lar radical suffers to a limited extent a still further dissociation, in some such manner as this:

$$2(C_6H_5)_2C.C_{10}H_7 \rightleftarrows 2(C_6H_5)C.C_{10}H_7 + C_6H_5 - C_6H_5$$

A small amount of a radical with a divalent carbon atom may thus be formed, and some biphenyl. Two molecules would then give rise to three and the freezing point would be lowered. We venture upon this explanation in a purely tentative way, and expect to subject other naphthyl derivatives to a careful study in this respect.

ANN ARBOR, MICH.

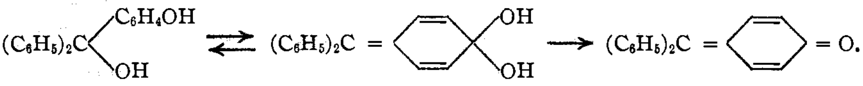
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TRIPHENYLMETHYL. XXVIII. TAUTOMERISM OF TRIARYLCARBINOLS.

BY M. GOMBERG AND L. C. JOHNSON.

Received June 13, 1917.

In a previous publication from this laboratory it was demonstrated[1] that in the triphenylmethane series the two tautomeric modifications, benzenoid and quinonoid, are actually separable from, and convertible into, each other. The first example of such separation was realized on *p*-hydroxytriphenylcarbinol,



(I) Benzenoid. (II) Quinonoid. (III) Diphenylquinomethane.

It was shown that the colored tautomer, on heating, loses water very much faster than the colorless, going over gradually into diphenylquinomethane.

Later[2] a convenient method was worked out for preparing readily in any desired amount the above carbinol. The method consists in the condensation of benzophenone chloride with phenol at room temperature and in absence of all catalyzers. That this ready condensation of benzophenone with phenol should have been overlooked until now is the more surprising as the equally ready condensation of phenol with benzotrichloride has been the source of innumerable investigations since the time of its discovery by Doebner in 1878.[3] The condensation of benzophenone chloride with phenol takes place, as has been shown, in three stages, and all the intermediate products have been isolated:

(1) Diphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_5)_2$.

(2) *p*-Hydroxytriphenylcarbinol, $(C_6H_5)_2C(OH)C_6H_4OH$.

(3) Di-*p*-hydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_4OH)_2$.

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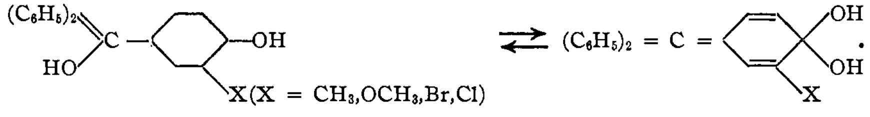
[1] THIS JOURNAL, 35, 1035 (1913).

[2] *Ibid.*, 37, 2575 (1915).

[3] *Ber.*, 12, 1462 (1879).

The applicability of this condensation reaction was later extended to other phenols. It was found[1] that *o*-cresol, guaiacol, *o*-bromophenol and *o*-chlorophenol condense with benzophenone chloride and give rise to classes of derivatives similar to those which are yielded by phenol itself. In this way nine additional pairs of tautomeric hydroxytriarylcarbinols were isolated, all containing one (or two) substituent in the *o*-position to the phenolic hydroxyl group.



(IV). (V).

In this paper are described results concerning the condensation of benzophenone chloride with meta-substituted phenols. We find that with *m*-cresol and with the monomethyl ether of resorcinol the condensation is realizable and that under proper conditions good yields of the carbinols are obtained. But as regards the occurrence of desmotropism in these carbinols our results proved contrary to expectation. The ease with which the two desmotropic forms of *p*-hydroxytriarylcarbinols had been obtained might lead one to believe that introduction of methyl or methoxyl groups in the *m*-position to the phenolic hydroxyl group would produce cases of tautomerism, analogous to those found when these groups are in the ortho position to the hydroxyl. This, however, is not the case; we could not obtain a colored form from either of our compounds. From this, one would be inclined to conclude that for some reason or other a group in the ortho position to the central carbon atom hinders quinonoidation. It may, in fact, be assumed that we have here a case of what has ordinarily been called steric hindrance, the migration of the hydroxyl group being prevented by the presence of the methyl or methoxyl group. This hypothesis cannot, however, be considered as established until more compounds have been investigated. We have found, in fact, that the introduction of two bromine or chlorine atoms in the *m*-cresyl compound produces a carbinol which is apparently capable of existence in the two desmotropic forms. The melting points of these two modifications proved in this case to be identical, but the difference in color, crystalline form, and rate of dehydration when heated indicate that the case is analogous to that of *p*-hydroxytriphenylcarbinol itself.

