10 Ag* cc.	Wt. of R ₃ CCl g.	Volume O ₂ absorbed STP	R ₃ C found % of calo.
	R ₃ C in sample g.	I ₂ ab-sorbed cc.	R ₃ C found % of calo.	cc.		R ₃ C in sample g.	cc.				
Diphenyl-biphenyl-methyl	0.520	13.73	84.4	13.79	Perchlorate	0.520	13.79	84.5	1.246	38.3	97.5
	0.522	13.65	83.6	13.90	Perchlorate	0.521	13.90	85.1			
	0.520	13.67	84.0	13.68	Acetate	0.521	13.68	83.9			
Diphenyl-naphthyl-methyl	0.574	16.60	84.9	16.91	Perchlorate	0.573	16.91	86.6	0.959	31.6	96.8
	0.573	16.31	83.5	16.84	Perchlorate	0.574	16.84	86.1			
	0.572	16.97	86.6	16.44	Acetate	0.561	16.44	86.0			
p,p'-Bi-phenylene-bis(diphenyl-methyl)	0.386	12.76	80.2	12.51	Perchlorate	0.377	12.51	80.4			
	0.386	12.92	81.3	11.76	Perchlorate	0.358	11.76	79.6			

†Stock solution: 5.234 gms. of R₃C in 100 cc. of 98% Br₂ prepared with Ag; shaken three days.
 ‡Stock solution: 5.753 gms. of R₃C in 100 cc. of 98% Br₂ prepared with Ag; shaken six days.
 §Stock solution: 1.936 gms. of R₃C in 50 cc. of 98% Br₂ prepared with Ag; shaken three days.
 ¶Separate sample prepared under identical conditions.

Analysis of Crystalline Hexaphenylethane

The isolation of crystalline hexaphenylethane was carried out in a bulb of the modified type described by Bachmann and Kloetzel⁵⁹. Solutions of triphenylmethyl in benzene prepared from triphenylchloromethane and mercury were siphoned into the bulb in a nitrogen atmosphere. After removal of the solvent at 50-60° under reduced pressure, the yellow oil was dissolved in hot acetone and allowed to crystallize over night. The next morning the solvent was drawn off and the crystals washed thoroughly with cold acetone. The crystals were dried alternately in a stream of nitrogen and in vacuum for one hour at 50-60°. The ethane thus prepared is free of solvent,--a 1.3 gm. sample heated at 65-70° for one hour and then at 85-95° for another hour suffered a total loss of only 0.8 mg.

In an atmosphere of carbon dioxide, samples of the crystalline material were transferred to small glass tubes which were then tightly stoppered. The tubes were carefully weighed and the samples transferred to 50 cc. Erlenmeyer flasks provided with ground glass stoppers. These flasks were immediately evacuated and filled with nitrogen by means of the

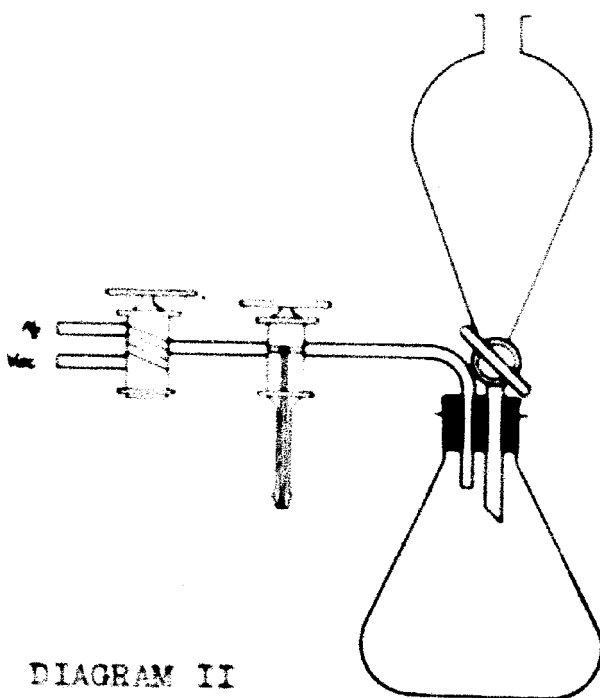


DIAGRAM II

apparatus shown in diagram II. Twenty-five cc. of 0.1 N iodine solution or 25 cc. of 0.1 N silver perchlorate solution was then introduced through the separatory funnel. With silver perchlorate, it was necessary to place several sharp glass rods in the flask, or first to dissolve the crystalline ethane in benzene or toluene; otherwise the crystals became coated with triphenylmethyl perchlorate and failed to react completely. After all the samples had been transferred in this fashion, the glass tubes were reweighed, the loss in weight in each case representing the quantity of ethane used.

