NOTE.

A Silver Plated Copper Gauze Electrode in the Zinc Determination.[1]—A silver plated copper gauze electrode can be made cheaply and is a good substitute for platinum in the electrolytic deposition of zinc, especially when alkaline cyanide solutions are employed. Copper gauze of a desirable mesh is cut to a convenient size, the ends are brought together to form a cylinder and all the edges folded down. The ends are joined by interlocking folds. The spiral is supported by means of a heavy copper wire which encircles the cylinder within the upper fold and is bent at right angles for connection to the support. The folds are then sewed together by means of a copper wire. The cylinder and rod are now immersed in a dilute cyanide silver bath and coated with silver by electrolysis, after which the unplated portion of the rod is cut off. A platinum wire is used for the anode connection. After each analysis, the zinc can be removed conveniently by the use of dilute hydrochloric acid.

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THE EXISTENCE OF FREE RADICALS.[2]

BY M. GOMBERG.

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I. Introduction.

From the time when Kekulé and Franchimont first prepared triphenylmethane, numerous attempts were made to prepare the analogous hydrocarbon, tetraphenylmethane, but seemingly without success. Victor Meyer then suggested that the general hypothesis of steric hindrance might be applied in this case in order to explain the apparent non-existence of tetraphenylmethane: *i. e.*, three phenyl groups take up so much space around the central carbon atom that there is no room left for a fourth so complex group as a phenyl. Soon after this explanation was given, it fell to my lot to work out a method[3] by means of which a hydrocarbon, supposedly tetraphenylmethane, was produced. It turned out to be quite stable, melting in the neighborhood of 300° and distilling undecomposed at 430°. In order to obtain more evidence as to the constitution of this hydrocarbon, an attempt was made to prepare for comparative study the next higher completely phenylated hydrocarbon, hexaphenylethane, which would be similarly constituted and for that reason possess properties presumably similar to those of tetraphenylmethane. Accordingly, triphenylchloromethane was subjected to the

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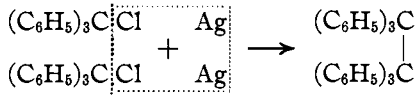
[1] See also Frary, *J. Ind. Eng. Chem.*, 5, 739, quoting L. A. Stenger.

[2] A paper read before the New York Section of the American Chemical Society, on the occasion of the presentation of the William H. Nichols Medal, March 6, 1914.

[3] *Ber.*, 30, 2043 (1897); THIS JOURNAL, 20, 773 (1898).

action of metals—sodium, silver, mercury, zinc—with the full expectation that the reaction would proceed normally and give rise to hexaphenylethane:[1]



$$\begin{matrix}(C_6H_5)_3C & Cl & & Ag \\ & & + & \\ (C_6H_5)_3C & Cl & & Ag\end{matrix} \longrightarrow \begin{matrix}(C_6H_5)_3C \\ | \\ (C_6H_5)_3C\end{matrix}$$

A hydrocarbon possessing the requisite composition ($C = 93.8\%$ $H = 6.2\%$) was actually obtained. But the unusual instability of this substance, its proneness to enter into most varied chemical reactions, and above all, its strikingly unsaturated character, precluded the natural inference that the hydrocarbon at hand was actually hexaphenylethane. The opinion was expressed that here was an instance of a compound with one atom of carbon in the trivalent state, *i. e.*, $(C_6H_5)_3C$, *triphenylmethyl*, a free radical. Subsequently it was found that many analogs of triphenylmethyl are capable of existence. In other words, there is a large class of such free radicals, a class of *triarylmethyls*.

A brief description of the most important properties of this strange class of compounds and a discussion of the arguments that have been advanced for and against the conception of free radicals will be the subject of my talk before you.

II. The General Reaction.

The mother substance is the hydrocarbon triphenylmethane, a colorless, fairly stable compound. By bromination we obtain triphenylbromomethane, a derivative of great activity. This bromide, and the analogous chloride, resemble in their general behavior the acid halides more than the alkyl halides. The halogen is easily replaced by other groups, and we may obtain a carbinol, an ether, an amine, an anilide, etc., all tolerably stable and all colorless compounds. What is true of the triphenylmethane is equally true of other triarylmethanes.

When a triarylmethylhalide, dissolved in benzene, is treated with some metal, like silver, in absence of oxygen the halogen is taken out by the metal and the unsaturated triarylmethyl is formed. The solution is invariably colored. The exact nature of the color so produced is dependent upon the nature of the three groups that are linked to the carbon atom. The triphenylmethyl itself gives in solution, as you notice, an orange-yellow color. But colors corresponding to all shades of the rainbow can be obtained by varying the nature of the three aryl groups in union with the central carbon atom. Let me illustrate this on the following triarylmethyl chlorides, to each of which some molecular silver has been added.

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[1] THIS JOURNAL, **22**, 757 (1900); *Ber.*, 33, 3150 (1900).

(1) $(C_6H_5)_3C.Cl$ gives an orange-yellow solution.[1]
(2) $(C_6H_5)_2.(p\text{-}CH_3C_6H_4).C.Cl$ gives an orange-red solution.[2]
(3) $(p\text{-}CH_3.C_6H_4)_3C.Cl$ gives a darker red solution.[3]
(4) $(p\text{-}BrC_6H_4).(C_6H_5)_2.C.Cl$ gives a brown-red solution.[4]
(5) $(o\text{-}BrC_6H_4)(C_6H_5)_2.C.Cl$ gives a red solution.[5]
(6) $(o\text{-}BrC_6H_4)(p\text{-}C_6H_4Cl)_2C.Cl$ gives a purple-red solution.[5]
(7) $(C_6H_5)_2.(\alpha\text{-}C_{10}H_7).C.Cl$ gives a dark brown solution.[6]
(8) $(p\text{-}NO_2C_6H_4).(C_6H_5)_2C.Cl$ gives a deep green solution.[7]

While the production of color in itself is characteristic, the susceptibility of the colored compound to the oxidizing influence of the air is by far its most striking feature. When, therefore, any one of these solutions be exposed to air the color will disappear. Let me illustrate this by the four examples: (1), (5), (7), and (8). This test, the production of color and the disappearance of it on exposure to air, is extremely delicate, a few mgs. of the material under examination suffice for the test.

III. Preparation of the Pure Triarylmethyl.

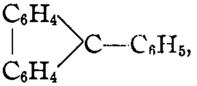
In order to prepare a triarylmethyl pure, the essential conditions are: (1) exclusion of moisture, to prevent the hydrolysis of the triarylmethyl halide itself; (2) absence of oxygen, to prevent the oxidation of the resulting unsaturated hydrocarbon; (3) avoiding exposure of the solutions to light—especially direct sunlight—to prevent autoöxidation; (4) avoiding even traces of acids, to prevent isomerization. Various contrivances can of course be used in order to insure the above conditions. Schmidlin, Schlenk and others have each described an apparatus answering these demands. The form of an apparatus which we have employed in our own laboratory, with very satisfactory results, was described some years ago.[8] It permits of the preparation, recrystallization, filtration, washing and drying of the final product without ever exposing it to the oxidizing influence of the air.

IV. Physical Properties of Triphenylmethyl.

Color.—The simple representative—triphenylmethyl itself—is in the solid state undoubtedly colorless, but it invariably becomes covered with a thin yellow coating, even if completely protected from the oxygen of the air. On the other hand, as the writer has demonstrated and has repeatedly called attention to the fact, the colorless triphenylmethyl

[1] Gomberg, THIS JOURNAL, 22, 757 (1900); *Am. Chem. J.*, 25, 320 (1901).
[2] Gomberg, *Ber.*, 37, 1631 (1904).
[3] *Ibid.*, 37, 1627 (1904).
[4] *Ibid.*, 37, 1635 (1904).
[5] Gomberg and Van Slyke, THIS JOURNAL, 32, 540 (1911).
[6] Gomberg, *Ber.*, 37, 1637 (1904).
[7] To be described in detail later.
[8] *Ber.*, 37, 2033 (1904).

goes into solution with the production of a distinct orange-yellow color in any solvent whatsoever. We must conclude that the compound, in dissolving, must undergo a change in molecular structure and that there are two modifications of triphenylmethyl, colorless and colored.[1] The credit belongs to Schmidlin[2] to have established by experiment that, even in solution, both modifications—the colorless and the yellow—exist side by side, in equilibrium with each other. There have been proposed several hypotheses in order to explain the difference in constitution between the colorless and the colored modification. We shall discuss them later.

That various analogous triarylmethyls may possess other than yellow color has already been called attention to. Some are colored even in the solid state. There is one hydrocarbon of this class,  $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\rangle C{-}C_6H_5$, which is colorless even in solution, but on heating, the solution assumes a deep blue fluorescence, almost as blue as the color of copper sulfate.

