[Contribution from the Chemical Laboratory of the University of Michigan.]

TRIPHENYLMETHYL. XXV. PREPARATION OF *p*-HYDROXYTRIPHENYLCARBINOL AND ATTEMPTS TO ISOLATE THE CORRESPONDING TRIARYLMETHYL.

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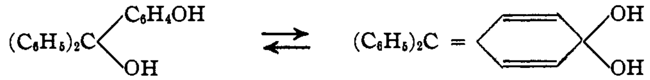
I. Introduction.

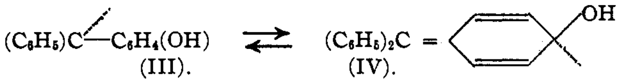
It has been shown lately[1] that a hydroxyl group in the triarylcarbinols, particularly in the *p*-position to the central carbon atom, increases greatly the tendency of the compound towards tautomerization. Triphenylcarbinol is known only in one, the colorless, state; its *p*-hydroxy derivative, however, has been obtained[2] in two distinct forms, the colorless and the colored, separable from each other and either readily changeable into the other merely by choice of suitable solvent. The distinctive behavior of these two carbinols is best explained, as has been shown, by assigning to them the two constitutions, respectively



(I). Colorless, benzonoid. (II). Colored, quinonoid.

The significance of this fact is evident. The existence of two desmotropic carbinols in equilibrium with each other implies, of itself, the theoretically probable existence of two desmotropic series of carbinol salts, each series derivable from its corresponding carbinol. Thus the hypothesis of the quinonoid structure of the colored carbinol salts, deduced previously wholly from the behavior of these salts themselves, receives strong additional support in the existence of the two desmotropic carbinols.

In view of the marked tautomerizing influence of the hydroxyl groups in the carbinols and in their salts, the questions naturally arise: What influence would a *p*-hydroxyl group in triphenylmethyl exert as regards the tendency of the free radical toward tautomerization? Would *p*-hydroxytriphenylmethyl, like the simple triphenylmethyl, exist as two forms in solution only, and as a solid, colorless? Would this *p*-hydroxylated free radical exist even as a solid in the two desmotropic forms (III) and (IV), as in the case with the corresponding carbinol? Or might the quinoid form of the *p*-hydroxytriphenylmethyl be the only one obtainable in the solid state?



(III). (IV).

For the preparation of the free radical *p*-hydroxytriphenylcarbinol

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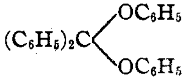
[1] Gomberg and West, This Journal, 34, 1533 (1912).

[2] Gomberg, *Ibid.*, 35, 1035 (1913).

must serve as the starting point. The methods previously used to prepare this carbinol are both tedious and extended. A far simpler synthesis has been devised during the course of this work, and since this method has proved to be efficacious in the preparation of many homologous and analogous hydroxy derivatives, a detailed study of the same has been undertaken.

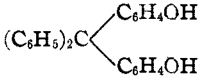
II. The Reaction between Benzophenone Chloride and Phenol.

In an unsuccessful attempt to prepare diphenoxydiphenylmethane (V) by the reaction of sodium phenoxide on benzophenone chloride, Mackenzie[1] obtained instead di-*p*-hydroxytetraphenylmethane (VI). He also noticed that the same product resulted from the direct action of phenol itself on benzophenone chloride. Through use of an analogous reaction, Smedley[2] prepared di-*p*-hydroxydiphenyldiphenylenemethane (VII) from fluorenone chloride and phenol. Zincke[3] made use of the reaction mentioned by Mackenzie, and obtained the same di-*p*-hydroxytetraphenylmethane, using a large excess of phenol and heating on the water bath for three days. On the other hand, Caro and Graebe,[4] long ago, condensed monohydroxybenzophenone chloride, and also dihydroxybenzophenone chloride, with phenol, employing sulfuric acid as the condensing agent, and obtained some benzaurine and aurine, respectively. More recently, Sachs and Thonet[5] have condensed benzophenone chloride with catechol, also by means of absolute sulfuric acid, and have obtained 3,4-dihydroxytriphenylcarbinol (VIII), but in the absence of sulfuric acid the ether of constitution (IX) was the principal product formed.



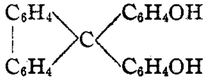
$(C_6H_5)_2C\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_6H_5\end{matrix}$

(V)



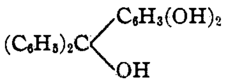
$(C_6H_5)_2C\begin{matrix}\diagup C_6H_4OH\\ \diagdown C_6H_4OH\end{matrix}$

(VI).



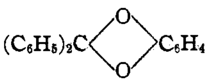
$\begin{matrix}C_6H_4\diagdown\\ |\qquad C\\ C_6H_4\diagup\end{matrix}\begin{matrix}\diagup C_6H_4OH\\ \diagdown C_6H_4OH\end{matrix}$

(VII).



$(C_6H_5)_2C\begin{matrix}\diagup C_6H_3(OH)_2\\ \diagdown OH\end{matrix}$

(VIII).



$(C_6H_5)_2C\begin{matrix}\diagup O\diagdown\\ \diagdown O\diagup\end{matrix}C_6H_4$

(IX).

Thus there were some indications in the literature that ketochlorides may be made to condense with phenols so as to yield a triarylcarbinol. As a rule, Friedel and Craft's reaction is seldom employed for condensations involving phenols. We found, however, that *p*-hydroxytriphenylcarbinol could, indeed, be obtained by this reaction from benzophenone chloride and benzene, fairly pure and in tolerably good yield, when carbon disulfide was employed as a solvent. At the same time we observed

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[1] *J. Chem. Soc.*, **79**, 1209 (1901).

[2] *Ibid.*, **87**, 1252 (1905).

[3] *Ann.*, **363**, 279 (1908).

[4] *Ber.*, **11**, 1350 (1878).