Samples of the ethane for oxygen absorption were weighed into constricted test tubes which were immediately filled with nitrogen, then with bromobenzene and quickly sealed.

The analyses in each case were made as described for triphenylmethyl solutions (page 35, 38). The results of the analyses are shown in Table III.

TABLE III

Analysis of Crystalline Hexaphenylethane by the Methods of OxygenAbsorption, Iodine Absorption and Silver Liberation

Sample No.	Oxygen Absorption			Iodine Absorption			Silver Liberation from AgClO_4	
	Ethane used, g.	Volume O_2 absorbed, cc. at STP	Ethane found, %	Ethane used, g.	N/10 I_2 absorbed, cc.	Ethane found, %	Ethane used, g.	Silver liberated in terms of N/10 Ag^+ cc.
1	0.7158 0.7825	33.9 37.0	102.9 102.6	0.4366 0.4385	15.55 16.09	86.6 89.2	0.4159 0.5241	15.45 19.07
2	0.6033 0.6269	28.5 29.7	102.6 102.7				0.3364 0.3509	12.02 12.82
3	0.6321 0.7628	29.7 36.2	101.6 103.2	0.2819 0.4088 0.3961	10.03 15.13 14.58	86.6 90.0 89.5		90.4 88.5
4	0.8535	40.3	102.5	0.5674 0.4915	21.11 18.05	90.5 89.4		
5	0.6608	30.0	100.8	0.5622 0.4926	21.55 19.00	93.3 93.9		
6	0.6845 0.6128	30.5 27.7	96.8 98.0	0.3641 0.4678 0.4932 0.3238	13.03 16.52 17.58 11.48	87.0 85.9 86.7 86.2		

sContained a small amount of peroxide.

Reduction of Silver Perchlorate and Silver Acetate
by Excess of Hexaphenylethane

These experiments were conducted in the manner described for the analyses in the immediately preceding section except that the silver salt was carefully weighed and allowed to react with a known excess of crystalline hexaphenylethane. With a 0.4224 gm. sample of anhydrous silver perchlorate and a 60% excess of hexaphenylethane, 98.9% of the silver salt was reduced to metallic silver. A 0.2601 gm. sample of silver acetate, allowed to react with an 80% excess of hexaphenylethane, gave 98.1% of the calculated amount of metallic silver. With 0.4994 gm. of silver acetate and 0.728 gm. of hexaphenylethane (theoretically equivalent quantities if the hexaphenylethane is pure), 92.5% of the original silver acetate was reduced.

Oxygen Absorption in the Presence of Pyrogallol

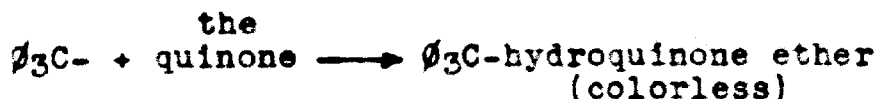
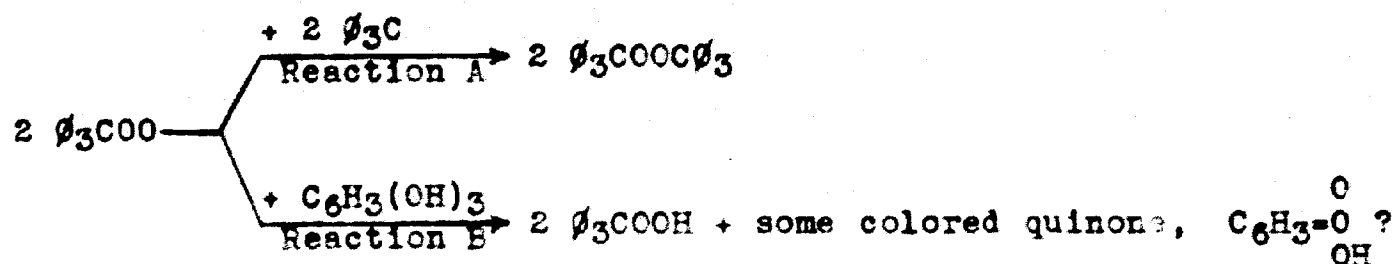
In order to reproduce as nearly as possible the conditions of Ziegler's experiments²⁶, 0.5 gm. samples of triphenylmethyl were prepared in toluene from triphenylchloromethane and mercury in constricted test tubes, the bottoms of which had been blown to thin bulbs which could be easily broken. After shaking for two days, the tube was placed in a Drechsel bottle containing a solution of 1 gm. of redistilled pyrogallol in 30 cc. of ethyl benzoate; in all other respects the apparatus was the same as for ordinary oxygen absorption. In starting the absorption, the thin bulb was broken under the surface of the ethyl benzoate solution before any oxidation could occur. This was done in order to prevent formation of the stable symmetrical peroxide, $\phi_3\text{COOC}\phi_3$ (Reaction A