Stability.—Triphenylmethyl, in the solid state, can be kept indefinitely. Samples sealed up in an atmosphere of carbon dioxide were found to be unimpaired on opening after having been kept five years. Triphenylmethyl melts at 145°. On distilling at 18 mm. pressure it decomposes, producing considerable quantities of triphenylmethane. With a better vacuum it may prove possible to distil it undecomposed.

Solvents of Crystallization.—The unsaturated character of triphenylmethyl is evidenced by its avidity to unite with a variety of solvents.[3] In fact, it is difficult to find solvents from which triphenylmethyl can be crystallized without its taking up solvent of crystallization. It unites with benzene, toluene, the three xylenes, ethyl benzene; with methylethyl ether, diethyl ether, methylpropyl ether, ethylpropyl ether, methylal anisol, benzylethyl ether, *o*-cresolmethyl ether, methylene oxide, etc.; with ketones, such as methylethyl ketone, diethyl ketone, methylpropyl and ethylpropyl ketone, acetyl acetone, methylhexyl ketone, acetophenone, etc.; with aldehydes;[4] with esters, such as formates, acetates, propionates, butyrates, carbonates, oxalates, malonates, succinates, benzoates, etc.; it unites with nitriles, with CS_2, with chloroform, with olefines. Particularly puzzling is the fact that when crystallized from petroleum ether the crystals so obtained contain actually petroleum ether of crystallization. Samples of American petroleum ether and of Kahlbaum ether, thoroughly washed with nitric acid and then with potassium permangan-

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[1] *Ber.*, 34, 2728 (1901); **35**, 1825, 2403 (1902).

[2] *Ibid.*, 41, 2471 (1908).

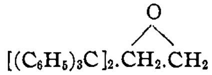
[3] Gomberg, This Journal, 23, 496 (1901); Gomberg and Cone, *Ber.*, 38, 1333, 2447 (1905); and some unpublished results.

[4] From results obtained by R. L. Jickling, in this laboratory, both aliphatic and aromatic aldehydes combine with triphenylmethyl.

ate, still give combinations with triphenylmethyl containing 14–15% of petroleum ether. We are at present investigating whether synthetic hexane, heptane, etc., are taken up by triphenylmethyl.

The combinations which are so formed are easily dissociated into the components near or at the boiling points of the respective solvents. The constancy and uniformity of composition is very striking, as can be seen from examples in the following table:

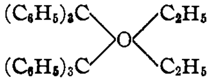
Aromatic hydrocarbon: $[(C_6H_5)_3C]_2.C_6H_6$
Ether: $[(C_6H_5)_3C]_2.(C_2H_5)_2O$
Ketone: $[(C_6H_5)_3C]_2.CH_3.CO.C_2H_5$
Aldehyde: $[(C_6H_5)_3C]_2.C_6H_5CHO$
Ester: $[(C_6H_5)_3C]_2.CH_3COOR$
Nitrile: $[(C_6H_5)_3C]_2.C_2H_5CN$
Olefine: $[(C_6H_5)_3C]_2.C_6H_{12}$
Ethylene oxide:

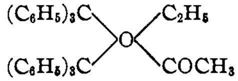


$[(C_6H_5)_3C]_2.\overset{O}{CH_2.CH_2}$

It is purely an incident that among the ketones, acetone, and among the esters, methyl- and ethyl-formate, do not give combinations with triphenylmethyl. It is more likely true that these solvents also combine with the hydrocarbon, but the temperature of dissociation lies very low, below ordinary room temperature.

From the constancy of composition it was at first inferred that these combinations occur, or are formed, in virtue of the tetravalency of the oxygen:





Lately, however, our studies have forced us to the conclusion that the assignment of constitutions with tetravalent oxygen to different compounds by various investigators was based in most cases upon erroneous and faulty experimental evidence. For this reason we would hesitate to defend our former point of view as regards the constitution of compounds produced by the combination of triphenylmethyl with ethers, ketones, esters, etc.

Conductivity.—Early in the development of this subject it became apparent that triphenylchloromethane, and also other triarylchloromethanes possess characteristics not unlike those of salts: they make perbromides, periodides, give double salts with metal halides,[1] etc. If

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[1] Norris and Sanders (*Am. Chem. J.*, 25, 55 (1901)) described the first double salt of this kind, namely, the aluminum chloride double salt. Soon after that, the writer prepared a number of analogous double salts from triphenyl- and tritolyl-chloromethane, with various metal halides (THIS JOURNAL, 23, 496 (1901); *Ber.*, 34, 2727 (1901)). Following this, Kehrmann and Wentzel described other double salts of this nature (*Ber.*, 34, 3818). Since then, large numbers of these derivatives have been described by various investigators.

salts—are they capable of conducting the electric current? Of course water could not be used as the solvent in this test, since the carbinol halides are readily hydrolyzed by it to the carbinols. Organic solvents known to possess more or less dissociating power were tried. Triphenylchloro- and bromomethane showed a ·measureable, but rather slight, conductivity in benzonitrile; in nitrobenzene, still less. Liquid sulfur dioxide was next employed, which, as you know from Walden's work, is as good an ionizing solvent for both inorganic and organic electrolytes as water itself. Walden[1] and we[2] in our laboratory, in Riga, found that these triarylmethyl halides behave truly like salts, in that they show a conductivity equal to that .of ethylamine, benzylamine; moreover, the molecular conductivity increases with dilution. It was thus definitely established that there are "*carbonium*" salts in the true sense of the definition applied to salts. The conclusion was tentatively drawn that the basic properties, in virtue of which the salt formation occurs, reside in the central carbon atom. This conclusion is still held by some, but we shall see later why this interpretation was given up in favor of another which appears to us to be more in conformity with the facts.

But, however, far more surprising than the apparent existence of the carbonium salts is the unexpected discovery that triphenylmethyl itself behaves exactly like an electrolyte when dissolved in liquid sulfur dioxide.[3] It, too, conducts the electric current quite well. It, too, possesses a higher molecular conductivity the more dilute the solution.

How is this strange phenomenon, a hydrocarbon behaving like an electrolyte, to be accounted for? Several explanations have been offered, but none of these is entirely satisfactory.

V. Chemical Properties.

Oxidation.—Foremost among the chemical reactions of triphenylmethyl, and all its analogs, is the readiness with which they unite with oxygen. We have seen this illustrated when the colored solutions of the various triarylmethyls lost their color on exposure to air. Permit me to illustrate this striking characteristic again, emphasizing this time the unusual *rate* of oxidation. On exposing to air a concentrated solution of triphenylmethyl in benzene (10%), it will be noticed that the clear solution in a very short time becomes covered with a crust of the insoluble oxidation product. The rate of absorption of oxygen is 50 cc. per 1 g. of material during the first minute of exposure.[4] Yellow phosphorus

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[1] *Z. physik. Chem.*, 43, 454 (1903).

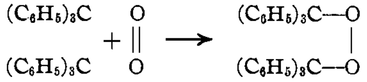
[2] *Ber.*, 35, 2404 (1902); Tousley and Gomberg, THIS JOURNAL, 26, 1516 (1904).

[3] Walden, *Z. physik. Chem.*, 43, 443 (1903); Gomberg and Cone, *Ber.*, 37, 2043 (1904).

[4] Gomberg and Cone, *Ber.*, 37, 3540 (1904).

hardly exceeds triphenylmethyl in the rate with which the latter unites with the oxygen of the air.

The compound formed in this reaction is a colorless, fairly stable substance and it has the constitution of a peroxide:



$$\begin{array}{l} (C_6H_5)_3C \\ (C_6H_5)_3C \end{array} + \begin{array}{c} O \\ \| \\ O \end{array} \longrightarrow \begin{array}{l} (C_6H_5)_3C{-}O \\ \qquad\quad\;\; | \\ (C_6H_5)_3C{-}O \end{array}$$

These peroxides, as a rule, are comparatively little soluble in the usual organic solvents such as benzene and ether, and thus their purification presents no difficulties. Consequently, the isolation of a peroxide in a reaction as described is positive proof that a compound containing a trivalent carbon atom is present. By the employment of this simple test we have proven the existence of a large number of free radicals.