In addition to the problem of the tautomerization of the carbinols the attempt was made to prepare the corresponding free radicals themselves. The hydroxyl group was found, however, in this, as in other similar cases, to increase the tendency toward quinonoidation to such an extent that the

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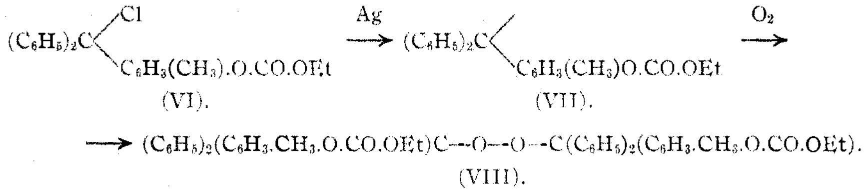
[1] THIS JOURNAL, 38, 1577 (1916).

carbinol chloride, necessary as a starting point for these experiments, could not be prepared. To overcome this difficulty it was decided to replace the hydroxyl with a less active group, and the carboëthoxyl group was chosen for this purpose.

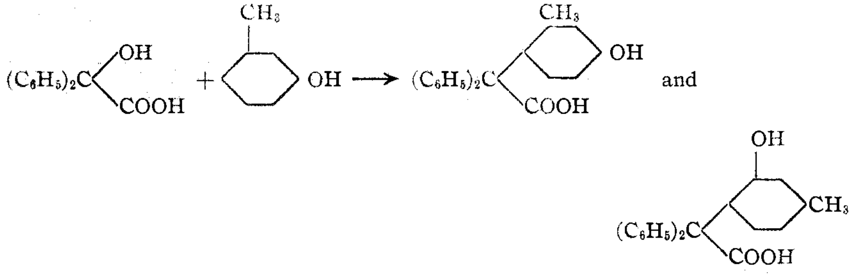


$$(C_6H_5)_2C{<}\begin{matrix}Cl\\ C_6H_3(CH_3).O.CO.OEt\end{matrix}\ \text{(VI)} \xrightarrow{Ag} (C_6H_5)_2C{<}\begin{matrix}\\ C_6H_3(CH_3)O.CO.OEt\end{matrix}\ \text{(VII)} \xrightarrow{O_2}$$

$$\longrightarrow (C_6H_5)_2(C_6H_3.CH_3.O.CO.OEt)C\text{—}O\text{—}O\text{—}C(C_6H_5)_2(C_6H_3.CH_3.O.CO.OEt).\ \text{(VIII)}$$

No difficulty was experienced in preparing the *o*-methyl *p*-carboethoxytriphenylmethyl (VII) in solution but all efforts to bring it to crystallization failed. We therefore resorted to the preparation and isolation of the corresponding peroxide (VIII) as a proof that the free radical had been produced.

In regard to the preparation of our material the following may be said. Bistrzycki and Zurbriggen[1] attempted to prepare *m*-cresyldiphenylcarbinol by warming *m*-cresyldiphenylacetic acid with sulfuric acid, the acetic acid derivative losing carbon monoxide and leaving the carbinol. In this they were unsuccessful for two reasons. First, the preparation of the substituted acetic acid from benzylic acid and *m*-cresol gives only a very poor yield of the desired product, an isomeric product with the hydroxyl group in the ortho position probably being formed at the same time:



Secondly, in the elimination of carbon monoxide they found that the yield of the carbinol was exceedingly poor and that the product was not always the same. Accordingly the properties of this carbinol have never been described. We have been able to prepare *m*-cresyldiphenylcarbinol pure and in very good yields by the condensation of the easily obtainable benzophenone chloride with *m*-cresol, the condensation taking place even in absence of any catalyzer:

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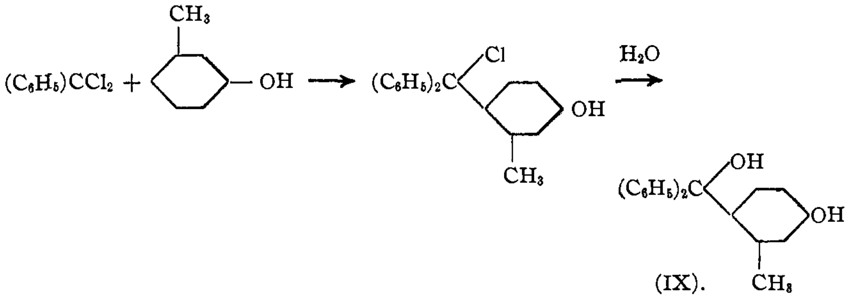
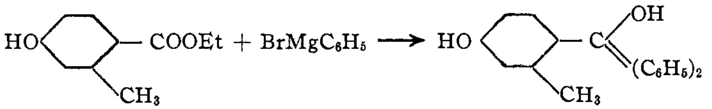
[1] *Ber.*, 36, 3558 (1903).

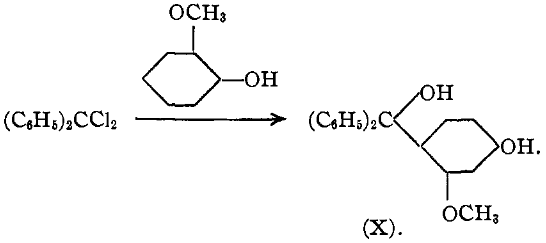


(IX).

