tillate, add to it 1 cc. of ether, shake, pour off the ether and allow it to evaporate on a watch glass. Crystals of acetoxime will remain on the glass if the distillation is not complete.

Add the distillate and 150 cc. more of hydrochloric acid to the acetoxime previously removed. Distil the acetone (about 60% is usually recovered) and evaporate the residual liquid to dryness on the steam-bath; yield, 210 to 300 g. of crude hydroxylamine hydrochloride or 53 to 77%. The crude product so obtained can be purified by recrystallization from $^1/_2$ its weight of hot water.

Preparation of Acetoxime.—If acetoxime is the desired product, the reduction, formation of the oxime and neutralization are carried out as before. The oily layer is separated and the aqueous layer extracted with two 100cc. portions of benzene. These 3 portions are mixed and the water which separates is added to the liquid which has just been extracted. The benzene solution of acetoxime is distilled, acetoxime passing over at 133–136° (the boiling point of the pure product is 135°); yield, 280 to 320 g.

The liquid which was extracted with benzene can be distilled to secure the acetoxime which invariably remains. This can be treated with hydrochloric acid and evaporated to obtain hydroxylamine hydrochloride as explained above; yield, 50 to 60 g.

Summary

1. A new method for the preparation of hydroxylamine hydrochloride has been described which (a) approximately halves the time necessary for the preparation; (b) is economical of ice; (c) gives a product free from ammonium salts.

2. An easy method is given for the preparation of acetoxime.

Seattle, Washington

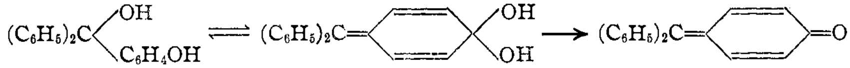
[Contribution from the Chemical Laboratory of the University of Michigan]

TRIPHENYLMETHYL. XXXI. TAUTOMERISM OF ORTHO-HYDROXY-TRIPHENYL CARBINOL; ORTHO-HYDROXY- AND ALKYLOXY-TRIPHENYLMETHYL

By M. Gomberg and D. Nishida

Received October 9, 1922

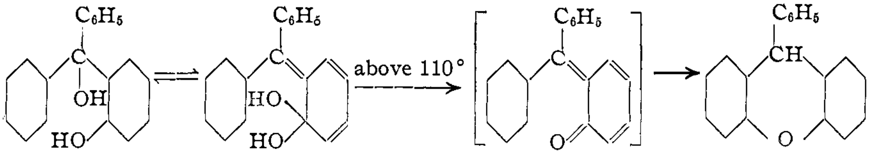
It has been shown in previous papers that *p*-hydroxy-triphenyl carbinol and many of its analogs are prone to tautomerize and, when heated, yield *p*-fuchsones, as for example,



The two tautomeric carbinols have been actually isolated in a number of instances. It has also been shown that the corresponding carbinol chlorides possess the tendency towards quinoidation even to a greater extent than do the carbinols themselves. In fact, the benzenoid form of these chlorides may be considered as non-existent. However, the quinonoid chlorides themselves are also extremely unstable and dissociate very readily, both in solution and in the dry state, into fuchsone and hydrochloric acid. On account of this extreme instability of the chloride it proved impossible to prepare *p*-hydroxy-triphenylmethyl. We have now investigated *o*-hydroxy-triphenylcarbinol from the same two points of view, namely, first, as regards its tendency to tautomerize and to yield *o*-fuchsone, and second, as regards the possibility of preparing the corresponding *o*-hydroxy-triarylmethyl radical. The investigation was further extended to the *o*-benzyloxy-, phenoxy-, methoxy-, and acetoxy-triphenylcarbinols, respectively.

Discussion of Results

Baeyer[1] found that *o*-hydroxy-triphenylcarbinol when heated to the temperature of its melting point (140°), gradually loses water, but did not succeed in isolating from the decomposition product any definite substance. On prolonged heating at higher temperature, or when subjected to vacuum distillation, the carbinol gave 9-phenyl-xanthane (IV). We have now found that when a solution of the carbinol in glacial acetic acid, carbon tetrachloride, benzene, toluene or xylene is warmed, the solution becomes brown. The coloration begins at 50–80°, according to the nature of the solvent, acetic acid giving the most intense color; the color intensity is increased by raising the temperature of the solution or the concentration of the solute. On cooling the solution, the color gradually decreases and almost completely disappears at the very same temperature at which the particular solution commenced to develop color when warmed. This color change is reversible at any temperature below 110°, and the carbinol is recoverable quantitatively. Above 110° the carbinol, in solution, slowly loses water; the product of dehydration, however, is not the anticipated *o*-fuchsone (III), but a colorless rearrangement product of it, namely, 9-phenylxanthane. The reactions are evidently as follows