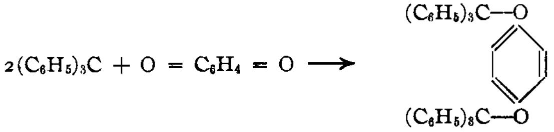
Addition of Iodine.—Next to the combination with oxygen, the behavior of triphenylmethyl towards halogens is very striking. It unites instantly with bromine, with chlorine, the reaction consisting in both substitution as well as addition. But with *iodine*, addition only takes place. Let me illustrate this by adding a solution of iodine in benzene to a similar solution of triphenylmethyl, and you notice that the dark color of iodine disappears instantly. Triphenylmethyl may be titrated in this manner with a standard solution of iodine.[1] In this reaction there is formed triphenylmethyliodide:

$$(C_6H_5)_3C + I \longrightarrow (C_6H_5)_3C{-}I.$$

Addition of Hydrogen.—As might be expected, triphenylmethyl adds hydrogen with the greatest ease, forming triphenylmethane. The hydrogenation can be carried out by adding a little zinc dust and some acetic acid[2] to a benzene solution of the unsaturated hydrocarbon. Or, in presence of finely divided platinum, hydrogen, as such, readily converts triphenylmethyl to triphenylmethane.[3]

$$(C_6H_5)_3C + H \longrightarrow (C_6H_5)_3CH.$$

Addition of Quinone.—Schmidlin[4] found that triphenylmethyl combines readily with quinone, giving stable compounds. He assigned to them the constitution:



Addition of NO and NO_2.—Schlenk and Mair[5] found that the oxides

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[1] THIS JOURNAL, 24, 597 (1902); *Ber.*, 35, 1822 (1902).

[2] *Ber.*, 36, 381 (1903).

[3] Schmidlin u. Garzia-Banus, *Ibid.*, 45, 3190 (1912).

[4] *Ber.*, 43, 1298 (1910).

[5] *Ibid.*, 44, 1170 (1911).

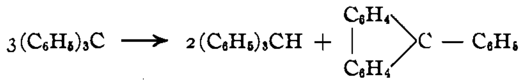
of nitrogen are taken up by triphenylmethyl with the greatest avidity. The products formed are nitroso- and nitrotriphenylmethane.

$$2(C_6H_5)_3C + NOCl \longrightarrow (C_6H_5)_3C—NO + (C_6H_5)_3CCl$$
$$(C_6H_5)_3C + NO_2 \longrightarrow (C_6H_5)_3C.NO_2.$$

Addition of Xylene.—Wieland and Müller[1] recently reported interesting results regarding the capacity of triphenylmethyl to combine with aromatic hydrocarbons in a way different from merely taking them up as solvents of crystallization. Wieland found that, on heating triphenylmethyl with xylene, dimethyltetraphenylmethane is formed:

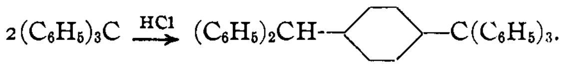
$$2(C_6H_5)_3C + C_6H_4(CH_3)_2 = (C_6H_5)_3C.C_6H_3(CH_3)_2 + (C_6H_5)_3CH.$$

Action of Light.—Solutions of triphenylmethyl in benzene are quite susceptible to light, especially direct sunlight.[2] Like most photochemical processes of this type, the reaction in this instance also is autoöxidation and reduction. Schmidlin[3] showed that the following reaction takes place:



$$3(C_6H_5)_3C \longrightarrow 2(C_6H_5)_3CH + \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\!>\! C - C_6H_5$$

Action of Acids.—Hydrochloric acid, and undoubtedly other acids, exert a peculiar catalytic influence upon triphenylmethyl. The unsaturated, unstable hydrocarbon is thus converted, in the presence of small quantities of acids, into an isomeric stable hydrocarbon.[4] This hydrocarbon was first prepared by Ullmann and Borsum[5] directly from triphenylchloromethane, and later by the writer from triphenylmethyl as mentioned above. It was first taken for the true stable hexaphenylethane. But Chichibabin[6] definitely proved its constitution to be that of *p*-benzhydryltetraphenylmethane:



Triphenylmethyl reacts also with phenols,[7] with diazomethane,[8] with substituted hydrazines,[9] etc. It may be mentioned, however, that it *does not* unite with cyanogen, nor with CO.[10]

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[1] *Ann.*, **401**, 238 (1913).

[2] Gomberg and Cone, *Ber.*, **37**, 3546 (1904).

[3] *Ber.*, **45**, 1345 (1912).

[4] *Ibid.*, **35**, 3914 (1902); **36**, 376 (1903).

[5] *Ibid.*, **35**, 2877 (1902).

[6] *Ibid.*, **37**, 4708 (1904); **41**, 2422 (1908).

[7] Schmidlin, *Ber.*, **45**, 3180 (1912); Gomberg and Cone, *Ibid.*, **37**, 2040 (1904).

[8] Schlenk u. Bornhardt, *Ann.*, **394**, 183 (1912).

[9] Wieland and Lecher, *Ibid.*, **381**, 214 (1911).

[10] Gomberg, THIS JOURNAL, **22**, 762 (1900).

VI. Constitution, First Period, 1900-1905.

Associated State.—It is obvious that the entire chemical behavior of triphenylmethyl finds its most consistent and most plausible explanation in the hypothesis that this hydrocarbon is a free radical containing a trivalent carbon atom. This explanation when first advanced was received without open opposition, but none the less with hesitancy, notwithstanding the fact that the extensive investigations by Nef have prepared us for the variability of the valence in carbon. The hesitation to acquiesce in the hypothesis of the trivalency of carbon received later its main support from the fact that the molecular weight of triphenylmethyl was found to be not 243, but double that. We used (1904) for the determination of the molecular weight by the cryoscopic method a wide range of solvents, freezing at various temperatures between 5° and 80°; such solvents as benzene, nitrobenzene, dimethylaniline, bromotoluene, phenol and naphthalene. Only in naphthalene did the molecular weight of triphenylmethyl drop considerably below 486, namely, to 410.

Here, then, was the dilemma: The entire chemical behavior of the unsaturated hydrocarbon speaks forcibly, almost exclusively, in favor of the trivalency of carbon. The only argument against this interpretation is the dimolecular state of the compound, one single physical constant. It did not seem, however, impossible to reconcile this apparent contradiction between the molecular weight, on the one hand, and the entire chemical behavior of the compound on the other hand. We have numerous examples among inorganic, as well as organic compounds, where substances in solution possess abnormally high molecular weights, double and triple that demanded by the composition and constitution of the compound in question. We say, under such circumstances, that the substance exists in the associated state, *i. e.*, several molecules unite to form a single aggregate. Is it not possible that triphenylmethyl, whatever be its molecular weight in the solid state, exists in solution in the associated state as dimolecular? Is not water itself polymolecular, the size of the aggregate varying with the temperature? Are not the organic nitriles, the acids, the acidamides di- or poly-molecular in solution? Is not association favored by the unsaturated state of the compound in question? And is not the associated state preëminently favored by solvents which lack the ionizing power, such, for instance, as the usual organic solvents? Why, then, may it not be assumed that triphenylmethyl is, perchance, in the associated state, *i. e.*, dimolecular? To quote from a paper of ten years ago:[1] "The depressions in the freezing point obtained with naphthalene as a solvent at the elevated temperature of 79–80° suggest the probability that at this temperature triphenylmethyl exists partially in the dissociated monomolecular state, as the molecular weights in this

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[1] *Ber.*, 37, 2049 (1904).

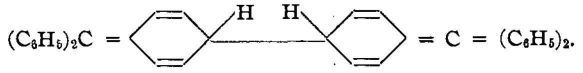
solvent are 407–420 as against 486 in other solvents. On the assumption that such dissociation may exist, be it to ever so small an extent, the behavior of the hydrocarbon becomes intelligible: through the action of oxygen or of iodine, the monomolecular form reacts first, the equilibrium is thus disturbed and it can only be restored through further and further dissociation of the dimolecular triphenylmethyl until all the compound has reacted."

$$\underset{\text{Solid}}{(R_3C)_n} \longrightarrow \underset{\text{Solution}}{(R_3C)_2} \rightleftharpoons R_3C.$$

Dimolecular Formulae.—The dimolecular state of the hydrocarbon was, however, the occasion for the suggestion of various structures for triphenylmethyl, all intending to do away with the interpretation involving the existence of free radicals.

(1) Markownikoff,[1] in 1902, expressed the opinion that "triphenylmethyl" is in reality hexaphenylethane. Assuming the latter to be extremely unstable, we can account for its decomposition reactions, by oxygen, by iodine, etc. But on what to base the assumption that hexaphenylethane must be unstable? How to account for it? No explanation was offered.

(2) Heintschel,[2] in 1903, suggested that the dimolecular state of the so-called triphenylmethyl, as well as its yellow color in solution, can be explained, perhaps, by the following formula:



(3) Vorländer,[3] in 1904, suggested that triphenylmethyl, dimolecular, must in some way be different from the actual hexaphenylethane, which, if prepared, would turn out to be stable, he believed. And so Vorländer put forward the indefinite notion of two isomers:

$[(C_6H_5)_3C]_2$	$(C_6H_5)_3C - C(C_6H_5)_3$.
Bistriphenylmethyl, hexaphenylethane A, unstable.	Hexaphenylethane B, stable.

It is indeed difficult to see the difference between this explanation and the notion of molecular combination or association.