[5] *Ibid.*, **37**, 3329 (1904).

that phenol acts directly without the help of the catalyst, upon benzophenone chloride in absence of solvent at room temperature. A careful study of the reaction between benzophenone chloride and phenol has been undertaken, and it has been found that the condensation proceeds in several successive steps. By observing the proper conditions during the course of the reaction, it is possible to get as the result almost exclusively any one of the three products: diphenoxy-diphenylmethane, *p*-hydroxytriphenylcarbinol, or di-*p*-hydroxytetraphenylmethane. The most suitable conditions for the preparation of each of these products will be given first, and an interpretation of the mechanism of this whole condensation reaction follows.

The Preparation of Benzophenone Chloride.—In studying the Friedel and Crafts synthesis, Boeseken[1] found that the reaction between carbon tetrachloride and benzene under the influence of the catalyst, aluminium chloride, proceeds in at least three steps:

$$\begin{array}{llll} CCl_4 & + C_6H_6 \longrightarrow & C_6H_5CCl_3 & + HCl \\ C_6H_5CCl_3 & + C_6H_6 \longrightarrow & (C_6H_5)_2CCl_2 & + HCl \\ (C_6H_5)_2CCl_2 & + C_6H_6 \longrightarrow & (C_6H_5)_3CCl & + HCl \end{array}$$

He was unable to isolate benzotrichloride, but by using an excess of carbon tetrachloride he obtained benzophenone chloride in good yield. We desire to emphasize the value of this reaction as an excellent means for the preparation of benzophenone chloride in large quantities.

We have obtained, by employing this reaction, benzophenone chloride in 90% yields by observing the following procedure: In a wide-mouth, two-liter bottle, 135 g. (1 mol) finely-divided aluminium chloride are suspended in 300 cc. carbon tetrachloride. To this are added through the course of an hour or more, 156 g. (2 mols) of benzene, mixed with about an equal volume of carbon tetrachloride. By cooling and shaking, the reaction mixture should be kept below 30°. The following morning the aluminium chloride is decomposed in the same bottle, preferably glass-stoppered, by adding a considerable quantity of ice at once and shaking vigorously. The temperature of the mixture is lowered to such an extent by the ice and the hydrochloric acid that hydrolysis of the benzophenone chloride is reduced to a minimum. The carbon tetrachloride solution, after drying over calcium chloride, is concentrated and the residue distilled in vacuum. The resulting product contains, as a rule, 90–95% benzophenone chloride, the balance being benzophenone. Redistillation in vacuum after addition of the calculated amount of phosphorus pentachloride gives pure benzophenone chloride.

Preparation of Diphenoxydiphenylmethane.—Mackenzie in his attempts to prepare diphenoxydiphenylmethane did not study the reaction between benzophenone chloride and phenol in any other solvent than an

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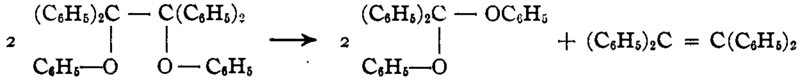
[1] Boeseken, *Rev. d. trav. chem.*, 24, 1 (1905).

excess of phenol, and for this simple reason failed. By carrying out the above reaction in benzene we have prepared the diphenoxy compound. The formation of this compound constitutes the first stage in the action of phenol upon benzophenone chloride, and in the presence of a solvent the reaction stops here and does not proceed any further.

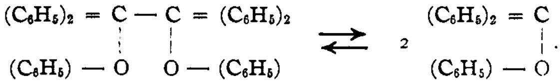
Molten phenol was added slowly to an equal weight of benzophenone chloride mixed with about ten times its volume of benzene, the reaction mixture being kept at about 50°. A stream of dry air was drawn, under slight vacuum, through the mass to remove the hydrogen chloride as formed, and thus prevent the decomposition of the diphenoxy derivative. Concentration of the benzene solution and addition of petroleum ether gave the diphenoxydiphenylmethane in clusters of white needles melting at 132° after recrystallization from alcohol. The yield was about 85% of the calculated amount.

Wieland[1] described as diphenoxydiphenylmethane a compound which he had obtained by heating the diphenyl ether of benzpinacone to 280°, resulting assumably as follows:



$$2\begin{array}{cc}(C_6H_5)_2C - & C(C_6H_5)_2\\ | & | \\ C_6H_5-O & O-C_6H_5\end{array} \longrightarrow 2\begin{array}{c}(C_6H_5)_2C - OC_6H_5\\ | \\ C_6H_5-O\end{array} + (C_6H_5)_2C = C(C_6H_5)_2$$

A sample prepared according to Wieland's method was found to be identical with the product from the reaction of benzophenone chloride and phenol in benzene solution. The melting point of a mixture of the two corresponds to that of either product, 132°. Thus our results corroborate Wieland's conclusion as regards the constitution of the diphenoxy derivative. Consequently, they also lend support to his conception of the constitution of the above mentioned diphenyl ether of benzpinacone and that of its dissociation product, the corresponding free radical, diphenylphenoxymethyl



$$\begin{array}{cc}(C_6H_5)_2 = C - & C = (C_6H_5)_2\\ \vdots & | \\ (C_6H_5) - O & O - (C_6H_5)\end{array} \rightleftarrows 2\begin{array}{c}(C_6H_5)_2 = C\\ |\cdot \\ (C_6H_5) - O\end{array}$$

Diphenoxydiphenylmethane is far more stable than dimethoxydiphenylmethane and its homologs, which, as described by Mackenzie, suffer decomposition even upon exposure to the air. Neither boiling water nor normal alkali has any effect upon the diphenoxy derivative. On the other hand, like its analogs, diphenoxydiphenylmethane is hydrolyzed by dilute acids, even by acetic acid, into benzophenone and the corresponding alcohol, *i. e.*, in this case, phenol.

Preparation of Hydroxytriphenylcarbinol.—Bistrzycki and Herbst[2] first prepared *p*-hydroxytriphenylcarbinol through elimination of carbon

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[1] *Ber.*, **44**, 2554.