I II III IV

Not only when in solution, but even as the solid, does the benzenoid

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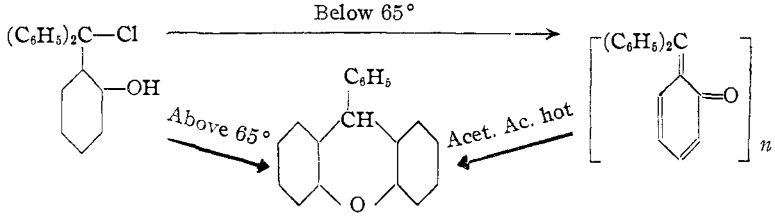
[1] Baeyer, *Ann.*, 354, 167 (1907).

carbinol tautomerizes to the quinonoid modification. It turns brown at 100°, and at 110°—which is 30° below its melting point—it commences to lose water; but here again the product of dehydration is 9-phenylxanthane.

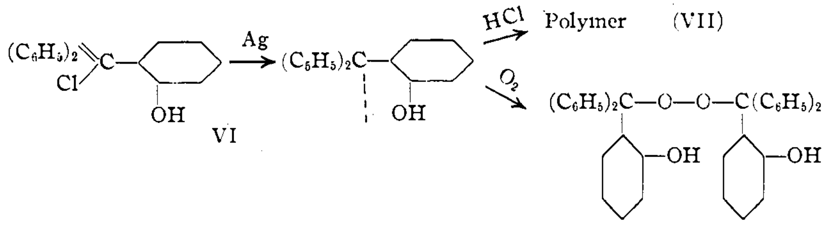
It appears thus that the quinonoid tautomer of the carbinol exists only at elevated temperatures, up to 110°, when it goes over into the *o*-fuchsone; that the latter is unstable at that temperature and isomerizes into xanthane. Indeed, as will be shown below, the conversion of the *o*-fuchsone into phenylxanthane may occur even at the temperature of about 65°.

o-Hydroxy-triphenyl carbinol chloride, when freshly prepared, is a white, crystalline compound, but it begins at once to lose hydrogen chloride and, simultaneously, assumes a brown color. This decomposition takes place slowly even below 10°, whether the carbinol chloride be in the solid state or in solution. Below 65°, the result is a dark brown jelly-like substance; but above 65° the main product of decomposition is 9-phenylxanthane. We did not succeed in converting the jelly-like substance into crystalline material, but it seems probable that it represents polymerized *o*-fuchsone. When this gum is heated with glacial acetic acid, the brown color disappears and phenylxanthane is produced. The decomposition of the chloride can be expressed as follows.



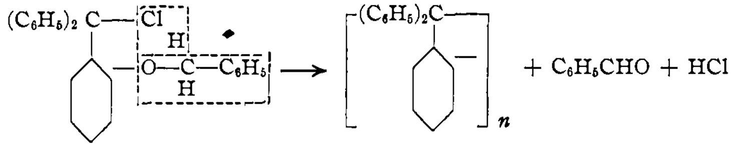
V

o-Hydroxy-triphenylchloromethane, being ever so much more stable than the isomeric *p*-hydroxy-compound, does actually give, upon treatment with metals, the corresponding triarylmethyl. Unfortunately, the isolation of the latter has proved impossible, for the reason that this carbinol chloride, as has been mentioned, decomposes in part with liberation of hydrogen chloride. The triarylmethyl, which may have resulted from the action of silver upon the portion of the undecomposed carbinol chloride, becomes thus subsequently polymerized under the catalytic influence of the acid into the corresponding stable benzhydryl-tetraphenylmethane derivative, in analogy to the similar behavior of many triarylmethyls. When, on the other hand, molecular silver is allowed to act upon the carbinol chloride with simultaneous introduction of air, then, in addition to the polymer, some hydroxy-triphenylmethyl peroxide is also formed. The reactions are as follows.



VI VIII

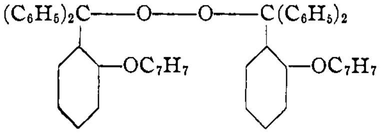
We hoped to obtain in the chloride of *o*-benzyloxy-triphenyl carbinol a compound sufficiently stable to yield the corresponding free radical. This expectation has not been fulfilled. The benzyloxycarbinol chloride is indeed considerably more stable than the hydroxy carbinol chloride. Nevertheless, like the latter, even at room temperature it suffers spontaneously a gradual decomposition, both in the solid state and when in solution. Placed in an air-tight bottle, the white crystals soon turn pink, hydrogen chloride is generated and a distinct odor of benzaldehyde becomes evident. At the temperature of 80° this decomposition is quantitative.