(4) Chichibabin,[4] in 1904 and 1905, came to the defense of the hexaphenylethane constitution. He, like Markownikoff, insisted that hexaphenylethane may be expected to be extremely unstable, readily decomposable, and consequently the triphenylmethyl is in reality nothing more than hexaphenylethane. Among the arguments adduced by Chichibabin

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[1] *J. Russ. Phys. Chem. Soc.*, 34, 140 (1902).

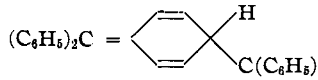
[2] *Ber.*, 36, 320 (1903).

[3] *Ann.*, 341, 1 (1905); 348, 155 (1906).

[4] *Ber.*, 37, 4708 (1904); *J. prakt. Chem.*, 74, 340 (1906).

in favor of this view was the well-known instability of trimethylene and its homologs, and other similar analogies. The fact that the saturated compound triphenylmethyl iodide gives triphenylmethyl peroxide on exposure to air appeared of particular significance to Chichibabin. Why then, said Chichibabin, could not *hexaphenylethane*, also saturated, give under similar conditions the peroxide? Chichibabin became a vigorous advocate of the hexaphenylethane formula.

(5) Jacobson,[1] 1905, disagrees with Chichibabin, and assigns to triphenylmethyl the following constitution, which is not unlike Heintschel's, a quinol-like constitution:



And, indeed, many of the reactions of triphenylmethyl are not unlike those of quinols.

(6) Flürscheim[2] (1905) thought it is hexaphenylethane, unstable, partly broken down into R_3C.

Thus, then, stood the question of the constitution of triphenylmethyl at the end of 1905. Leaving out Heinstchel's formula, there was in the field: (1) The idea of the associated molecule, associated but none the less in equilibrium with the monomolecular free radical; (2) the hexaphenylethane formulation, based upon the assumption that this, unlike all other saturated hydrocarbons, is, or rather ought to be, extremely unstable; (3) Jacobson's quinol formula. Each of these three explanations had followers, but undoubtedly the "free radical" idea was most favored, and was most widely adopted.

VII. Constitution, Second Period, 1905-1910.

We now enter upon the second period of our hypothesis. These questions presented themselves: Is it possible to show by *experimental* evidence whether a hydrocarbon of the type of hexaphenylethane *is* or *is not* stable? Is it possible to test experimentally the validity of Jacobson's suggestion? Upon the nature of the answers to these two questions the acceptance or the rejection of the hypothesis relative to the existence of free radicals depended. Let us follow each line of the inquiry separately.

Phenylated Ethanes.

One of the fundamental arguments in favor of the probable instability of hexaphenylethane was the well-known fact that the unsymmetrical tetraphenylethane seemed impossible of preparation. Anschütz[3] proved definitely that all methods, perfectly logical and reasonable in themselves, which have been employed by the many investigators to obtain the un-

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[1] *Ber.*, **38**, 196 (1905).

[2] *J. prakt. Chem.*, **71**, 505 (1905).

[3] *Ann.*, **235**, 150 (1886).

symmetrical tetraphenylethane, invariably resulted in giving the *symmetrical* compound.

$$(C_6H_5)_3C - CH_2(C_6H_5); \qquad (C_6H_5)_2CH - CH(C_6H_5)_2.$$

Unsymmetrical tetraphenylethane. Symmetrical tetraphenylethane.

The conclusion became prevalent that the unsymmetrical hydrocarbon could not exist, owing to its instability. The cause of such instability was implied to be of the same nature as that of the supposed instability of tetraphenylmethane, namely, the lack of capacity on the part of a carbon atom to hold more than three complex groups. From the presumed instability of the unsymmetrical tetraphenylethane it was further surmised that the more complex hydrocarbons, pentaphenyl- and hexaphenylethane, may reasonably be expected to be still more unstable and, consequently, less likely to exist as such.

In an attempt to improve upon the original method of the synthesis of tetraphenylmethane, it occurred to Dr. Cone and myself[1] to apply the Grignard reaction, being unaware, because of the very brief mention in the *Chemiker Zeitung* only, that Freund and Beck[2] had used the same reaction just previous to us:

$$(C_6H_5)_3CCl + BrMgC_6H_5 = (C_6H_5)_3C.C_6H_5 + MgClBr.$$

The reaction proceeded as expected, but the yield of the desired hydrocarbon was very unsatisfactory. Again we explained the result to ourselves by the hazy, but none the less useful notion of steric hindrance, *i. e.*, there is but little room left around the same carbon atom for the fourth phenyl group. In order to test the plausibility of this explanation, it was decided to couple triphenylchloroethane with magnesium benzylchloride, placing, in this manner, the fourth phenyl group at a further distance from the central carbon atom.

$$(C_6H_5)_3C.Cl + ClMgCH_2C_6H_5 = (C_6H_5)_3C.CH_2C_6H_5 + MgCl_2.$$

It was indeed a most welcome surprise that this reaction did proceed, and almost quantitatively, too. We were able to obtain any amount of the long-sought-for hydrocarbon. It turned out to be a very stable substance, beautifully crystalline, distilling in a vacuum at 270–280° unchanged, and was oxidized with considerable difficulty by CrO_3. All in all, this hydrocarbon showed no resemblance to triphenylmethyl. Moreover, a revision of some of the methods that have been previously employed by others,[3] and have been reported as unsuitable, convinced us that several investigators have actually had this hydrocarbon in their hands, but through lack of proper purification did not recognize it as such.

The next step was to prepare pentaphenylethane. Here a number of

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[1] *Ber.*, 39, 1461 (1906).

[2] *Chem. Ztg.*, 1905, 768; *Ber.*, 39, 2237 (1906).

[3] Hanriot and Saint Pierre, *Bull. soc. chim.*, [3] 1, 774 (1889).

difficulties were encountered. But finally this hydrocarbon, too, was prepared, by the action of magnesium upon a mixture of triphenylchloromethane and diphenylbromomethane:

$$(C_6H_5)_3CCl + Mg + BrCH(C_6H_5)_2 = (C_6H_5)_3C—CH(C_6H_5)_2 + MgClBr.$$

So far as we could notice at the time, pentaphenylethane presented no resemblance to the elusive triphenylmethyl. True enough, we noticed that on heating the hydrocarbon to its fusion point, 180°, some decomposition occurred. But on the other hand, we encountered no difficulty in recrystallizing pentaphenylethane from various solvents; no oxidation on exposure to air was observed.

The successful preparation of the two higher phenylated ethanes, above described, made it now seem more probable than ever that the hypothetical hexaphenylethane ought also to be a *stable* compound and that it also could be prepared if only the conditions requisite for this process could be found. Alas, neither we nor anyone else of the many who have tried it have till this day found the requisite conditions. Hexaphenylethane still remains a figment of the imagination. And so the idea began to take root more and more generally that, after all, there is no difference between the so-called triphenylmethyl and the hexaphenylethane, that the former is in reality the latter. Add to this the insistent emphasis which Chichibabin[1] laid upon his discovery that pentaphenylethane is, after all, not so very stable, that it is decomposed by hydrochloric acid at 150°, and that it absorbs oxygen at its melting point, at 180°—and you have at least a *formal* analogy, if not a real one, between pentaphenylethane and triphenylmethyl. That the analogy is purely formal can hardly be doubted. The difference is so great between the surpassing susceptibility of triphenylmethyl on the one hand, and the violent conditions necessary for the decomposition of the pentaphenylethane on the other hand, that one is equally justified in emphasizing the *lack* of analogy between these two hydrocarbons as the *existence* of the analogy, depending entirely upon the subjective view point.

Be that as it may, these two factors taken together, the failure to prepare a stable hexaphenylethane and the apparent lesser stability of pentaphenylethane than was attributed to it, these two factors had much to do with shaking the confidence of chemists that hexaphenylethane, as such, ought to be a stable substance and unlike triphenylmethyl. Henceforth the hexaphenylethane constitution for triphenylmethyl began to appear in the literature more frequently, at least as one of the more probable constitutions. It is self-evident that such a constitution could at best account for the *colorless* triphenylmethyl alone, the existence of the

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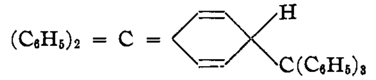
[1] *Ber.*, 40, 367 (1907). Compare also Cone and Robinson, *Ibid.*, 40, 2160 (1907); Schlenk and Herzenstein, *Ibid.*, 43, 3542 (1910); Norris, Thomas and Brown, *Ibid.*, 43, 2945 (1910).

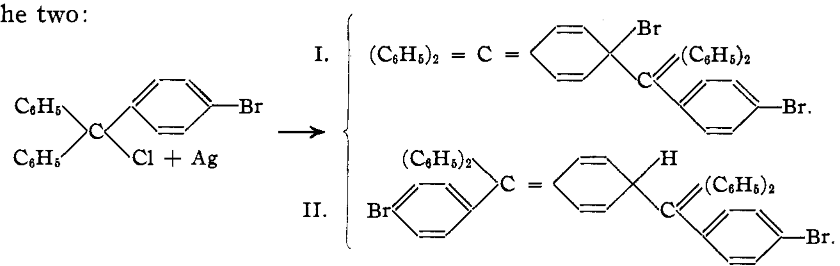
second, colored modification being explicable only with the help of some additional hypothesis.