below). As soon as the oxidation had begun, the solution, presumably because of dehydrogenation of pyrogallol by the peroxide radical, $\phi_3\text{COO}\cdot$, assumed a deep red color. From this point on, the total absorption of oxygen is governed by the manner of manipulation. If oxygen is introduced rapidly, the solution retains its red color to the end, and a total absorption of not more than 80-90% of the calculated results in about one hour. If, however, with the initial appearance of the red color, the solution is swirled without further access to oxygen, it is decolorized by the still unoxidized triphenylmethyl. If the oxygen is henceforth introduced intermittently in small amounts, then the red color is alternately reformed and discharged, and the total oxygen absorption in about one hour amounts to only 50-60% of the calculated.

We interpret these results as follows: It is known that triphenylmethyl reacts readily and irreversibly at room temperature with simple quinones such as benzoquinone:



and the resulting colorless ethers are stable compounds⁶⁰. In the oxidation of triphenylmethyl in the presence of pyrogallol, the dehydrogenation of pyrogallol by the intermediate radical, $\phi_3\text{COO}\cdot$, must result in the formation of a corresponding quinone, a highly colored compound. With excess of unoxidized triphenylmethyl still present, addition of the free radical to this quinone may ensue, and thus, a stable triarylmethyl ether, devoid of the capacity to absorb oxygen, will be formed. The final result will therefore be a low oxygen absorption.



On the other hand, by rapid introduction of oxygen, the formation of the unsymmetrical peroxide, ϕ_3COOH , occurs rapidly and thus, the side reaction of the free radical with the quinone will be minimized. The oxygen absorption in this case must approach nearer to that calculated for exclusive formation of ϕ_3COOH .

Further experimental difficulty arose in that the endpoint of the absorption is uncertain. Initially the absorption is rapid, but this is followed by a slow and appreciable absorption which continues for hours. This secondary oxidation is caused in some way by the system, triphenyl hydroperoxide + pyrogallol.

One gram of pure triphenylmethyl hydroperoxide, prepared according to the directions of Wieland and Maier⁶¹, was shaken in the absorption apparatus at room temperature with a solution of 1 gm. of pyrogallol in 30 cc. of ethyl benzoate. Immediately on mixing, the solution began to assume a reddish color which increased in intensity over a period of several hours. Simultaneously a slow absorption occurred, amounting in two hours to 1.8 cc. of oxygen; in seventeen hours to 7.1 cc. The reddish-brown product was decolorized by addition of triphenylmethyl in the absence of oxygen.

Triphenylmethyl Esters from the Reaction of
Triphenylmethyl with Silver Salts

The esters listed below were isolated as follows: One-hundredth of a mol of triphenylmethyl in 30 cc. of benzene, prepared from triphenylchloromethane and mercury, was added, in the absence of air, to a suspension of 0.15 mol of the corresponding silver salt in 10 cc. of benzene. After shaking over night at room temperature, the mixture was warmed, filtered from metallic silver and excess of silver salt, and extracted with small portions of benzene. The filtrate was concentrated under reduced pressure at 50° to a nearly colorless oil.

Triphenylmethyl acetate was crystallized from petroleum ether; yield, 85%; m.p., 55-6°. The product is identical with that prepared by the method of Gomberg and Davis³².

Triphenylmethyl benzoate crystallized in clumps of short colorless needles from benzene or carbon tetrachloride; yield, 80%; m.p., 169-70°.

Anal. calc. for $C_{26}H_{20}O_2$: C; 85.66 H; 5.53

found: C; 85.55 H; 5.56

Hydrolysis: calc. $\%CO_2$; 33.23

found; 33.4

Triphenylmethyl-phenylacetate crystallized with some difficulty from petroleum ether as colorless glistening rhombs; yield, 82%; m.p., 75-6°.

Anal. calc. for $C_{27}H_{22}O_2$: C; 85.70 H; 5.86

found: C; 85.40 H; 5.97

Hydrolysis: calc. $\%CH_2CO_2$; 35.70

found; 35.9

Triphenylmethyl p-chlorobenzoate crystallized from benzene and petroleum ether in fine colorless needles; yield, 89%; m.p., 163-8°.