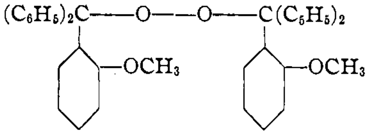
IX X

The very interesting hydrocarbon (X), unsaturated to the extent of two hydrogen atoms, undergoes instant polymerization. Although not crystalline, it was obtained sufficiently pure for analysis, and the results point to the composition $(C_{19}H_{14})_4$.

With metals, benzyloxy carbinol chloride behaves like the hydroxy carbinol chloride. Like the latter, it gives the free radical, but this is rapidly polymerized by the hydrogen chloride which results, as indicated above, from the spontaneous dissociation of a portion of the carbinol chloride. According to whether the reaction is carried on in the absence or presence of oxygen, either the stable polymer alone of the free radical, or the polymer and the triarylmethyl peroxide (XI) is produced.



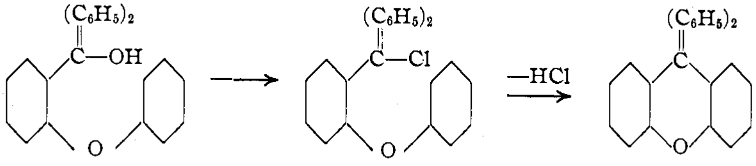
XI



XV

o-Phenoxy-triphenyl carbinol proved even less suitable than the benzyloxy compound for the purpose of obtaining the corresponding free radical.

The chloride suffers spontaneously complete intramolecular condensation with the production of 9,9-diphenylxanthane.



XII XIII XIV

o-Methoxy-triphenyl carbinol, although resembling so very closely in constitution the benzyloxy carbinol gives, nevertheless, a carbinol chloride which is quite stable. On treatment with metals the chloride gives the free radical (XVII) which, of course, is in equilibrium with its association product, dimethoxy-hexaphenylethane (XVI). The radical is crystalline and almost colorless when first prepared, but when dried it becomes light yellow. Its solutions are reddish-brown, a much darker color than that of triphenylmethyl solutions. On exposure to air the solutions absorb oxygen with avidity and give the peroxide (XV) of the free radical with a yield of about 80%.

The free radical unites with iodine, giving the corresponding triarylmethyl iodide, and the equilibrium state is reached when about 65% of the theoretical amount of iodine has been taken up.

o-Methoxy-triphenylmethyl chloride and the bromide show decided electrolytic conductivity in liquid sulfur dioxide. The free radical also conducts, but much less than the halide salts.

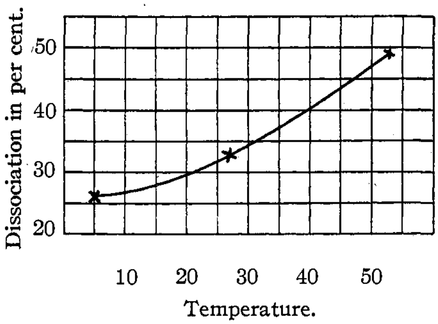


Fig. 1.—Dissociation curve.

Molecular-weight determinations of this hexa-arylethane indicate a considerable degree of dissociation—much more than that of hexaphenylethane. The dissociation increases to some extent with the dilution of the solute, and it increases markedly with the rise of temperature. The striking effect of temperature is brought out in Fig. 1.

When the colored solution of dimethoxy-hexaphenylethane is shaken with excess of oxygen the color instantly disappears, but is restored again after a very short interval, a reaction common to nearly all triarylmethyls. From the number of such successive decolorizations some have endeavored to deduce what the extent of the dissociation is of the hexa-arylethane, colorless, into the free triarylmethyl, colored. Gomberg and Sullivan[2]

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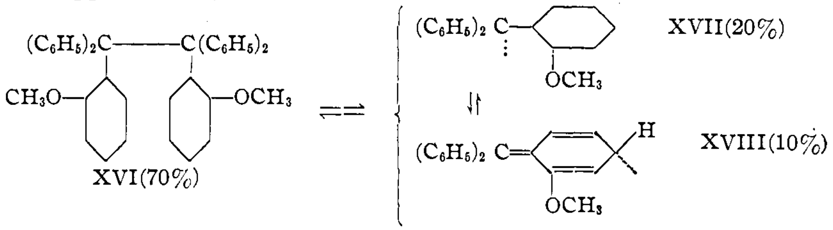
[2] Gomberg and Sullivan, This Journal, **44**, 1830 (1922).

called attention to the fallacy of this argument. By means of the apparatus described by them, we have now determined on the one hand the number of such color discharges of our radical, and on the other hand the amount of oxygen absorbed in each single operation. The results show indubitably that only about $^1/_{10}$ of the hexa-arylethane present in solution exists as the colored compound. Contrasting this figure with the actual amount of dissociation, as determined by the cryoscopic method, namely, 30%, it becomes obvious that only about $^1/_3$ of the total amount of the monomolecular free radical is colored, and the remaining $^2/_3$ is colorless. The benzenoid (XVII) and quinonoid (XVIII) tautomers are in this instance approximately in the ratio of 2:1.