Quinol Formula of Jacobson,



Competing with the hexaphenylethane hypothesis for recognition as the constitution of the dimolecular triphenylmethyl was the quinol formula of Jacobson, suggested in 1905. Unfortunately the author of this suggestion, like the defenders of the hexaphenylethane constitution, apparently took no cognizance of the fact, at that time well established, that there are two modifications of triphenylmethyl, the colorless and the colored. Which of these two should be represented by the quinol formula? If it be the colored modification, as was probably intended by Jacobson, how to account for the remarkable facility with which it isomerizes into the colorless modification through merely evaporating the solvent? It is an axiom with organic chemists that the presence of a "quinone" ring in the molecule imparts to the compound the attribute of the color. Whether the presence of a quinol ring may exert a similar influence was by no means certain at that time. Indeed, the known facts pointed to the contrary.[1] For this reason the writer[2] did not favor the quinol formula until after the experiments described in the following pages had clearly demonstrated that triphenylmethyl behaves as if it actually contained some kind of a quinoid nucleus. And later, when the quinol hypothesis, modified, was adopted by the writer, it was only in order to explain the constitution of the colored modification, and not of the colorless isomer.

In deciding to subject the validity of this quinoid hypothesis to the test of the experiment, we were guided by the following idea:[3] Suppose we start with the mono-*p*-bromotriphenylmethylchloride, and allow metallic silver to act upon it. On the basis of the quinol hypothesis the first step of the reaction must consist in the formation of a triphenylmethyl analog, the constitution of which, *in solution*, must be one of the two:



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[1] Zinke and Krügener, *Ann.*, 330, 68 (1904); *Ann.*, 320, 189 (1902).

[2] *Ber.*, 38, 2457 (1905).

[3] Gomberg and Cone, *Ber.*, 39, 3274 (1906); Gomberg, *Ber.*, 40, 1880 (1907).

If there be any doubt which of these two reactions, I or II, are likely to take place, one may start with a triarylmethyl halide that contains a para bromine atom in each of the three nuclei, as has been done in later experiments. But let us consider the simple problem, when there is only one brominated nucleus, and let us assume that the quinoidation takes place exclusively in the substituted ring. It is evident that the bromine atom in the quinone nucleus must now become labile, since the stabilizing effect of the benzene or "aromatic" nucleus is now wanting. Consequently this bromine atom should be easily taken out by metallic silver. On the basis that the reaction is quantitative, it can be readily seen, the silver will remove first of all one atom of carbinol-chlorine from each molecule of bromo-triphenylchloromethane, with the subsequent formation of compound I; and now, from the latter, the silver can take out only one bromine atom, and not the two. In other words, each brominated triphenylchloromethane can in this process lose no more than one and one-half atoms of halogen, one atom of chlorine and one-half atom of bromine. Now, we have tested these presuppositions on a large number of examples, and found this rule to hold absolutely true: the amount of halogen removed, over and above the carbinol-chloride, is always $^1/_2$ atom. You will ask, what results, if the one atom of bromine in the quinone nucleus is taken out? The answer is, we get once more a compound containing a trivalent carbon atom—still an unsaturated radical—and this in its turn may combine with another like radical and give rise to a compound of similar quinoid formulation, but twice as complex. Suffice it merely to state here, that we calculated how much bromine one may expect to remove if two, and also if all three nuclei contain bromine in the para position; and the calculated amounts, $^3/_4$ and $^7/_8$ of an atom, coincided to a remarkable degree with the quantities actually found at that time. All subsequent work confirmed these results.[1]

The above results seemed convincing that a quinoid constitution of some nature for the colored modifications of triphenylmethyl must and should be taken into account. However, by themselves, these results did not suffice to prove the correctness of the quinol formula. But strong corroborative evidence was soon obtained, evidence which proved the validity of the method described above and which also made it obvious how a colorlesss modification may, through tautomeric changes, give rise to a colored triphenylmethyl. Such evidence was supplied by the study of the quinocarbonium salts.

Quinocarbonium Salts.

The probable quinoid character of triphenylmethyl threw a flood of light on many phenomena which were at that time subjects of much

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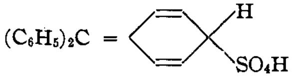
[1] *Ber.*, 39, 3294 (1906); *Ibid.*, 40, 1886 (1907); *Ann.*, 370, 181 (1909); *Ibid.*, 376, 208 (1910); Gomberg and Van Slyke, THIS JOURNAL, 32, 538 (1911).

debate. Baeyer strenuously opposed Kehrmann's view that the colored solutions of triphenylcarbinol in strong acids are due to the formation of quinoid salts of the type II, rather than of benzoid type I.

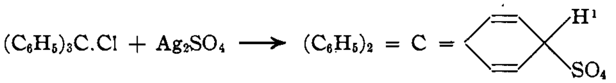
(I) $(C_6H_5)_3C—SO_4H$

(II)

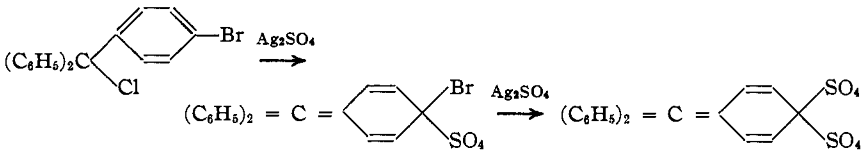


In the light of the results with triphenylmethyl our adherence to Baeyer's view began to waver. We then undertook to test the validity of these views by the same method that was employed in the case of triphenylmethyl. Contrary to Baeyer's previous findings, the verdict of our experiments was positive; these salt-like bodies were proven to be quinoid in their constitution.

When triphenylchloromethane or any of its analogs is treated with Ag_2SO_4 a double transposition takes place. Silver chloride precipitates out and triphenylmethyl sulfate is formed. This reaction is best carried out in methyl sulfate as the solvent, since the triarylmethyl sulfates are soluble in it. But, notice: while the chlorides are colorless, the sulfates resulting from them are intensely colored. This in itself is strongly suggestive that the sulfates must have a different constitution than the chlorides. And because of the color attribute the assumption is reasonable that the constitution of the sulfates is presumably quinoid.



Positive proof in regard to the quinoid character of the sulfates was found in the behavior of para-brominated triphenylmethyl chlorides. We found, namely, that when *p*-bromotriphenylcarbinolchloride is subjected to the action of Ag_2SO_4, the reaction consists in removing not only the "carbinol" chlorines, but equally so the "nucleus" bromine.[2] The interpretation can be none other than this:



To fully appreciate the cogency of this argument in favor of the quinoid constitution of the sulfates, one must bear in mind that *p*-brominated triphenylcarbinols are entirely unaffected by Ag_2SO_4—they remain colorless and their nucleus bromine is not taken out. The sulfates, therefore, differ from the corresponding carbinols not merely in possessing color, but in acquiring at the same time a change in the brominated nucleus, a change

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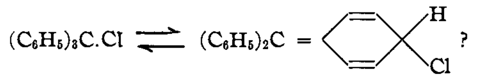
[1] SO_4 = one-half equivalent.

[2] *Ber.*, 40, 1847 (1907); Gomberg and Van Slyke, THIS JOURNAL, 32, 540 (1911).

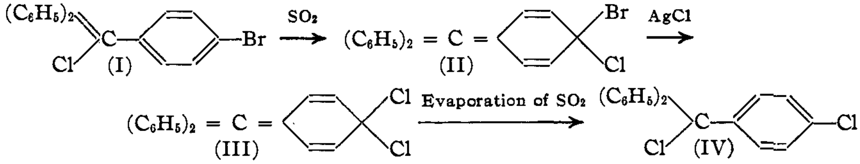
which indicates that the nucleus which contains the bromine atom has lost its stability—and is consequently no longer the true benzene nucleus.

Having thus connected positively by actual experimental evidence the color-formation of the sulfates with their simultaneous acquisition of the quinoid state, the attention was next directed to the chlorides. In the early part of this paper it has been mentioned that triphenylchloromethane and its analogs dissolve in liquid sulfur dioxide with pronounced color and behave in this solvent like true salts. On the evaporation of the solvent the original colorless chloride is again obtained. The question arose, may not the production of color be accompanied also in this instance by the conversion of the chloride while in solution in liquid sulfur dioxide, to the quinoid state:



Is it not probable that the triarylmethylchlorides may exist in two tautomeric forms—benzoid and quinoid, depending upon the nature of the solvent?