Anal. calc. for $C_{26}H_{19}ClO_2$: C; 78.28 H; 4.80

found: C; 7793 H; 477

Hydrolysis: calc. $\text{Cl} \rightarrow \text{CO}_2$; 39.01

found: 39.7

Triphenylmethyl carbonate prepared by this method was contaminated with triphenylmethyl peroxide which was separated by extracting with a small amount of warm benzene. On concentrating, a 35% yield of triphenylmethyl carbonate⁶² was obtained.

The esters prepared by this method are identical with those obtained by the reaction of triphenylchloromethane with the respective silver salts.

Triphenylmethyl perchlorate was prepared by addition of a solution of 0.5 gm. of silver perchlorate in 15 cc. of toluene to 0.47 gm. of crystalline hexaphenylethane dissolved in 10 cc. of toluene. The mixture of metallic silver and triphenylmethyl perchlorate was filtered off in the absence of moisture, washed with benzene and extracted with 4 cc. of hot nitrobenzene. Addition of benzene and cooling caused crystallization of the perchlorate; yield, 0.15 gm.; m.p., 148-9°. The residue from the nitrobenzene extraction was washed with acetone and the solid obtained by evaporation of the acetone filtrate was recrystallized from carbon tetrachloride. The product was 0.26 gm. of pure triphenylcarbinol. As previously mentioned (page 17) the above esters are not affected by long shaking with molecular silver in benzene.

Synthesis of Some New Triarylmethyl Acetates and Perchlorates

The acetates listed below were synthesized as follows: a mixture of 3 gms. of the respective chloromethane, 3 gms. of silver acetate and 60 cc. of dry benzene was refluxed in the absence of moisture for two hours. The hot solution was separated from the insoluble silver salts and the residue extracted with small portions of warm benzene. The combined filtrate was then concentrated to an almost colorless oil which usually solidified on scratching under petroleum ether.

Diphenylbiphenylmethyl acetate crystallized as finely divided colorless crystals from petroleum ether; yield, 88%; m.p., 92-3°.

Anal. calc. for $C_{27}H_{22}O_2$: C; 85.7 H; 5.86

found: C; 85.8 H; 5.95

Hydrolysis: calc. CH_3CO_2 ; 12.43

found; 11.90

Phenyldibiphenylmethyl acetate crystallized in colorless plates from benzene and petroleum ether; yield, 91%; m.p., 92-3°.

Anal. calc. for $C_{33}H_{26}O_2$: C; 87.2 H; 5.64

found: C; 87.2 H; 5.75

Hydrolysis: calc. CH_3CO_2 ; 10.35

found; 10.31

p,p'-Biphenylene-bis-(diphenylmethyl acetate) was obtained as pale yellow plates from benzene and petroleum ether; yield, 90%; m.p., 186-7°.

It is intended to prepare these same esters by means of the reduction of silver acetate and silver perchlorate by the corresponding triarylmethyl radicals.

Anal. calc. for $C_{42}H_{34}O_4$: C; 83.7 H; 5.69

found: C; 83.7 H; 5.67

Hydrolysis: calc. CH_3CO_2 ; 14.3

found; 13.9

The perchlorates listed below were prepared as follows: To a hot solution of 0.01 mol of the respective carbinol in 50 cc. of acetic acid and 5 cc. of acetic anhydride was added dropwise a 10 to 20% excess of 70% perchloric acid. After cooling, and in some cases after adding a little dry benzene to induce crystallization, the colored salt which precipitated was transferred to a sintered glass funnel which was fitted with a stopper carrying a calcium chloride tube and a dropping funnel. The crystals were washed with a cold mixture of acetic acid-acetic anhydride, dry benzene and finally with dry ether. After drying in a stream of dried air for twenty to thirty minutes the salt was transferred to a vacuum desiccator containing phosphorus pentoxide and soda lime. The yields were 93 to 98%.

Diphenylbiphenylmethyl perchlorate was obtained as scarlet plates which appeared green-gold by reflected light. The melting point was 164-5°.

Anal. calc. for $(C_{25}H_{19}) \cdot ClO_4$: ClO_4 ; 23.74

found: ClO_4 ; 23.8

Phenyldibiphenylmethyl perchlorate separated as greenish-brown needles which appeared deep red when powdered or when dissolved in acetic acid. The perchlorate melted with decomposition at 199-200°.

Anal. calc. for $(C_{31}H_{23}) \cdot ClO_4$: ClO_4 ; 20.00

found: ClO_4 ; 20.1

p-Phenylene-bis-(diphenylmethyl perchlorate) was obtained as a chocolate-brown powder. The sample melted when placed in a bath previously heated to 113-4°.

Anal. calc. for $(C_{32}H_{24}) \cdot (ClO_4)_2$: ClO_4 ; 32.7

found: ClO_4 ; 32.6

p,p'-Biphenylene-bis-(diphenylmethyl perchlorate) precipitated as a deep red powder which melted if placed in a bath not lower than 115°. If placed in the bath at 100° the compound sintered gradually and occasionally exploded at 160-200°. If placed in the bath at above 115° it melted immediately.