XVI(70%)

XVII(20%)

XVIII(10%)

The question must remain open whether the quinoidation occurs in the methoxy-phenyl ring or in one of the two unsubstituted rings. The surmise is justified that both quinonoid forms may be present, with the first tautomer predominating.

Experimental Part

1. **Tautomerization of *o*-Hydroxy-triphenyl Carbinol.**—The carbinol was prepared according to the method of Baeyer and Diehl, from methyl salicylate and phenylmagnesium bromide, with a yield of 75–80%.

When recrystallized from acetic acid or from benzene it is obtained in snow-white, well defined crystals, but contains solvent of crystallization which, however, is readily removed when the crystals are gently heated. From carbon disulfide, carbon tetrachloride, ether or petroleum ether the carbinol crystallizes free from solvent.

Analyses. Calc. for $C_{19}H_{16}O_2.C_2H_4O_2$: loss, 17.84. Found: 17.94. Calc. for $C_{19}H_{16}O_2.C_6H_6$: loss, 22.03. Found: 21.72.

Table I

Color Change in Glacial Acetic Acid

Concn. of solution %	Temperature Color appears on heating °C.	Color disappears on cooling °C.	Color at 100°
1.0	65	60	pink
2.5	60	55	light brown
5.0	55	50	brown
7.5	50	50	dark brown
10.0	50	50	dark brown
20.0	50	50	dark brown

The solutions of the carbinol are colorless at room temperature but develop a reddish-brown color when warmed, this phenomenon being particularly striking in acetic acid. Solutions were prepared containing various concentrations of the purest carbinol in glacial acetic acid (99.98%); 2 cc. of each was sealed in test-tubes of 1 cm. diameter, the tubes placed in a sulfuric acid bath, warmed gradually to 100° and, after being kept at this temperature for 5 minutes, were cooled slowly to room temperature, again. The results are recorded in Table I.

The comparative influence of different solvents was determined by a similar set of experiments upon solutions containing in each case 5% of the carbinol, and the results are given in Table II.

TABLE II

COLORATION OF CARBINOL IN VARIOUS SOLVENTS

Solvent	Temperature Color appears on heating °C.	Temperature Color disap. on cooling °C.	Color at 100°
Benzene	75	68	pink
Toluene	80	75	pink
Xylene	80	75	pink
Bromobenzene	80	75	pink
Carbon tetrachloride	70	65	pink, deep
Amyl alcohol	..	..	colorless
Pyridine	..	..	colorless
Aniline	..	..	colorless
Nitrobenzene	..	..	colorless

After the experiment, pure carbinol was isolated from each solution.

The coloration of the carbinol, that is, the tautomerization, is greatly hindered by the presence of small amounts of water in the solvent and is completely prevented by larger amounts. The following set of experiments (Table III) on 5% solutions of the carbinol shows how remarkable the influence of water is on this color change.

TABLE III

INFLUENCE OF WATER UPON THE COLORATION

Conc. of acetic acid %	Temperature color appeared °C.	Color at 100°
100.0	55	brown
99.5	70	pink
99.0	88	light pink
98.0	95	slight pink
97.0	110	......
96.0	no color at 120	......

Conversion of the Carbinol into 9-Phenylxanthane (Formula IV).—While small amounts of water greatly hinder tautomerization, the presence of a dehydrating agent seems to have no pronounced influence provided, of course, that the temperature is kept below 110°; 5% solutions of the carbinol in acetic acid containing 5, 10, 20 and 50% of acetic anhydride were heated to 100° and gradually cooled, and the color changes were compared with those of solutions in pure acetic acid. The changes were practically unaffected by the presence of acetic anhydride within the range of temperature mentioned, except that samples containing much anhydride in the solution, even when cold, retained a slight yellow color, and small amounts of acetylated carbinol, in addition to the original carbinol, were isolated from these solutions.

When boiled with acetic acid the carbinol loses a molecule of water and slowly changes to phenylxanthane. It is completely converted into the xanthane, even at the temperature of only 110°, provided the water split off from the carbinol is either broken up or removed. The addition of acetic anhydride to the acetic acid accomplishes this purpose. When the temperature is raised to 110° and kept at this point for some time, the color of the solution, which is dark brown at the first stage, gradually turns to yellow and finally to light yellow. A 5% solution of the carbinol in glacial acetic acid containing 10% of acetic anhydride was used in these experiments. At 100° there was no apparent diminution of color, even after several hours' heating. At 110° the color was discharged in $1^2/_3$ hours; at 120°, in 1 hour; at 140°, in 30 minutes.