It now appeared possible to settle this question by experiment.[1] *p*-Bromotriphenylchloromethane was dissolved in benzene, ether, and toluene. The solutions were *colorless*. They were shaken with carefully dried silver chloride for days and weeks, but not the slightest change occurred. But when the same reaction was carried out in liquid *sulfur dioxide* as the solvent, then there was found to take place a complete exchange of the Br by the chlorine of the silver chloride and on evaporating the solvent *p-chloro*triphenylmethylchloride was obtained. This admits of only one interpretation:



Later, still more incontrovertible proof in favor of the quinoid character of the colored triarylmethylchlorides was obtained. The following idea suggested itself: If it be true that *p*-bromotriphenylmethylchloride in liquid sulfur dioxide is in the quinoid state (II), then the two halogen atoms must become of equal function in the molecule, both being now linked to one and the same carbon atom in the quinoid nucleus. Therefore, on the evaporation of the solvent and in the consequent restoration of the benzenoid form, the bromine will have an equal chance with the chlorine to shift to the carbinol carbon atom. The result must be the formation of some *p-chloro*triphenylmethylbromide as well as of the original *p-bromo-*

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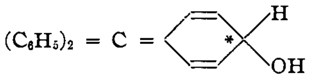
[1] *Ber.*, 40, 1860 (1907); *Ann.*, 370, 190 (1909); 376, 208 (1910).

triphenylmethylchloride, the relative amounts of the two depending upon their possible relative solubility. Experiment completely verified this presupposition.[1] Merely dissolving compound I in liquid sulfur dioxide and then allowing the latter to evaporate, induces the chlorine and bromine to exchange their relative positions.

Thus, the evidence seemed indisputable that the color formation of the sulfates and the chlorides is intimately connected with the change of the benzenoid to the quinoid form. Furthermore, since the manifestation of color and the salt-like properties of these substances are also simultaneous, the conclusion seems warranted that both of these phenomena are results of one and the same cause, *i. e.*, tautomerization to the quinoid state.[2] Consequently, these salts were named *quinocarbonium* salts, corresponding to the hypothetical *quino*carbonium base:

$(C_6H_5)_3C.OH$

Carbinol, *pseudo-base*



Quinocarbonium base

For obvious reasons the basicity was now assumed to lie in the quinone nucleus, in the C*, and not in the central carbon atom as had been originally supposed. It may also be added, that lately a number of the carbinols themselves were found capable of existing both in the quinoid state as well as in the benzoid.[3] Hence quinocarbonium bases themselves are no longer hypothetical bases.

The pursuit of this new idea, as to the function of the quinoid nucleus in imparting basicity to the molecule, was so alluring, and seemed to promise so much, that the subsequent work led us further and further away from the original problem, *i. e.*, from the immediate problem of the constitution of triphenylmethyl. It led us into the realm of the carboxonium and carbothionium salts, into that of various other oxonium salts and we found ourselves in opposition to the prevailing ideas as regards the tetravalency of oxygen in these classes of substances.

The Equilibrium Formula.

Whether our speculations respecting the valence of oxygen and the basicity of carbon be correct or not[4] may be left out of the present discussion. The significant conclusions from the results just described are these:

(1) Triphenylmethyl, *in solution*, behaves as if it had the quinol structure, either as a temporary phase or as one in equilibrium with some other phase. (2) Compounds of the type $R_3C - X$ possess the tendency to

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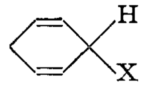
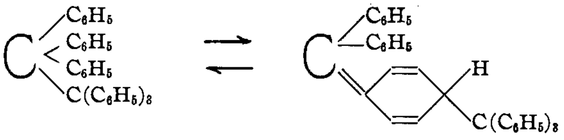
[1] *Ber.*, 42, 406 (1909).

[2] Compare Hantzsch, *Ber.*, 39, 2478 (1906).

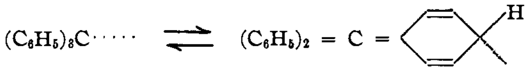
[3] THIS JOURNAL, 35, 1135 (1913).

[4] Anschütz, in the eleventh edition of *Richter's Chemistry* (1913), adopts the quinoid constitution of these salt-like compounds, as advocated in this paper.

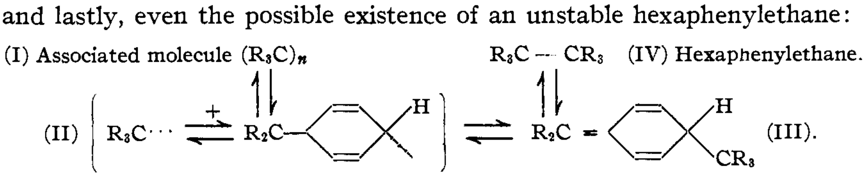
tautomerize to the quinoid modification R$_2$C =  (3) Since the nature of the group X may apparently vary within wide limits, then, as a corrolary to the second conclusion, it follows that hexaphenylethane, considered as a triphenylmethane derivative, may also possess the tendency toward tautomerization, and in this manner give rise to a compound of the quinol constitution:



While these new facts demanded, undoubtedly, some modifications in the simple monomolecular constitution as originally assigned to triphenylmethyl, they did not seem of such a nature as to set aside entirely the "trivalent carbon" hypothesis. Whether we assign to the dimolecular triphenylmethyl the constitution of an associated molecule, or of hexaphenylethene, or of a quinol, the chemical reactions of the unsaturated hydrocarbon are explicable only if we assume that it possesses the capacity to dissociate into free radicals. This, in my opinion, was to remain an essential part of whatever explanation might be advanced in order to account for the enigmatical behavior of this class of compounds. We need only to assume, and this assumption is perfectly consistent with the facts outlined above, that the tendency towards tautomerization is not limited to the triphenylmethane compounds alone, wherein C is tetravalent, but is also shared by the triphenylmethyl radical itself:



We then arrive at an explanation which embraces all the factors that enter into the discussion: The unsaturated character of triphenylmethyl, the existence of the two, colorless and colored, modifications, the dimolecular state in solution, the probability of the quinol-like constitution, and lastly, even the possible existence of an unstable hexaphenylethane:



This explanation assumes triphenylmethyl to exist in solution in various phases of constitution, all in equilibrium with each other. It accounts satisfactorily for all the facts. It becomes a matter of comparatively little consequence whether the colorless modification is assumed to be associated triphenylmethyl or hexaphenylethane. Either one would tend to give, in solution, the dimolecular triphenylmethyl of the quinol type, namely, the associated molecule through dissociation and hexaphenylethane through tautomerization. And the quinol thus produced must be in equilibrium with its products of dissociation, that is, with the two tautomeric free radicals. In other words, we can accept the quinol formulation as an intermediate phase only, and even then provided that at the same time we attribute to such a quinol the capacity to dissociate into the two free radicals.[1] It is the actual existence of these free radicals that accounts for the strange behavior of triphenylmethyl. It matters little whether the equilibrium be largely in favor of II, III, or IV, for it is a mobile, a tautomeric equilibrium. And as such it tends to restore itself as the one or the other phase is used up in a particular reaction, until the whole has reacted. Indeed, the relative equilibrium between II, III, and IV may be expected to vary with the nature of the solvent, with the temperature, and with the nature of the individual triarylmethyl under consideration.

Two Modifications of Triphenylmethyl in Solution.

Our attention should now be directed to a paper by Schmidlin,[2] in 1908, which must be considered as one of the most important contributions in this field.

The puzzling fact that the colorless triphenylmethyl gives colored solutions was first[3] attributed to possible slight oxidation. But it was soon definitely settled, in 1902, that "triphenylmethyl was white when freshly prepared. . . . .While colorless itself, the solutions of triphenylmethyl are always yellow, no matter what solvent be employed."[4] From that time on attention was repeatedly[5] called to this fact, *i. e.*, to the existence of these two modifications of triphenylmethyl, easily convertible into each other merely through changes of phase from solid to solution or *vice versa.* Schmidlin, however, observed that solutions of the colorless hydrocarbon

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[1] Gomberg, *Ber.*, 40, 1880 (1907); 46, 228 (1913). In presenting the above "equilibrium formula" for the first time, the writer called attention to the fact that such a formulation is consistent with the facts whether we look upon the dissociation products as ions or as free radicals. The ionic interpretation became the one most widely adopted (J. Schmid, F. Henrich, Stewart, Fehling's Dictionary, etc.), although the writer himself clearly gave preference to the free-radical conception: "Die Hypothese bezüglich der Existenzfähigkeit von freiem Triphenylmethyl hat demnach den besonderen Vorteil, dass wir alle Reactionen des Kohlenwasserstoffs erklären können, ohne die Ionisationstheorie soweit ausdehnen zu müssen, das sie zu nichts anderem als zu einem leeren Spiel mit Worten wird." (*Ber.*, 40, 1884.)

[2] *Ber.*, 41, 2471 (1908).

[3] *Am. Chem. J.*, 25, 335 (1901).

[4] THIS JOURNAL, 24, 602 (1902); *Ber.*, 35, 1825 (1902).