Anal. calc. for $(C_{38}H_{28}) \cdot (ClO_4)_2$: ClO_4 ; 29.1

found: ClO_4 ; 28.9

Treatment of diphenyl-1-naphthylcarbinol with $HClO_4$ in acetic acid-acetic anhydride resulted in the initial formation of a deep green color which rapidly faded to a brownish-red. A colorless precipitate was isolated and identified as 9-phenyl-1,2-benzofluorene⁶³. The yield was 35%.

Synthesis of 9,9'-Diaryldifluoryls

9,9'-Diphenyldifluoryl⁴¹ (XV).- In a 50 cc. glass stoppered Erlenmeyer flask 3 gms. of 9-phenyl-9-chlorofluorene was dissolved in 50 cc. of dry acetone containing 7.5 gms. of anhydrous sodium iodide. The flask was flushed with nitrogen, stoppered and placed on the shaking machine. The acetone solution gradually assumed the deep red color of iodine and simultaneously a mixture of finely divided sodium chloride and colorless crystals of the ethane precipitated. After shaking over night the mixture was quickly filtered with suction through a Jena funnel. The adhering

iodine was removed by washing with acetone and the sodium chloride by thorough washing with water. After final washing with a small amount of acetone the remaining crystals were dried for two hours in a vacuum desiccator over phosphorus pentoxide; yield, 2.63 gms.; m.p., 254-6° (corr.) in nitrogen. The melting point reported by Schlenk and Herzenstein is 254°³⁴. Their product was prepared by the action of copper on the chloromethane.

Anal. calc. for $C_{38}H_{26}$:	C; 94.57	H; 5.43
	found: C; 94.27	H; 5.60

A sample of our hydrocarbon was converted to the corresponding peroxide, m.p., 193-4° in 75% yield.

A carefully weighed sample of the chloride was treated with sodium iodide as before and the iodine liberated in the reaction was titrated with standard sodium thiosulfate solution.

Wt. of chloromethane, 1.055 gm.	Calc. cc. N/10; 38.12
	found; 38.14

9,9'-dibiphenyldifluoroyl (XVI).— Six gms. of 9-biphenyl-9-chlorofluorene was dissolved in 100 cc. of dry acetone containing 10 gms. of anhydrous sodium iodide and the mixture shaken over night. The precipitate which formed was filtered in an atmosphere of nitrogen, washed with acetone, water and finally with acetone. In some cases the product was recrystallized from benzene in a nitrogen atmosphere. The yields were 80-90%.

Schlenk^{34b}, and Scherp⁶⁴, have reported the melting point as 175-6° and 175° respectively. Our product began to melt, in air, at 175°, but did not completely liquefy below 181°. In an atmosphere of nitrogen the melting point was 236°, with decomposition to a red liquid.

From 0.1 gm. of our ethane 0.081 gm. of the peroxide, m.p., 192-3°, was obtained by passing a stream of oxygen through the refluxing benzene solution for one hour.

2,2'-di-1-naphthyldifluoryl (XVII).- Five gms. of 9-(1-naphthyl)-9-chlorofluorene was dissolved in warm acetone and, in the bulb used for the isolation of hexaphenylethane, was treated with a solution of 7.5 gms. of anhydrous sodium iodide in 25 cc. of dry acetone. The liberation of iodine occurred rapidly and a citron-yellow precipitate was formed. After swirling the mixture for 45 minutes, the bulb was placed in the refrigerator for one hour. The solid was separated by forcing the mother liquor under nitrogen pressure through the stopcock at the bottom of the bulb. After washing with water until the filtrate was free of halide ion, the precipitate was washed with acetone and dried alternately in a vacuum and in a nitrogen atmosphere for one and one-half hours.

Dissolved in 15 cc. of bromobenzene, 1.00 gm. of this material absorbed 18.1 cc. of oxygen (STP). This corresponds to 47% of the calculated amount.

Two grams of the same product was dissolved in 25 cc. of benzene and allowed to oxidize slowly in air. The resulting solution was clear but deep red in color. The benzene was evaporated at room temperature and the resulting mixture of solid and red oil was washed with cold benzene. The solid was 0.84 gm. (40%) of nearly pure peroxide, m.p., 174-7°, which was obtained as colorless crystals possessing the correct melting point, 182-3°¹⁶, on recrystallization from benzene.