In order to make sure that the hydroxyl group in the compound which we obtained was in the para position to the methane carbon atom and not in the ortho as in the compound described by Bistrzycki, we prepared a small amount of the same *p*-hydroxy compound by the Grignard method. The preparation by this latter method was found to be quite laborious but it made certain the structure of the resulting carbinol, and the identity of this with the compound made by our condensation method was easily established:

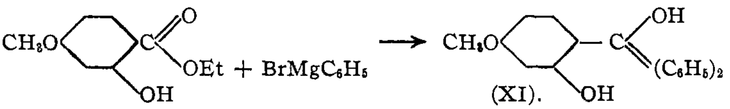


Our second compound, the corresponding methoxy-derivative, was obtained almost as readily by the action of the monomethyl ether of resorcin on benzophenone chloride.



(X).

In order to prove that this compound was in fact *o*-methoxy-*p*-hydroxytriphenylcarbinol (X), it seemed very desirable to prepare it by the Grignard method, using an ester of 4-hydroxy-2-methoxybenzoic acid as a starting point. But the difficulties in the way of obtaining this acid forced us to adopt an indirect method in order to prove the constitution of our compound. We have prepared, accordingly, by the Grignard method the isomeric *o*-hydroxy-*p*-methoxytriphenylcarbinol, using the ethyl ester of the more readily obtained *o*-hydroxy-*p*-methoxybenzoic acid:



(XI).

It is quite reasonable to suppose that in the carbinol made from benzophenone chloride either the hydroxyl or methoxyl group would occupy a position para to the central carbon atom, resulting in either compound (X) or (XI). Thus a demonstration of the fact that the carbinols prepared by the two methods were *not* identical was considered a proof that the product of the benzophenone chloride reaction was *not* the ortho-hydroxy, and, therefore, must be the desired *o*-methoxy-*p*-hydroxytriphenylcarbinol.

EXPERIMENTAL.

m-Cresyldiphenylcarbinol.

24 g. (1 mol) of benzophenone chloride are mixed with 27 g. (2.5 mols) of *m*-cresol and allowed to stand several days, the mixture being cooled at first to prevent rise of temperature due to the heat of the reaction. After neutralizing with dilute ammonia steam is passed into the flask, and the distillate is extracted with ether to recover the excess of cresol. The solid residue in the flask is digested with warm 5% sodium hydroxide solution, the small amount of insoluble oil being benzophenone. The alkaline solution is extracted with benzene to remove benzophenone which seems to be held in solution by the carbinol, filtered, the benzene removed by a stream of air and the carbinol precipitated by means of carbon dioxide. The precipitate, which is usually granular, is allowed to settle, the solution poured off, and the precipitate dissolved in ether. The ether solution is then dried over calcium chloride, the ether evaporated under reduced pressure, the temperature being kept below 50°. The resulting thick oil is dissolved in benzene, which solution on standing deposits well-formed colorless crystals. The yield of crystallized carbinol is 60–70% of the calculated quantity. If only the theoretical amount of cresol is taken for the reaction the yield is very much poorer, nearly half of the benzophenone chloride being recovered as benzophenone.

The carbinol is only slightly soluble in benzene, 200 cc. of this solvent being required for solution of 1 g. of carbinol at room temperature. It is readily soluble in the other usual organic solvents, crystallizing from a number of these with solvent of crystallization. It is best obtained pure by dissolving in ether and adding low-boiling petroleum ether, which causes precipitation of well-formed colorless crystals, melting at 114°.

Calc. for $C_{20}H_{18}O_2$: C, 82.72; H, 6.25; Mol. wt., 290. Found: C, 82.54; H, 6.25; Mol. wt., 287, 294.

The molecular weight was determined by the method of Menzies,[1] measuring directly the lowering of the vapor pressure of benzene.

Synthesis by Grignard Reaction.—In order to prove beyond doubt the constitution of the above-described carbinol it was synthesized by the Grignard reaction from bromobenzene and the ethyl ester of 5-hydroxy-2-

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[1] THIS JOURNAL, **32**, 1615 (1910).

carboxy-1-methylbenzene. The requisite acid was prepared from *m*-cresol and carbon tetrachloride by heating with sodium hydroxide in sealed tubes, using the Reimer and Tiemann method according to Schall.[1] The separation of the acid from a reddish material formed during the heating process was not easily accomplished, even with the use of animal charcoal, and the yield of the acid when finally purified was very small. The acid was freed from the small amount of isomeric 5-hydroxy-4-carboxy-1-methylbenzene by washing with chloroform, in which the latter is soluble. The acid, insoluble in chloroform, was fairly pure, and melted without further purification at 174°.