[2] *Ibid.*, **34**, 3073 (1901); **35**, 3133 (1902).

monoxide from *p*-hydroxytriphenylacetic acid by means of concentrated sulfuric acid. This step is accomplished with satisfactory yield, although the preparation of the acid by condensation of mandelic acid with phenol involves a rather laborious process. Baeyer and Villiger[1] obtained the identical product by demethylating *p*-methoxytriphenylcarbinol by boiling the latter in a mixture of acetic and sulfuric acids for twelve hours, the methoxy carbinol having been prepared by Grignard's synthesis from anisic ester and phenyl bromide. Gomberg[2] demethylated the methoxy carbinol by means of aluminium chloride in benzene solution, a method which gives at the same time more or less diphenylquinomethane and other by-products. A highly satisfactory method of preparing this carbinol is offered by the reaction of benzophenone chloride and phenol under the following conditions:

Molten phenol (3–4 mols) is chilled in a flask in such a way as to be evenly distributed on the interior surface. Benzophenone chloride (1 mol) is then added, the mouth of the flask being protected by a calcium chloride tube. The reaction begins at once with evolution of hydrogen chloride, and an occasional rotation of the flask brings fresh portions of the phenol into reaction. After ten hours or more at a temperature between 20 and 25°, the mass is subjected to steam distillation in the same flask to remove the excess of phenol. The residue is digested with 5% alkali and the alkaline solution extracted with ether in order to remove any benzophenone which may be present.[3] After filtration the dissolved ether is removed from the alkaline solution by a stream of air. Addition of ammonium chloride or treatment with carbon dioxide liberates the carbinol and the dihydroxy-tetraphenyl compound in the form of a paste, which changes on standing to a granular mass. As a means of separation of the carbinol from the tetraphenyl derivative, a small amount of which is also likely to be formed together with the triphenyl-carbinol, either alcohol or 95% acetic acid may be used, as the tetraphenylmethane compound is soluble in either solvent to an extent of not more than 0.1 g. in 100 cc. Using about 6 cc. alcohol to each gram of the mixed products dissolves the carbinol and leaves a fine suspension of the tetra compound. The filtration, often quite troublesome, may be facilitated by the addition to the alcoholic suspension of a few cc. of a concentrated aqueous

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[1] *Ber.*, **36**, 2791 (1903).

[2] THIS JOURNAL, **35**, 209 (1913).

[3] This extraction is necessary at this point not only to remove the benzophenone in suspension but also the benzophenone held in solution by the sodium salt of the carbinol. The solubility of benzophenone under these conditions has been verified by a blank experiment in which it was found that benzophenone, insoluble itself in alkali, was jointly soluble with the carbinol in *n*-NaOH. In the extraction a large amount of ether is to be avoided since the carbinol through hydrolysis of its salt is also removed to some extent by this solvent.

solution of sugar. Addition of water and a few drops of ammonium hydroxide to the alcoholic filtrate precipitates the carbinol in a beautiful crystalline form. Though hardly essential, the carbinol may be recrystallized from benzene in order to remove traces of the tetraphenyl derivative.

Following the above method we have obtained with samples of 12–18 g. of benzophenone chloride yields of 90 to 98% of the calculated amount of the carbinol, with but a few hundred milligrams of the by-product, di-*p*-hydroxytetraphenylmethane. The difficulty of controlling the temperature of the viscous reaction mixture may cause at times the formation of a gram or more of the tetra compound and a corresponding decrease in the yield of carbinol. If only two mols of phenol are taken for condensation with one mol of the ketochloride the reaction mixture may be allowed to stand longer, 3–4 days, without fear of having much of the tetraphenyl compound formed. A few typical examples, tabulated below, will serve as illustration:

Chloride.	Phenol.	Temperature.	Time.	Carbinol.	"Tetra."
12	10	40–50°	1 hr.	8.7 g.	0.2 g.
12	20	0–20	1	8.0	0.3
12	17	25–35	1	10.8	1.8
12	20	20–25	15 hrs.	13.4	1.2

Preparation of Di-*p*-hydroxytetraphenylmethane.—As has been mentioned, this product is obtained when benzophenone chloride and phenol are heated together. The use of sodium phenolate dissolved in excess of phenol, is, we believe, without any advantage in this reaction. Nor is it necessary to heat the reaction for the length of time given by Zincke, three days. According to our experience, the reaction is practically completed at the end of a few hours, with a yield of 90–95% of the calculated amount.

Since di-*p*-hydroxytetraphenylmethane is the final product in the series of the three successive reactions between benzophenone chloride and phenol, it should then be possible to prepare it under suitable circumstances from any of the two intermediate products. This is in reality the case, as will be shown in discussing the mechanism of the reaction.

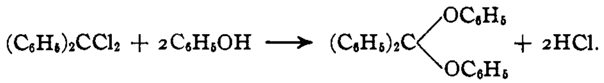
Di-*p*-hydroxytetraphenylmethane crystallizes from acetic acid in glistening, white flakes or needles, melting at 286° without decomposition. It forms a diacetyl derivative by boiling in three times its weight of anhydride together with a small amount of sodium acetate, as described by Zincke.

Mechanism of the Reaction.

The reaction between benzophenone chloride and phenol proceeds, as mentioned, in several steps.

(1) The first stage of the reaction consists most probably in the forma-

tion of the diphenylether of benzophenone, whatever the experimental conditions of the method employed.

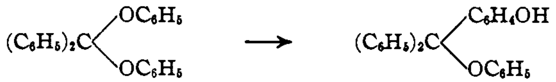


$$(C_6H_5)_2CCl_2 + 2C_6H_5OH \longrightarrow (C_6H_5)_2C\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_6H_5\end{matrix} + 2HCl.$$

(I).