[5] *Ber.*, 35, 2403, 2407 (1902); THIS JOURNAL, 25, 1276 (1903); *Ber.*, 36, 3929 (1903); 37, 2047 (1904); 38, 2455, 2457 (1905); 40, 1880 (1907).

are at first also colorless, but acquire color only after a few seconds' standing. Following up the observation, he was able to establish definitely that the colorless triphenylmethyl is only partially converted into the colored modification, that even in solution the two modifications exist side by side, in equilibrium with each other. He found that this equilibrium is greatly influenced by the nature of the solvent, by temperature, etc.,[1] and that under ordinary conditions the equilibrium is approximately one part of the colored to nine parts of the colorless modification.

Schmidlin also proved that of the two forms the colored modification is by far the more reactive. Thus, when a yellow solution of the hydrocarbon is shaken with air, the color disappears through the conversion of the colored hydrocarbon into the colorless peroxide. But in a few seconds, the yellow color of the solution reappears, due, of course, to the transformation of some more colorless into the colored modification of triphenylmethyl until the equilibrium is again restored.

These important results of Schmidlin did not, of course, invalidate in the least the theoretical conclusions in regard to the constitution of triphenylmethyl that have been set forth in the preceding pages, for these conclusions invariably took into consideration the existence of two modifications of triphenylmethyl. But Schmidlin's results did emphasize in the most striking manner that the relation of these two modifications to each other is even more intimate than had been previously supposed, and they also served to emphasize again that no constitution of triphenylmethyl could be considered satisfactory which did not account for the ready transformation of the two modifications into each other.

Tentative explanations in regard to the relation between the two modifications of triphenylmethyl were not lacking. In 1902[2] it was ascribed to the ionization of the hydrocarbon in solution into two oppositely charged ions, R_3C^+, R_3C^-. In 1905, a simple suggestion was made by Flürscheim,[3] namely, that the colorless hexaphenylethane dissociates in solution into colored free radicals, triphenylmethyl. In 1906,[4] for the first time, positive experimental evidence was obtained that the change of the colorless into the colored form is accompanied by the production of some kind of a quinoid constitution. In the same year, a little later, but independently, Chichibabin[5] suggests the possible existence of tautomerism between hexaphenylethane and some kind of colored quinol, according to Heintschel or to Jacobson; but on the next page, in the same paper, he cites evidence which, he thinks, "spricht gegen die quinoiden Structur-

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[1] It varies also with concentration of solution (Piccard, *Ann.*, **381**, 347 (1911)).

[2] Gomberg, *Ber.*, **35**, 2403 (1902); 40, 1882 (1907).

[3] *J. prakt. Chem.*, **71**, 505 (1905).

[4] Gomberg, *Ber.*, **39**, 3297 (1906).

[5] *J. prakt. Chem.*, **74**, 342 (1906).

formeln des Triphenylmethyls," an opinion which he most strongly upholds in his next paper.[1] In 1907, based upon evidence from extensive experiments, the "equilibrium formula" was suggested, *i. e.*, associated molecule (or hexaphenylethane) ⟶ quinol ⟶ free tautomeric radicals; the production of color being due either to the dimolecular quinol or to the *quinoid* monomolecular radical.

The "equilibrium formula" is in full harmony with the facts known up to the present, but the explanation—hexaphenylethane ⟶ triphenylmethyl, is finding a wider acceptance, largely because of its simplicity.

We have now reached the end of the second period of the hypothesis relative to the existence of free radicals. During this period the trivalency hypothesis still had its adherents. Werner (1906), Schmidlin (1908), Wieland (1909), and many others spoke in favor of it. And yet, on the whole, the majority of chemists, I think, came to look upon triphenylmethyl either as unstable hexaphenylethane, or as a quinol, some admitting probable partial dissociation into radicals or ions, others refusing to admit it. Anschütz, in the tenth edition of Richter's Organic Chemistry (1905), gives equal weight to the two interpretations, the free radical and hexaphenylethane. W. A. Noyes, in the German edition of his Organic Text (1907) speaks of it as hexaphenylethane. Nernst, in the fifth edition of the Theoretical Chemistry (1907), leaves out the mention of the trivalency of carbon which was recorded in the preceding edition. Henrich, in the first edition of his "*Anschauungen über organische Chemie*" (1908), gives preference to the equilibrium idea. So does Stewart in his "Recent Advances in Organic Chemistry" (1910). Holleman-Walker, in the third English edition (1910), are undecided between triphenylmethyl and hexaphenylethane. Jacobson and Stelzner, in the second edition of Meyer and Jacobson's *Lehrbuch*, speak of triphenylmethyl in the early part of the first volume (p. 65, written in 1905), as a free radical, but in the latter part of the first volume (p. 788, written in 1907), as a substance of double the molecular weight, with probable dissociation into parts. Many other similarly divergent views could be cited.

VIII. Constitution, Third Period (1910–).

Monomolecular Triarylmethyls.—As the hexaphenylethane and the quinol constitution were gaining ascendency over the simple triphenylmethyl idea, and all because of the double molecular weight, and as the actual reality of free radicals was appearing to many more and more dubious, a paper by Schlenk,[2] 1910, gave a new turn to the subject.

In studying analogs of triphenylmethyl, he prepared the following compounds:

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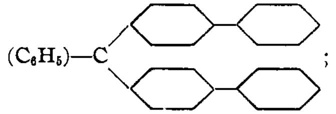
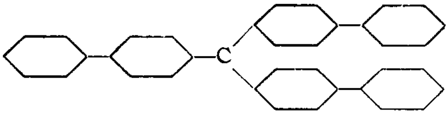
[1] *Ber.*, 40, 3970 (1907).

[2] Schlenk, Weickel u. Herzenstein, *Ann.*, **372**, 1 (1910); *Ber.*, **43**, 1754 (1910).





He found that these analogs resemble triphenylmethyl itself in every characteristic. They are colored, the intensity increasing with the number of *bi*-phenyl groups; they are unstable, readily absorb oxygen from the air and form peroxides, etc. But when the molecular weight of these unsaturated triarylmethyls was determined he found, unexpectedly, that some of these hydrocarbons exist largely as monomolecular. To be more specific: The tri-*bi*-phenylmethyl was found to be entirely monomolecular; the di-*bi*-phenyl, to the extent of 80% monomolecular; and the mono-*bi*-phenyl only to the extent of 15%.

There can be but one inference—these compounds exist as free radicals. And as the characteristic reactions of these bodies are entirely similar to those of triphenylmethyl itself, the reactions of the latter must also be due to the presence of more or less of the actual, free, triphenylmethyl radical, whatever its immediate predecessor. The supposed existence of free radicals, with carbon trivalent, becomes therefore indisputable.

With the recognition of the highly important fact that some triarylmethyls exist as wholly monomolecular the only serious obstacle and argument against the hypothesis of free radicals vanished. Soon after that, many other analogs of triphenylmethyl were found to be monomolecular.[1]

Attention was now again directed to the molecular weight of triphenylmethyl itself. The molecular-weight determinations that have been made in 1904[2] indicated that at least in naphthalene monomolecular triphenylmethyl may be assumed to exist as such. Wieland[3] now computed that the amounts of the monomolecular hydrocarbon, as calculated from these molecular-weight determinations—17% in naphthalene, 5% in benzene—are of the same order of magnitude as the equilibrium ratio between the colorless and the yellow modification in solvents as found by Schmidlin. From this he draws the inference that the yellow modification is in reality monomolecular triphenylmethyl. Later, Piccard,[4] Schmidlin,[5] and also Schlenk and Mair,[6] employing diverse methods, arrived at the conclusion

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[1] Schlenk and Rennig, *Ann.*, 394, 180 (1912); Chichibabin and Korjagin, *J. prakt. Chem.*, 88, 516 (1913).

[2] Gomberg and Cone, *Ber.*, 37, 2037 (1904).

[3] *Ber.*, 42, 3029 (1909).

[4] *Ann.*, 381, 347 (1911).

[5] *Ber.*, 45, 3180 (1912).

[6] *Ann.*, 394, 179 (1912).

that *all* solutions of triphenylmethyl contain actually monomolecular triphenylmethyl, the amount of this in benzene at 80° reaching 25–30% of the whole amount of the hydrocarbon dissolved.

Some Unsettled Questions.—But while the existence of free radicals, with carbon as trivalent, is thus firmly established, some of the minor features of this subject are not as yet as completely cleared up as one might judge from the current literature.