The Decomposition Product of 1-Naphthyl-fluoryl.- A

solution of 6 gms. of 9-(1-naphthyl)-9-bromofluorene in 50 cc. of dry benzene was shaken with 12 gms. of molecular silver in a glass stoppered graduate cylinder. Within an hour a heavy precipitate of the ethane was formed but on prolonged shaking this precipitate redissolved, owing to the formation of a more soluble polymerization product. However, the original deep red-brown color was not completely dispelled on long shaking. After five days, the flask was opened, and the solution was filtered from the silver and silver bromide. The resulting red solution was heated with norite, filtered and concentrated at room temperature. Addition of petroleum ether to the warm benzene solution caused the precipitation of 1.4 gms. of a slightly pink amorphous powder. This product was purified by reprecipitation from benzene by means of petroleum ether. The faintly colored product decomposed at approximately 220° when an attempt was made to purify it by vacuum sublimation at 0.05 mm. pressure but did not melt in air at 280° . A molecular weight determination by the Rast method⁶⁵ gave an average value of 1215. The analysis corresponds very nearly to that calculated for a polymer of 1-naphthylfluoryl, the low carbon value being due most likely to the presence of a small amount of oxygen-containing impurity.

Anal. calc. for $(C_{23}H_{15})_x$: C; 94.8 H; 5.19

found: C; 93.8 H; 5.34

Reactions of Diphenyl- and Dibiphenyldifluoryl with
Silver Perchlorate and with Iodine

9-Phenylfluorylpyridinium Iodide.(page 22).- To 1.4 gms. of 9-9'-diphenyldifluoryl in a 50 cc. glass stoppered Erlenmeyer flask was added a solution of 0.75 gm. of iodine in a mixture of 5 cc. of pyridine and 40 cc. of benzene. A few sharp glass rods were introduced, the air space was flushed with nitrogen and the flask tightly stoppered. After shaking at room temperature for three days the light brown precipitate was filtered and washed with benzene. The yield was 55%. The compound sintered at 177° and melted at 183-6°.

Anal. calc. for $C_{24}H_{18}NI$: I; 28.4

found: I; 28.3

Estimation of Iodine Absorbed and Silver Liberated

These reactions were conducted with the crystalline ethanes as described for crystalline hexaphenylethane. At temperatures above 25° the tightly stoppered flasks were placed in a water bath controlled to within $\pm 3^\circ$ of the desired temperature. The results are shown in Tables IV and V.

TABLE IV

Diphenyldifluoryl with Silver Perchlorate and with IodineDiphenyldifluoryl with Excess Silver Perchlorate

Exp. No.	Wt. of ethane, g.	Silver liberated in terms of N/10 Ag ⁺ , cc.	Ethane reacted, %	Conditions of reaction
1	0.4241	14.22	80.9	75° for 5 hrs.
	0.4436	14.27	77.6	75° for 5 hrs.
2	0.4497	13.63	73.1	80° for 5 hrs.
	0.6508	15.76	58.4	80° for 5 hrs.
	0.4086	15.88	93.8	25° for 3 days
3	0.4879	18.76	92.8	25° for 5 days
	0.3478	13.12	91.0	25° for 5 days
4	0.5379	20.72	93.0	25° for 3 days
	0.3600	13.18	88.4	25° for 2 days
	0.3162	11.50	87.8	25° for 3 days

Diphenyldifluoryl with Excess Iodine^a

Exp. No.	Wt. of ethane, g.	N/10 I ₂ absorbed, cc.	Ethane reacted, %	Conditions of reaction
1	0.3430	12.26	86.2	75° for 1 hr.
	0.3711	14.76	71.6	75° for 1 hr.
3	0.4689	19.81	101.5	25° for 3 days

Silver Perchlorate with Excess Diphenyldifluoryl[†]

Exp. No.	Wt. of AgClO ₄ , g.	Wt. of ethane, g.	Ag liberated in terms of N/10 Ag ⁺ , cc.	Ag ⁺ reduced found, %	N/10 Ag ⁺ not reduced, cc.	Ag ⁺ not reduced found, %
5	0.5560	0.7223	23.89	89.1	1.83	6.8
	0.4898	0.9839	22.04	93.2	0.97	4.1
	0.5929	0.9218	26.01	91.0	2.16	7.5

^aThe endpoint in these titrations was obscured by the formation of a turbid precipitate (see page 22).

[†]The reaction mixtures in each case were shaken at 25° for 3 days.