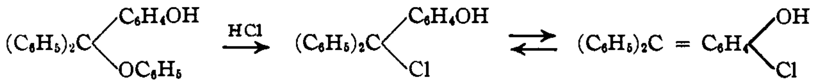
If the hydrochloric acid is being removed as formed, the reaction stops here, and the ether is the final product. Thus, the ether is formed when the chloride and the phenol are allowed to act upon each other in the presence of a solvent like benzene or carbon disulfide, in either of which the hydrochloric acid is but little soluble. But when no such solvent be present, then the viscous reaction mixture, containing during the course of the reaction always an excess of phenol, retains a certain amount of the hydrochloric acid, and the concentration of this acid becomes relatively great. The diphenyl ether, as soon as formed, is then subject to the action of the acid, and then there ensues the second stage of the condensation.

(2) In the second stage of this reaction the diphenoxy compound suffers an *intramolecular rearrangement* with respect to but one of the phenoxy groups (II). The resulting monophenyl ether, like all similar compounds, must be, to some extent, decomposed by hydrogen chloride with the formation of the chloride of p-hydroxytriphenylcarbinol, which, as has been shown, exists largely in the quinoid state (II*a*). This latter reaction is, however, quite subordinate, but enough of the quinonoid chloride is formed to account for the intense fuchsine-like color of the reaction mixture at this stage.



$$(C_6H_5)_2C\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_6H_5\end{matrix} \longrightarrow (C_6H_5)_2C\begin{matrix}\diagup C_6H_4OH\\ \diagdown OC_6H_5\end{matrix}$$

(II).



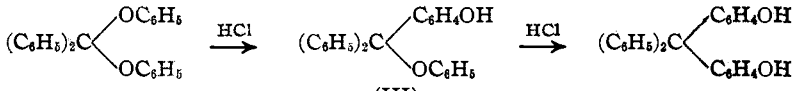
$$(C_6H_5)_2C\begin{matrix}\diagup C_6H_4OH\\ \diagdown OC_6H_5\end{matrix} \xrightarrow{HCl} (C_6H_5)_2C\begin{matrix}\diagup C_6H_4OH\\ \diagdown Cl\end{matrix} \rightleftarrows (C_6H_5)_2C = C_6H_4\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}$$

(II*a*).

If the condensation be now stopped, after the reaction mixture has stood 1–3 days, and the whole treated with water, then the monophenoxyether, as well as the carbinol chloride, will yield by hydrolysis chiefly p-hydroxytriphenylcarbinol as the final product.

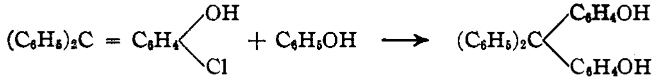
The following experiments illustrate the ease with which the diphenoxy compound undergoes an intramolecular rearrangement with respect to but one phenoxy group when subjected to the action of acid at room temperature, and with regard to both phenoxy groups at higher temperature. In a quantitative experiment 1.45 g. of substance gave, when exposed to an atmosphere of dry hydrogen chloride at room temperature, 0.67 g. *p*-hydroxytriphenylcarbinol but *no* di-*p*-hydroxytetraphenylmethane. A 3 g. sample, when treated similarly but at 50°, gave 1.3 g. of the carbinol and 0.5 g. of the tetra compound, together with some unchanged diphenoxy derivative.

(3) But if, instead of hydrolyzing the reaction mixture after 2–3 days' standing, the reaction be allowed to proceed still further, then the process enters upon its third stage. The monophenoxy compound suffers in its turn, under the influence of the hydrochloric acid, an intramolecular rearrangement with respect to the second phenoxy group, and di-*p*-hydroxytetraphenylmethane is formed (III). At the same time, the variable, but never large, amount of chloride produced in (II*a*) condenses with phenol, in the presence of the anhydrous hydrochloric acid, and it, too, gives the same tetraphenyl derivative (III*a*).



$$(C_6H_5)_2C\left<\begin{matrix}OC_6H_5\\OC_6H_5\end{matrix}\right. \xrightarrow{HCl} (C_6H_5)_2C\left<\begin{matrix}C_6H_4OH\\OC_6H_5\end{matrix}\right. \xrightarrow{HCl} (C_6H_5)_2C\left<\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}\right.$$

(III).



$$(C_6H_5)_2C = C_6H_4\left<\begin{matrix}OH\\Cl\end{matrix}\right. + C_6H_5OH \longrightarrow (C_6H_5)_2C\left<\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}\right.$$

(III*a*).

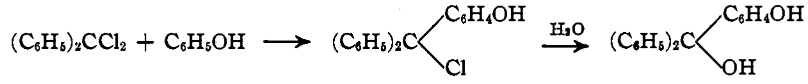
That the pure diphenoxymethane can actually be changed by hydrochloric acid at elevated temperatures (50°) to the tetraphenyl compound has already been shown. The following experiment illustrates the condensation of the carbinol chloride with phenol:

Hydrochloric acid gas was passed into a mixture of 4 g. *p*-hydroxytriphenylcarbinol and 10 g. phenol at 50° and, after a short time, 3.5 g. of the tetra compound were isolated. In acetic acid solution, 3 g. carbinol and 3 g. phenol gave, after passing in hydrogen chloride, 2.8 g. of the tetraphenyl derivative.

Thus, it will be seen that di-*p*-hydroxytetraphenylmethane is the result of three successive reactions, one etherification and two intramolecular rearrangements. The velocity of the second intramolecular rearrangement must be very much slower than that of the first, so that at room temperature, even after several days' standing, there is but little of the tetraphenyl derivative formed as compared with the amount of the triphenylcarbinol.

Every intermediate product mentioned in the explanation here offered as to the mechanism of the condensation reaction has been isolated, except one, the monophenyl ether of *p*-hydroxytriphenylcarbinol. Nor have we succeeded in synthesizing it, in any way, directly from the carbinol. And it is not surprising, if we may judge from the extreme sensitiveness towards hydrolyzing agents of its nearest analog and prototype, monophenoxytriphenylmethane.[1] We have, however, obtained very satisfactory evidence in regard to the formation of our monophenoxy compound in an indirect manner.