When the brown color of the solution had disappeared, a few drops of water were added, and the phenylxanthane crystallized in white, pearly crystals, melting at 144–145°. The yield was almost quantitative. The substance was identified by analysis and, further, by a comparison with a sample of the same compound that had been prepared according to the method of Ullmann and Engi,[3] by reduction of 9-phenyl-xanthenol with zinc dust and acetic acid.

Dehydration of the Solid Carbinol.—Experiments were conducted, using for each experiment a fresh sample of 1 g. of carefully purified and thoroughly dried carbinol. The material was placed in a tube, heated to the desired temperature, while a stream of dry carbon dioxide or hydrogen passed through the tube and carried off the water into a weighed calcium chloride tube.

TABLE IV

DEHYDRATION OF THE CARBINOL BY HEATING

Temp ° C.	Time Hours	Water driven off % of Calc.
90	5	. . .
100	5	2.2
110	5	68.0
110	10	88.2
120	5	79.0
120	10	94.2
130	3	80.6
130	5	100.8
140	5	103.0

It is evident that an appreciable amount of water is split off by heating the solid carbinol even as low as 110°, which is 30° below its melting point. The substance remaining in the tube in the last two experiments was

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[3] Ullmann and Engi, *Ber.*, **37**, 2372 (1904).

almost pure phenylxanthane, the yield being about 95% of the calculated. If air is used instead of hydrogen or carbon dioxide in order to drive out the water, some oxidation of the xanthane to xanthenol occurs, and this causes difficulty in the purification of the product.

o-**Hydroxy-triphenylchlormethane.**—Ten g. of the carbinol was dissolved in 100 cc. of absolute ether, calcium chloride added and the solution saturated with dry hydrogen chloride. After the filtered solution had been thoroughly dried, it was concentrated under reduced pressure to about 20 cc., and 30 cc. of petroleum ether was added. The crystals that separated were then filtered and washed with petroleum ether, while protected from the moisture of the air. The product was dried, first over sulfuric acid, then over freshly ignited soda lime. The yield was 4–6 g. The crystals were perfectly colorless when first obtained, but became brown even while in the desiccator.

Analysis. Calc. for $C_{19}H_{15}OCl$: Cl, 12.03. Found: 11.61.

The chloride is quite soluble in the usual organic solvents except petroleum ether, and is readily hydrolyzed by moisture. Even while protected against moisture it gives off hydrogen chloride, the rate of the decomposition depending mainly upon the temperature, as can be seen from the results in Table V. One g. of the chloride was taken for each experiment, and the porcelain boat containing the sample was placed in a tube and kept at a definite temperature. The hydrogen chloride given off was swept out by a stream of carbon dioxide (not air) and collected in standard silver nitrate solution.

TABLE V

DECOMPOSITION OF CHLORIDE IN ONE HOUR

Temp. °C.	HCl liberated G.	HCl liberated % of total
40	0.0023	2.3
50	0.0035	2.8
60	0.0185	14.8
70	0.0240	19.4
80	0.0430	32.6
90	0.0687	55.5

It is evident that the decomposition rapidly increases at 60°. Heating for 6 hours at that temperature, or for 4 hours at 80°, sufficed to expel about 90% of all the acid. The nature of the product left in the boat depended upon the temperature at which the sample was heated. If above 65°, then the residue consisted nearly all of pure 9-phenylxanthane; if below 65°, then it consisted of a dark colored gummy substance. The latter could not be brought to crystallization, but it was undoubtedly a polymerized product of *o*-fuchsone; it contained no phenylxanthane, but was readily converted into the latter by boiling acetic acid.

Similar experiments were carried out with the chloride in solution in carefully dried xylene. The results were in general similar to those given above. At the temperature of 25° about $^1/_4$ of all the acid was expelled in 24 hours, and more rapidly at higher temperatures. Here again, below 65°, the polymerized fuchsone was produced; above 65°, phenylxanthane was formed.

Action of Molecular Silver upon the Carbinol Chloride.—Preliminary experiments established that the chloride gives up its halogen to the metal quite readily. Shaking for 1 hour in benzene gave 65% of the total chlorine as silver chloride, 4 hours gave 84% and after that there was hardly any increase even in a week's time. These results indicate, since hydrogen chloride acts hardly at all upon metallic silver, that in the concentrations we employed, 4 to 5%, about 20 to 30% of the carbinol halide has dissociated into fuchsone and hydrogen chloride. Consequently, at best only 70–80% of the carbinol chloride employed was converted into the triarylmethyl; however, due to the acid present even that amount did not remain as such. The gradual diminution of the amount of triarylmethyl initially produced is shown strikingly by the following experiments. Bromobenzene, because of its low vapor pressure, was used as a solvent. In case of Expt. 1, the solution of the carbinol chloride in a small test-tube was placed in a bottle in which some molecular silver was suspended, also in bromobenzene. The bottle was connected with a gas buret and the whole filled with oxygen. The sample tube was then broken and the shaking was continued until no more oxygen was absorbed. In the other experiments, the mixture of carbinol halide and metal was shaken for indicated periods of time before breaking the test-tube. The amount of oxygen absorbed is an index of the amount of the triarylmethyl present.