TABLE V

Dibiphenyldifluoryl with Excess Silver Perchlorate
and with Excess Iodine^a

Exp. No.	Iodine Absorption			Silver Liberation		
	Wt. of ethane, g.	N/10 I ₂ ab- sorbed, cc.	Ethane found, %	Wt. of ethane, g.	Ag liber- ated in terms of N/10 Ag ⁺ , cc.	Ethane found, %
1	0.2568	7.48	92.3	0.3105	8.34	85.2
2	0.3671	9.89	85.6	0.458	12.48	87.2
				0.448	12.13	86.0
3	0.3506	9.74	88.3	0.4751	13.03	87.3
				0.6776	18.75	88.1

Silver Perchlorate with Excess Diphenyldifluoryl

Wt. of AgClO ₄ , g.	Wt. of ethane, g.	Ag liber- ated in terms of N/10 Ag ⁺ , cc.	Ag ⁺ reduced, found, %
0.3003	0.7952	14.04	97.0
0.2931	0.7427	13.92	98.5

^aAll reaction mixtures were shaken at room temperature for three days.

Reaction of Pentaarylethanes with
Silver Perchlorate and with Iodine

For reactions at room temperature, the samples were weighed into 50 cc. glass stoppered Erlenmeyer flasks, 30 cc. of 0.1 N silver perchlorate in toluene was added, the air was replaced

by nitrogen and the flasks tightly stoppered. The samples at 60° were shaken in a thermostat which was controlled to $\pm 0.5^\circ$.

For reactions at 100° and at the boiling point, samples of the ethanes were weighed into a 50 cc. round bottom flask which was fitted with a condenser by means of a ground glass joint. The condenser was fitted with a three-way stopcock leading to a mercury trap. Thirty cubic centimeters of 0.1 N silver perchlorate solution in toluene was added, the air in the system was replaced by nitrogen, and the flask heated to 100° on the steam bath or to the boiling point with a small flame.

The analyses were made as described for triphenylmethyl solutions.

TABLE VI

The Reaction of Silver Perchlorate with Pentaarylethanes

<u>Pentaphenylethane</u>			<u>Triphenyldibiphenylethane</u>		
<u>Wt. of ethane, g.</u>	<u>Conditions of reaction</u>	<u>Ag liberated, % of calco.</u>	<u>Wt. of ethane, g.</u>	<u>Conditions of reaction</u>	<u>Ag liberated, % of calco.</u>
0.1825	25° - 4 months	43.0	0.4896	25° - 5 wks.	26.0
0.2006	25° - 4 months	45.0	0.4344	25° - 5 wks.	24.0
0.2956	60° - 4 days	20.8	0.2615	60° - 4 days	40.5
0.3396	60° - 4 days	28.2	0.5952	60° - 4 days	39.7
0.3320	60° - 4 days	23.2	0.3891	60° - 4 days	41.6
0.4065	100° - 45 min.	28.9	0.4787	100° - 45 min.	39.7
0.3540	100° - 45 min.	36.9	0.4101	100° - 45 min.	51.7
0.2788	100° - 4 hrs.	18.9	0.5000	100° - 4 hrs.	55.4
0.2972	100° - 4 hrs.	21.6	0.4434	110° - 10 min.	65.1
0.2810	110° - 10 min.	65.6	0.4515	110° - 30 min.	71.0
0.3715	110° - 10 min.	72.9	0.4626	110° - 1 hr.	78.0
0.4050	110° - 1 hr.	78.8	0.5105	110° - 1½ hrs.	56.6
0.3531	110° - 1½ hrs.	44.1	0.4649	110° - 3 hrs.	32.3

Pentaphenylethane with Iodine

<u>Wt. of ethane, g.</u>	<u>Conditions of reaction</u>	<u>I₂ absorbed, % of calco.</u>
0.3164	115° - 1 hr.	91.48
0.3110	115° - 1 hr.	89.68
0.1588	100° - 4 hrs.	94.9

Endpoints obscured by formation of a turbid precipitate.

Biradicals

9,10-Diphenylanthracene and Silver Perchlorate.- A solution of 0.50 gm. of 9,10-diphenylanthracene³⁶ and 0.85 gm. of anhydrous silver perchlorate in 35 cc. of xylene was refluxed at the boiling point for five hours. No precipitation of metallic silver occurred and only a slight yellow-green color appeared in the solution. After cooling, the silver perchlorate was extracted with water and the xylene solution concentrated under reduced pressure. With addition of alcohol and cooling, 0.41 gm. of nearly pure hydrocarbon, m.p., 247-9°, was recovered.

Synthesis of p-Phenylene-bis-(diphenylmethyl) (XXIII) and the Reactions with Silver Perchlorate and Iodine.- To 4.00 gms. of p-phenylene-bis-(diphenylchloromethane) in a 50 cc. glass stoppered Erlenmeyer flask containing a few sharp glass rods was added a solution of 6 gms. of anhydrous sodium iodide in 45 cc. of dry acetone. The air was replaced by nitrogen and the stoppered flask shaken for five hours. The precipitate which formed was rapidly filtered, washed with acetone and water and finally with a little acetone. The dried product was 3.26 gms. (94%) of finely divided halogen-free crystals, which bear the appearance of powdered potassium dichromate⁶⁶. The melting point in air was identical with that reported by Wittig and Kröhne⁶⁷, 250-4°. In a nitrogen atmosphere the melting point was 264-6°.