An examination of Equations I and II will show that on this basis for every molecule of benzophenone chloride *two molecules of phenol* must take part in the reaction. On the other hand, should the formation of the carbinol proceed according to the simple scheme (IV) then only one molecule of phenol would be required for the formation of the carbinol. Hence, the amount of phenol, whether one or two mols, requisite for a quantitative, or approximately quantitative, yield of the carbinol from one mol of the ketochloride serves to decide whether the monophenoxy compound is really formed as the intermediate product in the condensation or not.



$$(C_6H_5)_2CCl_2 + C_6H_5OH \longrightarrow (C_6H_5)_2C{<}\begin{matrix}C_6H_4OH\\Cl\end{matrix} \xrightarrow{H_2O} (C_6H_5)_2C{<}\begin{matrix}C_6H_4OH\\OH\end{matrix}$$

(IV).

The results given in Table I were obtained by carrying out the experiments with all due precautions as to purity of materials employed and constancy of temperature (20–22°), etc. On the assumption that in the experiments of Series I and II all the benzophenone chloride entered into condensation, the calculated yield of the carbinol is 8.96 g. When at the same time some tetraphenyl derivative is produced a correspondingly smaller yield of the carbinol is, of course, to be expected.

TABLE I.

	Series I. $RCCl_2 + C_6H_6O$ 7.7 g. + 3 g. gave		Series II. $RCCl_2 + 2C_6H_6O$ 7.7 g. + 6 g. gave		Series III. $2RCCl_2 + C_6H_6O$ 15.4 g. + 3 g. gave	
Time of reaction.	Carbinol.	Tetra.	Carbinol.	Tetra.	Carbinol.	Tetra.
After 2 days	3.88 g.	None	6.05 g.	None	3.15 g.	None
After 10 days	4.62	None	7.42	0.43	3.95	None
After 20 days	5.61	Trace	7.39	0.87	4.25	None
After 30 days	6.00	0.11	7.73	0.93	4.76	None

A comparison of the results obtained in the two sets of experiments, Series I and II, shows plainly that two molecules of phenol give not far from the theoretical amount of the carbinol at the end of ten days, 87%, while with one molecule of phenol only a little more than half of that amount of the carbinol is obtained, *i. e.*, 51%. With the increase of the time the difference between the results in I and II becomes less, but the difference in the yields still remains sufficiently pronounced to make it apparent that two molecules of phenols are requisite in order that the one molecule of the ketochloride should be completely used up in the condensation.

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[1] Baeyer, *Ber.*, **42**, 2625 (1909).

In other words, if the monophenyl ether is actually an essential intermediate product in the formation of the *p*-hydroxytriphenyl carbinol, and if the condensation thus involves one molecule of benzophenone chloride with two molecules of phenol simultaneously, then we are dealing, fundamentally, with a trimolecular reaction. But if, on the other hand, the condensation is not as complex as here intimated, and if it proceeds according to Equation IV, then, clearly, we are dealing strictly with a dimolecular reaction. However, while, on the one hand, the velocity of reaction may perchance vary in a dimolecular irreversible reaction according to which of the two components is increased in amount, and is thus made to function as solvent, on the other hand, the yield of the product should be the same in both cases when, at the end of a reasonable period of time, the final equilibrium has been practically reached.

An inspection of the results of the experiments in Series II and III in Table I shows the following: With one mol ketochloride and two mols phenols the yields are 67, 86, 92 and 97% at the end of 2, 10, 20 and 30 days, respectively. With two mols ketochloride and one mol phenol the yields for the same intervals are: 35, 44, 47 and 53. Indeed, the comparison of the experiments in Series II and III shows convincingly that the reaction is not dimolecular, and that *two* molecules of phenol are essential for a quantitative yield of the triphenylcarbinol.

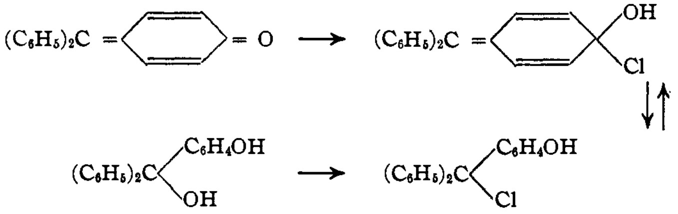
The fact, however, that even with one molecule of phenol, Series I, a yield of the carbinol amounting to 70%, instead of the expected 50, is reached finally at the end of a month, is quite readily explained by the subordinate reaction II*a*. As therein indicated, phenol is being regenerated, and this, in its turn, will combine with some more unused benzophenone chloride. That the reaction II*a* is slow, and that it soon reaches the conditions of equilibrium, can hardly be doubted, for otherwise how could diphenoxydiphenylmethane be formed so readily and so completely as it does in reality form in the first stage of the condensation?

The condensation here described has been studied so much in detail because of the promise that this reaction might find application in the synthesis of other hydroxylated triarylcarbinols. Results that have been obtained in this laboratory so far indicate that in reality it may find such application, but that, at the same time, individual ketones and phenols may show a deviation from the general course of this reaction.

III. Concerning the Free Radical, *p*-Hydroxytriphenylmethyl.

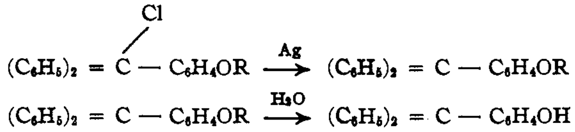
The general method for the preparation of free radicals in the triaryl methyl series consists in subjecting the triarylmethyl halide to the action of metals.

Unfortunately, *p*-hydroxytriphenylcarbinol chloride cannot be used according to this general reaction. This had also been found to be the case with the chlorides of *p*-hydroxybenzo-γ'-pyranols[1] and of *p*-hydroxyxanthenols.[2] The cause for this exceptional behavior we believe to be the same in all cases, namely, the chlorine and the hydroxyl group are linked to one and the same carbon atom in these carbinol chlorides. The formation of the above *p*-hydroxy chloride takes place by exposing in the solid form either fuchsone or *p*-hydroxytriphenylcarbinol to gaseous hydrochloric acid. The resulting products are identical, hence we must assume the usual equilibrium between the two tautomeric isomers.