TABLE VI

OXYGEN ABSORPTION BY *o*-HYDROXY-TRIPHENYLMETHYL

Wt. of chloride G.	Time of previous shaking Hours	Oxygen absorbed Vol. at normal state Cc.	Oxygen absorbed % of the theoretical
1.002	..	15	40
1.018	0.5	9.0	23
0.903	1	6.2	19
1.151	5	7.3	17
1.024	12	3.2	8

The Peroxide (VIII) and the Polymeric Substance (VII).—For the preparation of the peroxide, 2 g. of the carbinol chloride in carbon disulfide was shaken with 2 g. of silver in presence of oxygen for 10 minutes. The filtered solution was allowed to evaporate spontaneously, the residue washed with ether and recrystallized from carbon disulfide. The yield was 0.5 g., and the white crystals melted at 131°. The peroxide is almost insoluble in ethyl acetate, ether, acetone, alcohol or petroleum ether, slightly soluble in benzene or chloroform, and is quite soluble in carbon disulfide. It is also soluble in warm alkali hydroxide solution.

Analyses. Calc. for $C_{38}H_{30}O_4$: C, 82.90; H, 5.49. Found: C, 82.75; H, 5.79.

The stable polymerized product of the triarylmethyl was prepared by shaking the carbinol chloride with silver in a closed tube until the color initially produced disappeared again, which required about 24 hours. The filtered residue was concentrated, and the product crystallized from a mixture of carbon disulfide and acetone as white crystals, melting at 237°.

2. ***o*-Benzyloxy-triphenyl Carbinol.**—Fourteen g. of *o*-hydroxy-triphenyl carbinol, dissolved in 60 cc. of 1 *N* sodium hydroxide solution, was heated with 9 g. (about 20% excess) of benzyl chloride and the mixture stirred.

The aqueous layer was decanted, the product washed with water and alcohol, and recrystallized from hot benzene. The yield was 17.6 g., which is 96% of the calculated amount, and the snow-white crystals melted at 172°. The carbinol is almost insoluble in petroleum ether or alcohol, slightly soluble in ether, acetone, carbon disulfide, carbon tetrachloride or chloroform, and quite soluble in hot benzene or hot acetic acid.

Analyses. Calc. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.06. Found: C, 84.90; H, 5.96.

***o*-Benzyloxy-triphenyl Carbinol Chloride.**—Eighteen g. of the carbinol was suspended in 200 cc. of benzene, calcium chloride was added and the solution saturated with hydrogen chloride, whereupon the carbinol chloride which had formed, dissolved. After the benzene solution had been thoroughly dried it was concentrated under reduced pressure to a small bulk and petroleum ether was added. The carbinol chloride separated in colorless crystals, with a yield of 17.5 g., or 91%. The substance melts at 146°.

Analysis. Calc. for $C_{26}H_{21}OCl$: Cl, 9.01. Found: 8.93.

The carbinol chloride, even when carefully protected against moisture, light and air, acquires a perceptibly reddish color in about a day or two, and some decomposition has occurred with production of hydrogen chloride and benzaldehyde (p. 193). The change in rate of decomposition with change of temperature was determined in the manner described for the hydroxy-triphenyl carbinol chloride. With the solid compound, 0.5g. samples were used; with the chloride in xylene solution, 1g. samples. During 1 hour's heating, the amount of hydrogen chloride expelled was: at 60°, 2.3% of the total; at 80°, 6%; at 90°, 9.5%; at 110°, 14%; at 130°, 18.3%. When the carbinol chloride was dissolved in xylene, then the decomposition was appreciable even at 25°, proceeding to the extent of 10% in 6 hours; at 100° to 120°, 70% of the total hydrogen chloride was expelled in 24 hours.

The Decomposition Products.—Three g. of the chloride was heated in a small fractionating flask at 140–150° and dry carbon dioxide passed through the flask. In about 3 hours 0.6 g. of a light-yellow oil condensed in the small receiver. The oil had the characteristic odor of benzaldehyde, boiled at 168° under 735 mm. pressure,[4] and on exposure to air gave benzoic acid.