Several peroxides may be formed. Our product was converted to the peroxide, of melting point 168-71°, which is formed by slow oxidation of the hydrocarbon in benzene solution⁶⁷. A solution of 0.30 gm. of the hydrocarbon in 35 cc. of benzene was allowed to oxidize in air over a period of four days, and there

was recovered 0.26 gm. of the pure peroxide.

The reactions with silver perchlorate and with iodine were conducted as described for crystalline hexaphenylethane.

TABLE VII

Iodine Absorption			Silver Liberation		
Wt. of hydro-carbon, g.	N/10 I ₂ absorbed, cc.	Hydro-carbon reacted, %	Wt. of hydro-carbon, g.	Ag liberated in terms of N/10 Ag ⁺ , cc.	Hydro-carbon oxidized, %
0.311	9.83	64.6	0.354	5.67	32.7
0.324	9.31	58.7	0.329	4.52	28.1
0.317	8.69	56.0	0.418	7.05	34.5

The Reaction of p-p'-Biphenylene-bis-(diphenylmethyl) with Silver Salts and Iodine.- This hydrocarbon was prepared in solution as described for triarylmethyls (page 37) and the reactions were conducted as described for those compounds. Data is included in Table II, page 42.

Tetraphenylhydrazine and Silver Perchlorate

Tetraphenylhydrazine was prepared according to the directions of Wieland⁶⁸. The reaction with silver perchlorate solution was conducted as described for other compounds. In addition to metallic silver, a very insoluble black organic material was precipitated. Its properties were not investigated. The silver titrations were conducted potentiometrically since a yellow color in the solutions obscured the usual ferric thiocyanate endpoint.

When heated with 0.1 N silver perchlorate to the boiling point of toluene, or when shaken with 0.1 N silver perchlorate in

toluene at room temperature for several days, 0.250 gm. samples liberated approximately 65% of the calculated amounts of metallic silver.

SUMMARY AND CONCLUSION

1. The reduction of silver salts by free radicals has been investigated.
2. Triarylmethyl radicals reduce a variety of silver salts, whether the salts be soluble or insoluble in organic solvents. The products of reaction are metallic silver and the corresponding triarylmethyl ester.
3. A method for the quantitative estimation of triarylmethyls, based on these reactions, has been studied. The results by this method have been compared with the results obtained by the method of iodine titration and by the method of oxygen absorption. These results could not be compared with the results by the method of oxygen absorption in the presence of pyrogallol since this method was shown to be unreliable.
4. The reduction of silver perchlorate, dissolved in toluene, affords a convenient qualitative test for the presence of free radicals. The relative rate of reduction provides a means of distinguishing between the dissociation tendencies of slightly dissociated ethanes.
5. A new method has been applied in the synthesis of several slightly dissociated, symmetrical ethanes.

Our conclusion concerning the determination of the purity of triarylmethyls is as follows.

We believe that silver salt reduction affords a reliable method for the estimation of the purity of triarylmethyl radicals. This conclusion is supported by the fact that the

iodine titration method, totally dissimilar in principle, gives results identical with those obtained by silver liberation. Moreover, although the method of oxygen absorption leads to results 10% higher than those obtained by these two concordant methods, a striking fact is noted; namely, that the maximum obtainable yields of the peroxides which form in the oxidation process are only 86-90% of the calculated^{21, 22, 47}. If these maximum peroxide yields be considered an index of the purity of triarylmethyls; the three methods of analysis may be compared as follows:

<u>maximum peroxide yield, % of calc.</u>	<u>maximum liberation of Ag, % of calc.</u>	<u>maximum absorption of I₂, % of calc.</u>
86-90	88-90	88-90

All of the above results are plausibly explained if it be assumed that triarylmethyls inherently contain approximately 10% of an impurity, susceptible to oxidation, but otherwise devoid of the properties characteristic of the triarylmethyl proper. This hypothesis is not without precedent. On the basis of independent considerations, Mitoff and Branch⁶⁹ have previously concluded that somewhere between 5 and 15% of the total oxygen absorption by triphenylmethyl may be attributed to the presence of an inherent impurity. The assumption appears most reasonable when applied to triphenylmethyl solutions. That the recrystallized, solid ethane, prior to re-solution, contains such an impurity, is unlikely.

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