On treatment with molecular silver a molecule of *hydrogen chloride* is split off instead of the usual single chlorine atom, giving consequently fuchsone and not the free radical, *p*-hydroxytriphenylmethyl.

From these results it became evident that the only promising procedure for the preparation of the free radical would be through protection or alteration of the *p*-hydroxyl group, according to the following scheme:



$$(C_6H_5)_2 = \overset{Cl}{C} - C_6H_4OR \xrightarrow{Ag} (C_6H_5)_2 = C - C_6H_4OR$$

$$(C_6H_5)_2 = C - C_6H_4OR \xrightarrow{H_2O} (C_6H_5)_2 = C - C_6H_4OH$$

in which $R = CH_3$, $COCH_3$, or COC_6H_5

Realizing, however, the difficulties usually encountered in the removal of any of these protecting groups, we turned first to the carboalkoxy groups, used so extensively and successfully by Emil Fischer as a temporary protection of hydroxyl groups, in his recent studies on tannins. A carboalkoxy group is readily removed through hydrolysis, thus restoring the hydroxy compound.

***p*-Carboethoxytriphenylcarbinol,** $C_2H_5O.CO.OC_6H_4.(C_6H_5)_2COH$.—Fourteen grams *p*-hydroxytriphenylcarbinol are dissolved in 55 cc. normal sodium hydroxide solution and a considerable amount of ice added to the solution. To the suspension of the sodium salt of the carbinol are added with vigorous stirring 6 g. (1.1 mol) chlorocarbonic ester. The resulting stiff paste upon becoming granular is filtered out. After drying partially, the product is recrystallized from alcohol by addition of water. The yield is quantitative. *p*-Carboethoxytriphenylcarbinol is readily solu-

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[1] Gomberg and Cone, *Ann.*, 370, 203 (1909).

[2] Gomberg and West, THIS JOURNAL, 34, 1562 (1912).

ble in benzene, ether, etc., crystallizing from these solvents upon addition of petroleum ether as white needles, melting at 119°.

***p*-Carboethoxytriphenylcarbinol Chloride.**—According to the usual method of preparing triarylcarbinol chlorides, this chloride is formed by passing gaseous hydrochloric acid into a benzene solution of the carbinol in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride, which, after washing with a mixture of ether and petroleum ether, melt at 98°.

Calc. for $C_{22}H_{19}O_2Cl$: Cl, 9.67. Found: Cl, 9.62.

The Action of Metals.—As has been mentioned, the usual result of the action of molecular silver or other metals on the chlorides of the triarylcarbinols in solution is the formation of the free radical with carbon in the trivalent state. The unsaturated nature of this class of compounds is illustrated, among others, by the avidity with which they unite with oxygen to form peroxides.

$$2R_3C + O_2 \longrightarrow R_3C - O - O - CR_3.$$

So characteristic is this reaction, that the isolation of the peroxide is now generally accepted as sufficient evidence of the existence of the corresponding free radical, though even temporary. Tested in this manner the carboethoxy-chloride gives rise unquestionably to its free radical.

***p*-Carboethoxytriphenylmethyl Peroxide.**—When treated with molecular silver out of contact with air a benzene solution of *p*-carboethoxytriphenylcarbinol chloride assumes, after several hours, a dark, cherry red color. On exposure to air this color disappears in a way analogous to that in the case of triphenylmethyl. Evaporation of the filtered benzene solution and washing the residue with ether to remove any unchanged chloride gives a relatively small amount of the peroxide, which, when crystallized from benzene, melts at 171°. Much better yields of the peroxide result from boiling the chloride and silver in benzene with a stream of dry air passing through the solution. Like other triaryl peroxides, *p*-carboethoxy peroxide is but slightly soluble in benzene and nearly insoluble in ether.

Calc. for $C_{44}H_{38}O_6$: C, 76.05; H, 5.52; Mol. wt., 694. Found: C, 75.73; H, 5.56; Mol. wt., 701.

All attempts to obtain the dihydroxy-peroxide by removing the carboethoxy groups alone in this peroxide resulted in the splitting of the product either to *p*-carboethoxytriphenylcarbinol or to *p*-hydroxytriphenylcarbinol. Warming the solution of the peroxide in a mixture of acetic and sulfuric acids (4 : 1) gives the former carbinol in good yield. The peroxide is not affected by boiling with a normal solution of alkali in water, but sodium ethoxide or a solution of potassium or barium hydroxides in methyl alcohol decomposes it to the hydroxy-carbinol.

Isomerization of the Free Radical.—The formation of the above-described peroxide proves definitely that the free radical, *p*-carboethoxytriphenylmethyl, is formed as the initial step of the reaction between the chloride and molecular silver. We next attempted to isolate the unsaturated free radical in the solid state by concentration of the colored solution of the same in an atmosphere of carbon dioxide. But the residue thus obtained proved to be colorless, was found to be entirely devoid of unsaturated properties, and would no longer yield a peroxide on exposure to air, either as the solid or in solution. Consequently we may assume that the free radical exists only temporarily, and must have been affected in some way during the subsequent stages of its isolation. In fact, even in the preparation of the peroxide through simultaneous action of silver and air upon the chloride, there is formed, as a coating on the silver, more or less of this colorless, saturated compound in addition to the peroxide. More of this substance, and relatively less of the peroxide, is obtained if the solution of the free radical is kept for some time previous to oxidation; still more, if the solution is heated. It is thus not surprising that we find upon boiling the benzene solution of the chloride with silver for several hours, that practically none of the peroxide can then be obtained. For under such treatment, the reactive free radical is transformed completely into this colorless, inert substance.