The residue in the flask, similar in appearance to rosin, was dissolved in ether and reprecipitated with alcohol. All efforts to get the material in crystalline form proved fruitless. The substance was, therefore, further purified by redissolving it in ether, adding alcohol cautiously, and repeating the process several times. A light-yellow powder was thus obtained, melting at 126–129°. It was easily soluble in ether,

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[4] The boiling point was determined by Schleiermacher's method. See Lassar-Cohn, "Arbeitsmethoden f. organisch-chemischen Laboratorion," Verl. von Leopold Voss., 4 Aufl, **1906**, p. 242.

benzene, chloroform or ethyl acetate, and slightly soluble in alcohol or acetic acid. See Formula X.

Analyses. Calc. for $C_{19}H_{14}$: C, 94.17; H, 5.83. Found: C, 92.90; H, 6.14. Calc. for $(C_{19}H_{14})_4$: mol. wt., 969. Found: in *p*-bromotoluene, 860; in *p*-dichlorobenzene, 869.

Action of Molecular Silver upon *o*-Benzyloxy-triphenylchloromethane.—Preliminary experiments showed that the carbinol chloride gives up its halogen to silver extremely readily, and with finely divided metal the reaction is completed in less than 30 minutes. After 1 hour's shaking, 94% of the total chlorine was present as silver chloride. Here again, as explained under hydroxy-triphenylchloromethane, the inference is justified that about 6% of the carbinol halide has broken down with production of hydrogen chloride. Because of this, the attempt to isolate the free radical as such was abandoned. The polymerizing effect of the acid upon the triarylmethyl which has been produced during the first stage of the reaction is evident from the results in Table VII. In Expt. 1, the halide and silver were shaken from the very beginning in presence of oxygen; in the others, for a definite interval of time in the absence of oxygen prior to oxidation.

TABLE VII

OXYGEN ABSORPTION OF THE REACTION PRODUCT

Wt. of chloride G.	Time of shaking; oxygen absent Hours	Oxygen absorbed Vol. at normal state Cc.	Oxygen absorbed % of the theoretical	Main product of the reaction
0.981	..	25.1	88.0	peroxide
1.008	1/6	20.5	69.8	peroxide
1.048	1/2	11.3	37.1	polymer
0.907	1	3.6	13.7	polymer
1.050	5	3.9	12.7	polymer
0.809	12	3.2	13.4	polymer

The Peroxide (XI) and the Polymerized Product.—The peroxide is almost insoluble in ether, ethyl acetate, alcohol, acetone, petroleum ether or carbon tetrachloride, and slightly soluble in chloroform, carbon disulfide or benzene. When the benzene solution of the peroxide is boiled for some time, slight decomposition takes place and the solution is colored brown. The snow-white crystals melt at 153°.

Analyses. Calc. for $C_{52}H_{42}O_4$: C, 85.44; H, 5.80. Found: C, 85.21: H, 6.05.

The polymer and the peroxide were separated by means of carbon tetrachloride, in which the polymer is soluble while the peroxide is not. The substance, consisting of fine white crystals, melts at 207°. It is fairly soluble in carbon tetrachloride, and quite soluble in benzene, carbon disulfide or ethyl acetate.

3. ***o*-Phenoxy-triphenyl Carbinol. (XII).**—This carbinol was prepared according to the method of Ullmann and Engi,[5] by the action of phenylmagnesium bromide upon the methyl ester of *o*-phenoxybenzoic acid. When a benzene solution of the carbinol was treated with dry

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[5] Ref. 3, p. 2368.

hydrogen chloride, the resulting product was not the carbinol chloride, but pure 9,9-diphenylxanthane (XIV), described by Ullmann and Engi, who obtained the same product by boiling a solution of the above carbinol in acetic acid with the addition of a few drops of sulfuric acid.

4. *o*-**Acetoxy-triphenyl Carbinol.**—This compound was prepared in the usual manner, by boiling the hydroxy carbinol with acetic anhydride and sodium acetate. Recrystallized from hot benzene, the white crystals melted at 246°. Unlike the hydroxy carbinol, the acetoxy derivative gives no coloration whatever when boiled with glacial acetic acid.

In the attempt to prepare the corresponding carbinol chloride, the carbinol was dissolved in ether and treated with dry hydrogen chloride. It was found that by this procedure the acetyl group was split off and there resulted *o*-hydroxy-triphenyl carbinol chloride.

5. *o*-**Methoxy-triphenyl Carbinol, the Carbinol Chloride and the Carbinol Bromide.**—Baeyer and Diehl prepared the carbinol from the methyl ether of methyl salicylate and phenylmagnesium bromide. We prepared our material by Grignard's reaction from benzophenone and *o*-anisyl iodide. It is quite stable and distils under reduced pressure, 30–36 mm., at 150–155°.

o-Methoxy-triphenylchloromethane was prepared from the carbinol according to our general procedure, in benzene solution with hydrogen chloride in presence of calcium chloride. Thirty g. of the carbinol gave 30 g. of the pure chloride, a 94% yield. The chloride does not split off hydrogen chloride nor methyl chloride, when heated even to 130°.