7 g. of the acid were dissolved in absolute alcohol and saturated with dry hydrochloric acid gas. After standing 48 hours the solution was concentrated slightly on the steam bath under reduced pressure and poured into water. The crude ester was extracted with six successive small portions of hot ligroin, which on cooling deposited clear, white crystals, all showing identical melting points. The boiling point of the ester was found to be 300°, the melting point of the distillate was 98°. Claisen[2] describes the ester as melting at 92–3° and boiling at 306–8°.

4.4 g. (0.025 mol) of the ester dissolved in absolute ether were added to an excess (0.15 mol) of phenylmagnesiumbromide and boiled for several hours. The addition compound was decomposed as usual, the carbinol dissolved in ether and steam-distilled, the residue dissolved in normal sodium hydroxide, the carbinol precipitated with ammonium chloride and dried in air. The yield was 5 g. of the crude carbinol.

Since the melting point of the carbinol, even when pure, is not sharp on account of gradual loss of water with simultaneous conversion into fuchsone, the identity of the compound made by the Grignard method with that made from benzophenone chloride was established by comparing three derivatives. For this purpose the carboethoxy, carbomethoxy, and benzoyl derivatives were made from the carbinols from the two sources, and the two sets of derivatives carefully compared. In each case the melting points of both series, as well as an intimate mixture of any corresponding pair, were found to be identical, thus definitely proving the identity of the carbinol prepared from benzophenone chloride with that prepared by the Grignard method.

Compounds of *m*-Cresyldiphenylcarbinol with Solvents.—*m*-Cresyldiphenylcarbinol possesses to an unusual extent the property of combining with various solvents when crystallized from them. Thus it was found to make combinations with acetic acid, alcohol, benzene, chloroform and carbon tetrachloride.

A sample freshly crystallized from glacial acetic acid was dried for 25

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[1] *Ber.*, **12,** 819 (1879).

[2] *Ann.*. **297,** 46 (1897).

minutes in a vacuum, dissolved in standard alkali and the excess of alkali titrated with acid.

Calc. for $C_{20}H_{18}O_2$ + $C_2H_4O_2$: $C_2H_4O_2$, 17.14. Found: acetic acid, 17.00.

From alcohol the compound forms on slow addition of water beautifully formed rhombic crystals. These were heated to constant weight at 90°.

Calc. for $C_{20}H_{18}O_2$ + C_2H_6O: C_2H_6O, 13.70. Found: loss in weight, 5.99.

A sample of 1.3190 g. crystallized from benzene lost 0.2837 g. on long standing at room temperature.

Calc. for $C_{20}H_{18}O_2$ + C_6H_6: C_6H_6, 21.2. Found: loss in weight, 21.5.

The product which contains chloroform of crystallization is unusually stable, decomposition being slow even above the boiling point of the solvent.

0.3787 g. heated 30 min. at 50° lost 0.0004 g. = 0.1%; heated 30 min. at 65° lost 0.0044 g. = 1.2%; heated 30 min. at 90°, total loss was 0.1086 g. = 28.7%. Calc. for one mol $CHCl_3$, 29.1%. Further heating at 90° caused a loss of less than 0.002 g. per hour.

The carbinol is only slightly soluble in cold carbon tetrachloride, and crystallizes from the hot solution with solvent of crystallization. A sample was heated at 70° to constant weight.

Calc. for $C_{20}H_{18}O_2$ + CCl_4: CCl_4, 34.70. Found: loss in weight, 33.76.

***o*-Methyl-*p*-carbomethoxytriphenylcarbinol.**—This compound was made by the general method of Fischer.[1] One gram of the carbinol dissolved in a very slight excess of normal sodium hydroxide solution was cooled with ice and treated with chlorocarbonic methyl ester. The compound was recrystallized from 70% glacial acetic acid, then repeatedly from chloroform until white. It melts at 118°.

***o*-Methyl-*p*-carboethoxytriphenylcarbinol,** $(C_6H_5)_2C(OH)C_6H_3(CH_3)$-$O.CO.OC_2H_5$.—This compound was prepared in the same manner as the preceding one, using chlorocarbonic ethy lester. The product was obtained pure on two crystallizations from 70% acetic acid, and was found to melt at 128°. This compound is soluble in the usual organic solvents with the exception of petroleum ether. Analysis of material dried in vacuum at 50–60° to constant weight gave the following results:

Calc. for $C_{23}H_{22}O_4$: C, 76.20; H, 6.12; Mol. wt., 362. Found: C, 76.40; H, 6.13; Mol. wt., 382.

The molecular weight was determined in boiling benzene.

***o*-Methyl-*p*-benzoxytriphenylcarbinol.**—This derivative was made by the Schotten-Baumann method, the carbinol being dissolved in 10% sodium hydroxide solution and shaken with an excess of benzoyl chloride. The resulting compound was dissolved in ether, the ether dried, and evaporated. The compound, when recrystallized from glacial acetic acid, melted at

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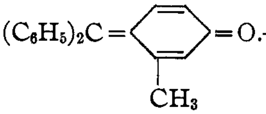
[1] This Journal, 36, 1170 (1914).