This new product is a white, amorphous powder insoluble in ether and but slightly soluble in boiling benzene or acetic acid. It melts at about 280° without decomposition. A sample from the last mentioned solvent gave an analysis corresponding closely to that calculated for the free radical. The molecular weight, determined according to the method of Menzies, proved, however, to be approximately twice that of the free radical.

Calc. for $C_{22}H_{19}O_3$: C, 79.72; H, 5.78; Mol. wt., 331. Found: C, 79.36; H, 6.04; Mol. wt., 680, 664.

The above results indicate that this unsaturated compound is either produced from the monomolecular free radical through polymerization, or more likely, is a metamer resulting from transformation of the dimolecular modification of the free radical. A change of this kind has been proved to take place in the case of the simplest free radical in this series, namely, triphenylmethyl. It was shown by Gomberg[1] that this dimolecular free radical is changed in benzene under the influence of hydrogen chloride, as a catalyst, to a stable isomer, the constitution of which has been definitely determined by Chichibabin[2] as *p*-benzhydryltetraphenylmethane.

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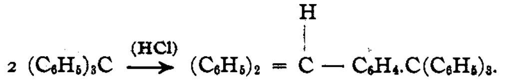
[1] *Ber.*, **36**, 378 (1903).

[2] *Ibid.*, **37**, 4708 (1904); **41**, 2422 (1908); Schmidlin, "Das Triphenylmethyl," p. 24.



$$2\ (C_6H_5)_3C \xrightarrow{(HCl)} (C_6H_5)_2 = \overset{\displaystyle H}{\overset{|}{C}} - C_6H_4.C(C_6H_5)_3.$$

Later Schlenk[1] found that this same transformation is brought about by the action of metallic sodium on the free radical in ether solution. The question arises: May not a similar metamerization take place spontaneously in the case of certain other radicals? In other words, may not the change of the free radical to its stable isomer proceed even without the presence of a catalyst, acid or alkali? We consider this entirely possible, and, at the present time, this is the most plausible explanation that we can offer for the relatively impermanent existence of the free radical, *p*-carboethoxytriphenylmethyl. We have modified the methods in attempting to prepare this radical by various means—by employing different solvents, by using mercury or copper instead of silver, by concentrating the solutions at very low pressure and temperature—but the result has invariably been the formation of the same stable metamer of the free radical.

Acetoxy- and benzoxytriphenylmethyl chlorides behave in this respect entirely analogously to the carboethoxy chloride. They, too, give free radicals which isomerize to stable metamers. The occurrence of such spontaneous transformations we believe to be far more frequent than has been assumed in the past. The apparent non-existence, or rather the marked instability, of the free radicals, tri-*p*-tolylmethyl, di-*p*-tolylphenylmethyl, *p*-tolyldiphenylmethyl,[2] tri-*p*-anisylmethyl,[3] etc., may be explained as due to a similar cause, namely, to the tendency to isomerize to more stable hydrocarbons.

***p*-Benzoxytriphenylcarbinol.**—Following the Schotten-Baumann reaction, 14 g. *p*-hydroxytriphenylcarbinol are dissolved in an excess of *N* NaOH, 14 g. benzoyl chloride added and the mixture thoroughly shaken for some time. The resulting oily precipitate solidifies on standing. Its benzene solution is extracted with 10% alkali and dried over calcium chloride. Addition of petroleum ether gives the benzoxy-carbinol in the form of small crystals, melting at 132° after recrystallization from glacial acetic acid. We have nothing to add to the properties as given by Bistrzycki and Herbst.[4]

***p*-Benzoxytriphenylcarbinol Chloride.**—This chloride is prepared by saturating a benzene solution of the carbinol with hydrogen chloride in the presence of calcium chloride. Addition of petroleum ether to the concentrated benzene solution gives white crystals of the chloride in nearly quantitative yield, melting point 105°.

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[1] *Ber.*, 47, 1665 (1914).

[2] Gomberg, *Ibid.*, 37, 1627 (1904).

[3] Schmidlin, "Das Triphenylmethyl," p. 153.

[4] *Ber.*, 34, 3077 (1901).

Calc. for $C_{26}H_{19}O_2Cl$: Cl, 8.90. Found: Cl, 8.74.

p-Benzoxytriphenylmethyl Peroxide.—With molecular silver, a solution of the benzoxy chloride gives the usual deep color of a free radical. On evaporation of this solution, however, a mixture of two substances is obtained, the one the inert isomer of the free radical and the other the peroxide. For identification the latter was prepared by simultaneous action of silver and oxygen on the chloride. The peroxide is slightly soluble in boiling benzene, nearly insoluble in ether, and melts at 167° with decomposition. This peroxide is also readily hydrolyzed to its corresponding carbinol by warming in a mixture of acetic and sulfuric acids.

Calc. for $C_{52}H_{38}O_6$: C, 82.29; H, 5.05. Found: C, 82.40; H, 5.40.

As in the case of *p*-carboethoxytriphenylmethyl, we were unable to isolate the free radical, *p*-benzoxytriphenylmethyl. On boiling the chloride and silver in benzene, the resulting highly-colored solution of the free radical loses its color, even during concentration, with the formation of the colorless isomer. A sample of the latter, recrystallized from acetic acid, melted at 266–9°, and gave an analysis and molecular weight corresponding closely to that calculated for the dimolecular free radical.

Calc. for $C_{52}H_{38}O_4$: C, 85.92; H, 5.27; Mol. wt., 726. Found: C, 85.70; H, 5.55; Mol. wt., 710.

p-Acetoxytriphenylcarbinol.—The following procedure has been adopted for the preparation of this carbinol: 20 g. of *p*-hydroxytriphenylcarbinol and 3 g. of anhydrous sodium acetate are boiled for two hours in 50 g. acetic anhydride. The product is precipitated by pouring the above solution into 100 cc. water and, if necessary, may be recrystallized from acetic acid. It possesses the properties described by Bistrzycki for this carbinol. The large excess of acetic anhydride, as employed by him, we believe to be unnecessary in the preparation of this compound.

p-Acetoxytriphenylcarbinol Chloride.—Gomberg[1] has prepared this chloride by the usual method, using calcium chloride as a dehydrating agent. We find it perferable to avoid the use of hydrogen chloride. The carbinol is suspended in an excess of acetyl chloride (2 : 3 mol) and the mixture heated until all goes into solution. The excess of solvent is removed by careful heating. Upon the gradual addition of petroleum ether and allowing to stand, the acetoxy chloride separates out slowly as white needles, melting at 88°. It is very soluble in benzene or ether but only slightly so in petroleum ether.