It has become customary to speak of the *colorless* triphenylmethyl as hexaphenylethane, in distinction to the colored modification as the actual free radical. But how vastly different is this modern conception of hexaphenylethane from the older idea! The *new* hexaphenylethane is an altogether different substance from what has been implied by that term before. Unstable it still is, and is indeed very easily broken down by a variety of reagents, but more than that: even if no extraneous force be present to break it up, the hydrocarbon still decomposes spontaneously in virtue of its inherent tendency to dissociate into two halves. And so we come in the case of hexaphenylethane to the same fundamental idea which the writer applied to the quinol formula. The quinol constitution, too, seemed acceptable as an intermediate phase only on the condition that the hydrocarbon be considered as possessing the capacity to dissociate spontaneously into two dissimilar free radicals. We mean real, actual dissociation, where the products are not of a fleeting temporary nature, but where they are entities and have a lasting existence. It is indeed far more probable, as we have expressed it in the equilibrium formula, that both the hexaphenylethane and the quinol formulae are but two tautomeric modifications of one and the same constitution, and that in solutions of the hydrocarbon, both exist side by side in equilibrium with each other. The results of the experiments described in the earlier part of this paper, the facility with which *p*-halogen in triarylmethyls can be removed must, in some way, be accounted for. The hexaphenylethane constitution does not explain them; but hexaphenylethane tautomerized accounts for those results completely, as completely as does a physically associated dimolecular molecule.

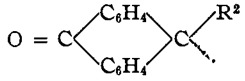
There is still another uncertainty which requires further study. It is now definitely established that the colored modification of triarylmethyls is monomolecular, and this applies even to those in the solid state, as for instance, to tri-*bi*-phenylmethyl. There is no better way at present at hand to explain this than by attributing to triphenylmethyl itself, as is done in the equilibrium formula, the capacity to undergo the same kind of tautomerization to the quinoid state as so many of its derivatives undergo. To say, as is being done, that hexaphenylethane is colorless and a radical with carbon in the trivalent state is colored, is to assert something for which at present there is no anology. Such a statement is not an explanation. It is an assertion which may be right, or wrong.

But after all, these are minor points. The really important issue—the existence of free radicals, the trivalency of carbon—that has been established.

IX. Analogs of Triphenylmethyl.

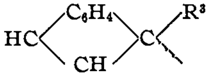
As has been mentioned in the introduction, triphenylmethyl is but an example, the simplest and most completely investigated example, of the class of the triarylmethyls. No systematic study of any particular subgroup of such free radicals has as yet been made or undertaken. The existence of about thirty-five free radicals has been demonstrated in our laboratory and as many more in other laboratories, and there is no reason to doubt that this new class of compounds will, in time, become fully as extensive as the classes of alcohols, ketones, acids, etc. Such instances of free radicals as are at present known, have been prepared with the idea to elucidate some definite feature of theoretical interest. It is now well established that the three aromatic groups around the central carbon atom may vary to any extent—some may be nitro-phenyl groups, or hydroxy-, methoxy-, bromo-, carboxy-phenyl, or they may be naphthyl groups. Also, as has been recently shown in our laboratory,[1] one of the three aromatic groups may be replaced by a non aromatic thienyl group, C_4H_3S. Furthermore, free radicals with a trivalent carbon atom have been obtained from compounds which belong to the following well-known series:

Anthracene series.........................



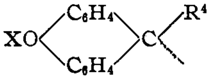
$$O = C \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} C \begin{matrix} R^2 \\ \cdot \end{matrix}$$

Indene series,..............................



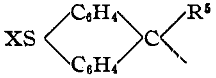
$$HC \begin{matrix} C_6H_4 \\ CH \end{matrix} C \begin{matrix} R^3 \\ \cdot \end{matrix}$$

Xanthone series...........................



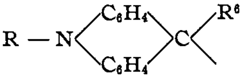
$$XO \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} C \begin{matrix} R^4 \\ \cdot \end{matrix}$$

Thioxanthone series......................



$$XS \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} C \begin{matrix} R^5 \\ \cdot \end{matrix}$$

Acridine series............................



$$R - N \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} C \begin{matrix} R^6 \\ \diagdown \end{matrix}$$

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[1] Gomberg and Jickling, THIS JOURNAL, **35**, 446 (1913).

[2] Liebermann, *Ber.*, **37**, 3340 (1904).

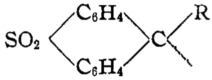
[3] Kohler, *Am. Chem. J.*, 40, 217 (1908).

[4] Gomberg and Cone, *Ann.*, **370**, 142 (1909); Gomberg and West, THIS JOURNAL, **34**, 1529 (1912).

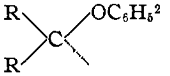
[5] Gomberg and Cone, *Ann.*, **376**, 183 (1910).

[6] Cone, THIS JOURNAL, **34**, 1703 (1912); and results to be published soon.

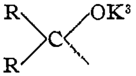
Benzophenone sulphone series ....



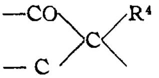
Diaryl-phenoxymethyl ....



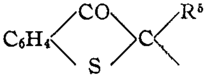
Aromatic ketones ....



Naphthalene series containing the group ......



Thio-indigo series ....



X. Historical.

Gay Lussac, in 1815, began his important studies upon cyanogen derivatives. He obtained cyanogen itself from mercuric cyanide and defined it as "a compound radical," functioning in its derivatives in the same manner as the elements, or "simple radicals," do in their derivatives, respectfully. According to Gay Lussac's idea cyanogen (CN), was a *free* radical. Dumas and Boullay later, in 1828, extended this fundamental notion of the existence of free radicals to organic compounds. They set up the theory that "etherin," —C_2H_4—, is the "compound radical" from which alcohol, ether, chloroethane, etc., are derived. In support of their contention they pointed to the existence of this radical in the free state, the gas ethylene. Liebig and Wöhler, 1832, published their memorable paper upon the "benzoyl radical." They defined a radical very much as we do now, "a never varying constituent of a series of compounds." Liebig did not oppose the idea concerning the existence of free radicals. On the contrary, he even predicted the possible isolation of alcohol radicals, which might be effected by the action of potassium on the iodides of such radicals. Berzelius and Dumas joined Liebig for a time, and their efforts were turned to discovering new radicals. Organic chemistry came to be defined as the chemistry of compound radicals. Much support was added to this view by the remarkable work of Bunsen. Between 1839 and 1843 he prepared various derivatives of "cacodyl," the chloride, the oxide, etc., and also the cacodyl itself, which he considered as a free radical, $As(C_2H_6)$, and to which was later given the more specific constitution $As(CH_3)_2$. Then followed the important work of

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[1] From results to be published soon.

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

[3] Schlenk and Weickel, *Ber.*, 44, 1182 (1911); 46, 2840 (1913)

[4] Pummerer, *Z. angew. Chem.*, 26, 549 (1913).

[5] Kalb and Bayer, *Ber.*, 46, 3881 (1913).

Frankland, and of Kolbe, 1849–1850. The former claimed to have isolated the radicals—*methyl, ethyl, etc.*—by the action of zinc upon the corresponding iodides, while Kolbe obtained the same radicals by the hydrolysis of the sodium salts of acetic, propionic and such acids. In vain did Gerhard and Laurent insist that the molecular formulas of all these so-called free radicals must be doubled, in accordance with Avogadro's hypothesis. The existence of free radicals was generally accepted as late as 1865, fifty years after Gay Lussac's introduction of this idea into chemistry. Even Kekulé for a time considered Frankland's "methyl" as distinct from ethane. But in 1864 Schorlemmer showed by experimental evidence that Frankland's and Kolbe's methyl and ethyl were nothing else than ethane and butane. From that time on, the question relative to the existence of free radicals was never seriously raised until the discovery of triphenylmethyl.

How parallel these two periods in the history of chemistry are! Now, as then, a methyl was prepared by the abstraction of halogen from the corresponding alkyl-halide. Now, as then, it was found that the molecular weight of the product must be doubled. But now, unlike as in the period of fifty years ago, it was possible to show, by physical and chemical evidence, that the product which results from the coupling of the radicals is at best unstable. It was possible to show that it does not retain its individuality, but tends to break down again and is in equilibrium with the truly free radicals. And so we find ourselves obliged to reintroduce the conception of free radicals, and also to introduce the supplementary notion of organic substances existing under certain conditions in a state of actual dissociation.

What the future holds in regard to this new revival of the much disputed question is difficult to foretell. As a working hypothesis it has fully justified its existence, it has opened a new branch of organic chemistry.

ANN ARBOR, MICH.

SYNTHESIS OF DEPSIDES, LICHEN-SUBSTANCES AND TANNINS.

BY EMIL FISCHER.[1]

Received April 30, 1914.

Gentlemen:

The substances mentioned in the title are ester-like derivatives of the phenol carbonic acids, to which belongs gallic acid, so widely distributed in the plant kingdom and discovered in 1786 by C. W. Scheele, as well

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[1] Address delivered before the Naturforscher-Versammlung, Vienna, Sept. 23, 1913; and published in *Ber.*, 46, 3253–89 (1913). Translated by Frank Rose Elder, Columbia University, and published here through the courtesy and with the consent of Excellent Fischer and of the editors of the *Berichte*.