103°. The acetyl compound, prepared by heating with acetic anhydride and sodium acetate, crystallizes from acetic acid in large, white crystals, melting at 136°.

Diphenyl-3-methylquinomethane,  $(C_6H_5)_2C=C_6H_3(CH_3)=O$.—On heating to a temperature slightly above that of its melting point *m*-cresyldiphenylcarbinol forms a thick red syrup which on longer heating crystallizes to reddish brown needles. The loss in weight corresponds to one molecule of water, the resulting product being very evidently diphenyl-3-methylquinomethane. This compound is readily soluble in benzene and other solvents, ether being an exception, 200 cc. of this solvent being required for solution of 1 g. of the substance. It is best purified by dissolving in a small amount of benzene and precipitating with ether. This procedure gives red needles melting at 183°.

The fuchsone may readily be hydrolyzed back into the carbinol by recrystallizing from dilute acetic acid.

Action of Hydrogen Chloride upon the Fuchsone.—A sample of this fuchsone was placed in a boat and a stream of dry hydrogen chloride passed over it until it ceased to gain weight. Gain in weight, 26.23%; the calculated amount for 2 mols HCl, 26.80%. Half of this hydrochloric acid is evolved quite readily when the addition compound is placed under reduced pressure, the remaining molecule only on long standing. This is in complete agreement with the observed behavior of other compounds of this type.[1] The carbinol chloride, intensely red, exists as the quinocarbonium salt, in combination with the extra molecule of acid.

Attempts to Obtain the Two Forms of the Carbinol.—Gomberg found that the colorless modification of *p*-hydroxytriphenylcarbinol was easily transformed into the colored modification by crystallizing from dilute acetic acid. He also found that exposure of either the white solid, or its benzene solution, to the direct rays of the sun or to ultraviolet light induced quinonoidation. By the same means Gomberg and Van Stone succeeded in tautomerizing many other carbinols. We find that *m*-cresyldiphenylcarbinol, contrary to expectation, behaves very differently. In an effort to obtain the colored modification we have tried recrystallization from acetic acid in varying strengths, also with the addition of acetic anhydride. Benzene containing a small amount of acetic acid was also tried, but in each case the result was the unchanged colorless modification. With stronger acids, as dichloroacetic, sulfuric, or a solution of hydrogen chloride in benzene, the color indicated the formation of a salt, and on dilution no colored crystalline product could be obtained. On exposure of the solid

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[1] THIS JOURNAL, 35, 1040 (1913).

white compound to sunlight the surface of the crystals turned yellow, but every attempt at recrystallization of this product resulted in obtaining only the colorless compound. A solution of the colorless compound in benzene was placed in a quartz flask and exposed to the direct rays of the sun. The solution assumed a brownish yellow color but on evaporation of the solvent no crystalline product could be obtained.

The Free Radical *o*-Methyl-*p*-carboethoxytriphenylmethyl.

The hydroxycarbinol when treated in benzene solution with dry hydrogen chloride was found to give the fuchsone hydrochloride which on treatment with silver splits off hydrogen chloride instead of chlorine. Consequently the carboethoxy-derivative was chosen for the attempt to isolate the free radical.

2-Methyl-4-carboethoxytriphenylchloromethane, Formula VI.—The carboethoxycarbinol is dissolved in benzene, saturated with dry hydrogen chloride and allowed to stand over fused calcium chloride. The benzene is evaporated under reduced pressure and an equal volume of petroleum ether added. On standing well-formed nearly colorless crystals separate. The small amount of color may be completely removed by boiling in petroleum ether with well-dried animal charcoal. The crystals melt at 96–7°.

Calc. for $C_{23}H_{21}O_3Cl$: Cl, 9.32%. Found: 9.27%.

2-Methyl-4-carboethoxytriphenylmethyl.—Preliminary experiments showed that the action of molecular silver upon the chloride was quite analogous to its effect on triphenylchloromethane but very much slower. In the latter instance, under similar conditions, nearly all the chlorine is taken out in fifteen to thirty minutes, while in the former it requires three to five days. A yellow color appeared in the solution at once, which, after a few days' shaking, increased to a deep cherry-red. When the solution is brought in contact with oxygen the color quickly disappears.

To determine the absorption of oxygen by the radical the following method was used. The chloride and the silver were sealed with benzene in a thin-walled test tube, only a fraction of a cc. of air being left for a cushion. After shaking three or four days the test tube was placed in a bottle connected by means of a tight stopper with a gas buret, both bottle and buret containing some benzene. The bottle was filled with oxygen and the test tube broken by shaking. The absorption of oxygen by the radical was complete within a very few minutes. Very careful control of the temperature by means of a large pail of water in which the bottle is immersed is essential to good results. After making correction for the vapor pressure of benzene, the barometric pressure, and temperature, the following results were obtained:

0.6623 g. of chloride yielded free radical which absorbed 0.0292 g. of oxygen. Calc. for peroxide formation, 0.278 g.

o-Methyl-p-carboethoxytriphenylmethyl Peroxide.—The principal product of the oxidation of the above-described free radical is the corresponding peroxide, and its formation as above described furnished indubitable proof of the existence of the free radical. The peroxide can conveniently be prepared and purified as follows: The benzene solution containing the free radical is exposed to air until only a pale yellow color remains, the solvent is then allowed to evaporate spontaneously and the product washed with a little ether. The product may be dissolved in warm benzene and an equal volume of ether added. On standing the peroxide deposits in minute, shiny crystals. The product melts at 141–2° with decomposition.