Calc. for $C_{21}H_{17}O_2Cl$: Cl, 10.53. Found: Cl, 10.52.

p-Acetoxytriphenylmethyl Peroxide.—This peroxide must be prepared by the simultaneous action of silver and oxygen on the chloride in solution. The resulting product, after recrystallization from benzene and

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[1] THIS JOURNAL, **35**, 200 (1913).

ether, melts at 172°. It is readily hydrolyzed to the corresponding carbinol.

Calc. for $C_{42}H_{34}O_6$: C, 79.46; H, 5.40. Found: C, 79.67; H, 5.80.

The acetoxy polymer was produced from the free radical under similar conditions as the other two polymers from their corresponding radicals. The white, amorphous powder, after purification, gave a product melting with decomposition at 255–270°. In its low solubility, its nonconversion through hydrolysis into the corresponding carbinol, and its lack of unsaturated properties, this polymer resembles the other analogs as described.

***p*-Carboethoxytriphenylmethyl Ether.**—Ten grams *p*-carboethoxytriphenylcarbinol chloride, 30 g. mercuric oxide and 50 cc. benzene were sealed and shaken for a month at room temperature. The resulting solution, after warming, was filtered from the mercuric oxide and chloride and concentrated. Upon addition of petroleum ether the product separated as a yellow, crystalline mass, which, after recrystallization from benzene and absolute ether, is white and melts at 219°.

Calc. for $C_{44}H_{38}O_7$: C, 77.84; H, 5.65; Mol. wt., 678. Found: C, 77.80; H, 5.74; Mol. wt., 694.

The *p*-carboethoxy ether resembles other triaryl oxides, being very readily hydrolyzed by acids. Thus it is converted into the carbinol by boiling in acetic acid or in alcohol containing a few drops of sulfuric acid.

As a rule, the carboethoxy group is easily removed by cold dilute alkali or aqueous ammonia, acetone or pyridine being added if necessary to increase the solubility of the products.[1] Treated in this manner, *p*-carboethoxytriphenylmethyl ether does lose its carboethoxy groups, but unfortunately suffers further hydrolysis to *p*-hydroxytriphenylcarbinol. Various conditions and hydrolytic agents of alkaline nature have been employed, but as yet it has been found impossible to remove only the carboethoxy groups and thus obtain the *p*-hydroxy-ether, a substance which has been the subject of controversy in the literature.

IV. Summary.

1. A detailed study of the reaction between benzophenone chloride and phenol has been carried out. Contrary to previous reports in the literature, the reaction was found to proceed in several successive stages, and the mechanism of the reaction has been studied.

2. A simple and excellent synthetic method for the preparation of *p*-hydroxytriphenylcarbinol has been devised, a method which promises to become general for obtaining analogous compounds.

3. *p*-Hydroxytriphenylcarbinol chloride on treatment with metals gives up hydrochloric acid and not chlorine, thus making it impossible to prepare the corresponding free radical according to the usual method.

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[1] Fischer, *Ber.*, 46, 3257 (1913).

p-Carboethoxy-, *p*-benzoxy-, *p*-acetoxycarbinol chlorides do give the respective free radicals, but these were found to be too unstable to be isolated as such, and consequently could not be used for the preparation of the hydroxytriphenylmethyl.

4. From the experimental facts obtained, an explanation is derived to account for the impermanent character of these free radicals, which may also serve to explain similar results previously reported by others, namely, a tendency of the radicals towards spontaneous polymerization or isomerization, or both.

ANN ARBOR, MICHIGAN.

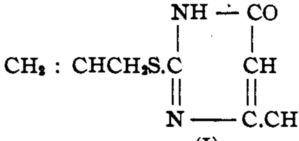
[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXXVII. THE ALKYLATION OF 2-MERCAPTOPYRIMIDINES.

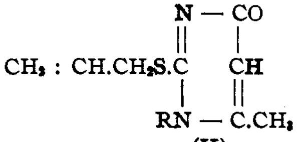
BY TREAT B. JOHNSON AND ROBERT C. MORAN.

Received August 20, 1915.

Johnson and Haggard[1] made the observation that, when 2-allylmercapto-4-methyl-6-oxypyrimidine (I) undergoes alkylation in alcoholic solution and in the presence of sodium ethylate, there is no tendency, apparently, for the alkyl group of the halide to substitute in position 3 of the pyrimidine ring to form a compound corresponding to Formula II. Either an imido ester combination (IV) is formed or a mixture of this with a 1-alkyl derivative as represented by Formula III. When allyl iodide was used the corresponding imido ester (IV) (R = $CH_2{:}CHCH_2$) was the only product formed. In other words, the sodium salt of this pyrimidine (I) exhibited an exceptional behavior towards alkyl halides, and the presence of the negative, unsaturated, allyl mercapto group in position 2 was favorable for the formation of oxygen derivatives.



(I).



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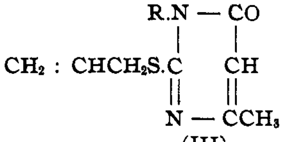

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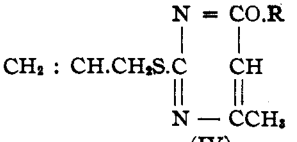

(IV).

In the light of these interesting results it was of especial interest to investigate the behavior on alkylation of a 2-mercaptopyrimidine containing a more negative radical than the vinyl group $CH_2{:}CH—$ in the com-

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[1] THIS JOURNAL, 37, 177 (1915).