Calc. for $C_{46}H_{42}O_8$: C, 76.42; H, 5.86. Found: C, 76.42; H, 5.94.

From 1.064 g. of chloride we were able to obtain 0.727 g. of peroxide, about 70% of the amount calculated. The determination does not take into account the solubility of the peroxide in the ether with which it was washed.

Attempt to Prepare the Free Radical as a Solid.—Several attempts were made to isolate the free radical in the solid state, using an apparatus to insure complete absence of oxygen. On evaporation of the benzene the thick syrup had a marked greenish tint. After standing for some time there was no sign of crystallization. Repeated experiments, wherein we had recourse to the addition of petroleum ether as well as other solvents, gave no better results.

In their work on p-carboethoxytriphenylmethyl, to which our free radical is analogous, Gomberg and Jickling found that the radical possessed a marked tendency to form a polymer or a stable non-reversible isomer, and that this did no longer absorb oxygen. It was thought that our compound, although more stable than Gomberg and Jickling's at room temperature, may have formed a similar polymer at the higher temperature at which the benzene was evaporated. In order to test this assumption tubes containing the carbinol chloride and silver in benzene were sealed and shaken at room temperature long enough to form the free radical, and were then placed in a bath at 100° before determining the oxygen absorption. The results appear to confirm our supposition. A tube shaken five days and heated at 100° for thirty minutes showed 69.4% of the theoretical absorption, while a tube shaken for the same length of time and then heated for one hour gave only 44.0% of the theoretical value.

In order, then, to avoid this polymerizing effect of heat upon the free radical the benzene solution in another preparation was evaporated without application of heat. The usual apparatus[1] was used, the evaporation being accomplished by allowing a slow stream of carbon dioxide to

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[1] *Ber.*, 37, 2034 (1904).

enter while maintaining a vacuum in the bulb. But here again, after standing for a few days, and even after the addition of petroleum ether, no crystals were obtained. On exposure to air, however, the solution still absorbed some oxygen forming the peroxide. The question as to why the free radical under these conditions fails to crystallize must remain for the present unanswered.

Dibromo-*m*-cresyldiphenylcarbinol.

m-Cresyldiphenylcarbinol is best brominated in acetic acid solution. It is advisable to brominate small portions at a time. In two instances, when we used 20 g. of the carbinol, the latter was almost completely decomposed by the bromine and the hydrobromic acid, and large quantities of tribromo-*m*-cresol were formed.

The following procedure is recommended: One gram of the carbinol is dissolved in acetic acid and two grams of bromine are added. The black oil which is at first precipitated crystallizes on standing overnight. To this as a nucleus, alternate portions of the acid solutions of carbinol and halogen are added, the perbromide being precipitated under these conditions as a bright red crystalline powder. The perbromide is filtered, washed with acetic acid, and, after short drying in air, is dissolved in ether. The ether solution is washed several times with a solution of sodium sulfite which removes all acetic acid and bromine. After drying with calcium chloride the ether is evaporated at as low temperature as possible, and benzene added. On standing the dibromocarbinol separates in well-formed, slightly orange-colored crystals. The compound can be obtained almost colorless on repeated recrystallization and then it melts at 148°.

Calc. for $C_{20}H_{16}O_2Br_2$: Br, 35.68. Found: Br, 35.58.

On recrystallizing from dilute acetic acid there is very little change in color. If, however, the compound be dissolved in hot glacial acetic acid the desmotropic modification is obtained on cooling in the form of yellowish red rosets. The composition and the melting point are the same as those of the colorless variety.

Calc. for $C_{20}H_{16}O_2Br_2$: Br, 35.68. Found: Br, 35.03.

If the acetic acid solution has been kept hot for some time small portions of the corresponding fuchsone (see below) will appear as deep red spots along with the much lighter crystals of the carbinol. The fuchsone may be easily separated mechanically from the main body of the crystals. If the colored carbinol be dissolved in alcohol and water added at once, the carbinol will precipitate with only very little change in color. If, however, the solution in alcohol be allowed to stand a few hours, then on addition of water the compound is obtained nearly colorless. The carbinol is quite soluble in ether, but less so in benzene and in alcohol, still less in chloroform and in carbon disulfide. Least of all it is soluble in carbon tetrachloride.

The colorless and the yellow modifications of the carbinol were very carefully purified, and the temperature at which they melt, respectively, was determined with great care, to see if a difference in the two could not be discovered. For this purpose the bath was heated to within a few degrees of the melting point of the carbinol before the tube containing the substance was introduced, thus reducing the amount of decomposition, or conversion of one tautomer into the other. The colorless tautomer melted at 146.5–147.5°, the yellow at 147–148°. An intimate mixture of the two was found to melt at 147–148°.

On heating samples of the two modifications placed in separate tubes, side by side in the same bath, a marked difference in the rate of dehydration was observed.

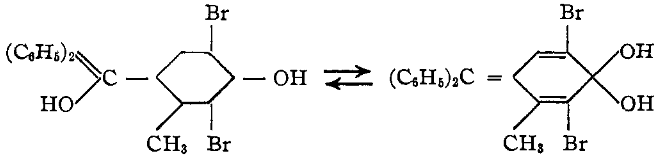
Temp.	Time of heating.	Colorless compound.	Colored compound.
90°	30 min.	No loss	No loss
110°	30 min.	No loss	0.25%
120°	30 min.	0.07%	0.52%
130°	30 min.	0.15%	1.48%
130°	30 min.	0.29%	2.24%

In each case the per cent. gives the total loss at the end of the stated period. After one hour's further heating the colorless modification also began to lose water more rapidly. The dehydration was continued at 130° until further heating caused a loss in weight of less than 1 mg. in three hours.

	Colorless.	Colored.	Calc. for loss. of one mol. H_2O.
The total loss was	4.01%	4.46%	4.02%

The water evolved was in each case collected in a calcium chloride tube in order to check the loss in weight.

We think our results justify the conclusion that the colored modification is the quinonoid, while the other is the benzenoid form. As it appears from our results the dibromo-*m*-cresyldiphenylcarbinol, in distinction from the unbrominated carbinol, exists in two desmotropic forms, quinonoid and benzenoid:



While both melt at the same temperature their behavior on heating, in addition to their difference in color, is sufficiently characteristic to differentiate the two forms.

2,6-Dibromo-3-methyl Diphenylquinomethane, $(C_6H_5)_2C : C_6H(CH_3)$-

Br_2 : O.—This compound remains as a residue after the evolution of water from either of the two modifications of dibromo-*m*-cresyldiphenylcarbinol. It is best prepared by heating a weighed amount of the dibromocarbinol in an open dish at 150° until the loss in weight just corresponds to one molecule of water. A longer heating causes decomposition. The fuchsone is soluble in benzene and only slightly so in ether, and can be crystallized from a mixture of the two. Crystallized from benzene it contains solvent of crystallization which is given off only very slowly at the boiling temperature of benzene. A sample thus prepared lost on heating in a vacuum for one hour at 75–80° only 0.44%, for another hour at 110–115°, 1.96%, and finally for one-half hour at 150–55°, 9.08%. On further heating the loss was very slow. Calc. for 1 mol of benzene, 8.32%.

From high-boiling petroleum ether the fuchsone crystallizes well.

Calc. for $C_{20}H_{14}OBr_2$: Br, 37.18. Found: Br, 36.89.

Dichloro-*m*-cresyldiphenylcarbinol, analogous to the above dibromide, was prepared by the action of chlorine in carbon tetrachloride upon the carbinol dissolved in chloroform. Crystallized from benzene, or carbon tetrachloride with the addition of petroleum ether, it comes out as white crystals, melting at 135–7°. But crystallized from glacial acetic acid the carbinol is yellow, melting, however, at the same temperature as the colorless modification. The relation apparently between these two tautomers is like that between the two bromides.

o-Methoxy-*p*-hydroxytriphenylcarbinol.

This compound was prepared from benzophenone chloride and resorcin mono-methyl ether, using exactly the same procedure as was used in preparing the corresponding cresyl compound. The methoxy derivative is more soluble in benzene than the cresyl compound, so that in the process of purification, after the addition of that solvent, the solution must be evaporated to a small volume. The compound melts at 132° with decomposition, but when the heat is raised gradually and kept around 120° for about 30 seconds, the carbinol may melt as low as 124°. Crystallized from 70% acetic acid, the compound shows no tendency toward tautomerization, as there is no sign of coloration, and the melting point is the same as when the compound is crystallized from benzene or alcohol. Like the cresyl carbinol, this carbinol also possesses a marked tendency to come out from various solvents with solvent of crystallization. Crystallized from carbon tetrachloride, it lost 23% on heating at 70°, calculated for 0.5 mol solvent, 20.1%; from benzene, it lost 12.7%, calculated for 0.5 mol solvent, 11.3%.

The constitution of this carbinol as *o*-methoxy-*p*-hydroxytriphenylcarbinol was established, as explained in the introduction, by its nonidentity with the only other isomer that could be formed in this reaction, and which in turn was prepared according to the Grignard method from the ester of *p*-methoxy-*o*-hydroxybenzoic acid by the action upon it of phenylmagnesiumbromide.

p-Methoxy-o-hydroxytriphenylcarbinol.—*p*-Methoxy-*o*-hydroxybenzoic acid was made by methylating resorcylic acid, using the general method of Ullmann and Wenner.[1] 7.7 g. (0.05 mol) of resorcylic acid were dissolved in 50 cc. of 10% sodium hydroxide solution and 12 cc. (0.1 mol) of dimethyl sulfate added. The mixture was shaken vigorously for a few minutes and allowed to stand overnight. Excess of alkali was then added and the mixture warmed on the steam bath for 30 minutes, cooled, and acidified with hydrochloric acid. The precipitated acid was recrystallized first from hot water, and lastly from benzene. The yield was 5.1 g., and the melting point 157°. Tiemann and Parrisius,[2] having made the compound by another method, give the melting point as 154°.

The ethyl ester was made in the usual manner by dissolving the above-described acid in absolute alcohol and saturating with HCl. The mixture was poured into water, the ester dissolved in ether, dried, the solvent evaporated, and the residue distilled. The main portion boiled between 272° and 274°.

The ester was converted into the *p*-methoxy-*o*-hydroxytriphenylcarbinol by the action upon it of phenylmagnesiumbromide. The carbinol is best recrystallized from glacial acetic acid, from which solvent it forms clear, white crystals. The compound melts to a very dark liquid at 154°, decomposing with evolution of gas at 158°.

This carbinol is thus seen to be essentially different from the carbinol obtained by the condensation of benzophenone chloride with resorcin monomethyl ether. The latter carbinol must, therefore, be the parahydroxy-derivative.

Summary.

1. The condensation of benzophenone chloride with *m*-cresol and with resorcinol monomethyl ether has been studied, and the principal products obtained were proven to be, respectively, *o*-methyl-*p*-hydroxytriphenylcarbinol, and *o*-methoxy-*p*-hydroxytriphenylcarbinol.

2. It was found that, strangely enough, the methyl and methoxyl groups in the ortho position to the central carbon atom greatly diminish the tendency of the above carbinols to form two desmotropic modifications. An impeding influence of this nature is entirely wanting, as has been previously reported, when these very same groups are in the meta position to the central carbon atom.

3. When *m*-cresyldiphenylcarbinol is brominated its latent tendency

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[1] *Ber.*, 33, 2476 (1900).

[2] *Ibid.*, 13, 2376 (1880).

toward tautomerization becomes apparent, the dibromocarbinol existing in the two modifications, benzenoid and quinonoid.

4. The free radical *o*-methyl-*p*-carboethoxytriphenylmethyl has been proved to be capable of existence in solution. While apparently more stable than the corresponding free radical, *p*-carboethoxytriphenylmethyl, it is, none the less, sufficiently prone toward polymerization or isomerization to a non-reversible isomer to preclude the possibility of its isolation by the ordinary means at present in use.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

IX. THE ELECTRONIC FORMULA OF BENZENE AND THE MOLECULAR VOLUMES OF THE CHLOROBENZENES.[1]

BY HARRY SHIPLEY FRY.

Received April 25, 1917.

Most of the papers of this series[2] have dealt with the interpretation of substitution reactions in the benzene nucleus, and other stereochemical problems, in terms of the electronic formula of benzene. Hence the evidence for the electronic formula of benzene has been found chiefly in chemical reactions rather than in particular physical properties, with the exception of the development of a relationship in the nature of a linear function between the systems of dynamic equilibria of the electromers of benzene and the oscillation frequencies of the seven bands which characterize the absorption spectrum[3] of benzene solutions.

The present paper is an attempt to show that other relationships may exist between the electronic formula of benzene and certain physical properties, notably, the molecular volumes of mono-, di-, tri-, tetra-, penta- and hexa-chlorobenzenes.

The distinctive feature of an electronic formula is the designation of the polarities of certain atoms or radicals constituting the compound. Such designations should not be arbitrary: they are based chiefly upon definite reactions[4]—hydrolyses, oxidations, reductions, etc.—which indi-

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[1] This paper constitutes Part IX of the series "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences." Read by title at the 53rd meeting of the American Chemical Society, New York City, September 27, 1916.

[2] Fry, THIS JOURNAL, **36**, 248, 262, 1035 (1914); **37**, 855, 863, 883, 2368 (1915); **38**, 1323, 1327, 1333 (1916). See also Fry, *Z. physik. Chem.*, **76**, 385, 398, 591 (1911); **80**, 29 (1912); **82**, 665 (1913); **90**, 458 (1915).

[3] Fry, "Dynamische Formeln und das Ultraviolettabsorptionsspektrum des Benzols," *Z. physik. Chem.*, **76**, 398 (1911).

[4] Fry, *Loc. cit.;* W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); Stieglitz, *Ibid.*, **23**, 796 (1901) and "Qual. Chem. Anal.," Chaps. XIV and XV of Vol. I; Jones, *Am. Chem. J.*, **50**, 414 (1913).