The carbinol bromide was prepared similarly to the chloride, by the action of hydrogen bromide in presence of calcium bromide; yield, 90%; m. p. 127–128°.

Analysis. Calc. for $C_{20}H_{17}OBr$: Br, 22.63. Found: 22.36.

Di-*o*-methoxy-hexaphenylethane and *o*-Methoxy-triphenylmethyl.—Five g. of methoxy-triphenylchloromethane and 5 g. of molecular silver were placed in a test-tube of about 100cc. capacity and the tube was almost completely filled with carbon disulfide. The reaction mixture was shaken for 12 hours. When the silver had settled to the bottom of the tube the clear solution was siphoned into the distilling bulb especially designed[6] for the work with free radicals. The solution was concentrated to about 10 cc. and an equal volume of petroleum ether added. On cooling, the hexa-arylethane, crystallized. The mother liquor was drained off, the crystals washed twice with low-boiling petroleum ether and dried in an atmosphere of carbon dioxide, with the bulb immersed in warm water at 50–60°. The yield is usually 2 to 3 g. of the pure compound, free from solvent of crystallization. The substance is extremely soluble in the usual organic solvents, but from carbon disulfide it can be successfully crystallized. The substance is first colorless, but on drying becomes slightly yellow; its solutions are dark orange color, with a reddish tint. The melting point, 117–121°, was determined in a U-shaped capillary tube, filled with carbon dioxide; when the temperature is being raised the color begins to appear at 110°.

Oxygen Absorption.—The absorption of oxygen by the free radical is very rapid, but hardly ever does the amount absorbed reach that calcu-

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[6] Gomberg and Schoepfle, THIS JOURNAL, 39, 1659 (1917).

lated from the equation. Quantitative measurements were made upon the triarylmethyl produced in solution from a definite weight of chloride, and also upon the previously isolated, crystalline, free radical as such.

TABLE VIII

OXYGEN ABSORPTION OF *o*-METHOXY-TRIPHENYLMETHYL

Wt. G.	Metal	Oxygen absorbed Vol. at normal state Cc.	Oxygen absorbed % of the theoretical
1.000[a]	mercury	33.8	93.3
1.126[a]	mercury	37.8	92.6
1.000[a]	mol. silver	34.2	94.4
1.203[a]	mol. silver	41.7	95.6
0.9552[b]	......	36.6	93.6
0.9136[b]	......	34.8	92.9

[a] Chloride. [b] Free radical.

Although the amount of oxygen absorbed is nearly quantitative, the actual amount of the peroxide formed is less than that which corresponds to the amount of oxygen taken up, just as has been found to be the case with other triarylmethyls; 1.156 g. of the compound gave 0.91 g. of peroxide; 0.897 g. gave 0.701 g. of peroxide, or about 82% of the theoretical amount.

The peroxide is insoluble in ether, alcohol, ethyl acetate, acetone or carbon tetrachloride and slightly soluble in benzene, bromobenzene, carbon disulfide or chloroform; the last two are the best solvents for recrystallization; m. p. 160–161°, with decomposition.

Analyses. Calc. for $C_{40}H_{34}O_4$: C, 83.20; H, 5.94. Found: C, 82.63; H, 5.88.

Action of Iodine upon *o*-Methoxy-triphenylmethyl.—The equilibrium was determined by titrating a weighed amount of the triarylmethyl with a 0.1 *N* iodine solution in benzene, with all requisite precautions against oxidation by the air. At the beginning, the reddish-brown color of iodine disappears instantly, then more slowly, and finally remains unabsorbed. The end-point can be determined by the change of color of the solution from the yellowish-brown of the free radical to a dark green, which is a resultant from the color of the free radical and that of iodine.

Subs., 1.675, 1.460, 2.030: 0.1 *N* I, 38.5, 35.0, 46.4 cc. Found: 63.1, 65.5, 62.9%.

The triaryl methyliodide was not isolated, but its presence in the solution was established through its conversion into the corresponding anilide, $(CH_3OC_6H_4)(C_6H_5)_2$-$C.NHC_6H_5$. This melted at 153°, and proved to be identical with a sample of the anilide prepared directly from the carbinol chloride and aniline.

The Molecular Weight of Di-*o*-methoxy-hexaphenylethane and the Degree of Dissociation into Free Radicals.—The molecular weight was determined by the cryoscopic method, using 3 different solvents. The apparatus used was of the Beckmann type, with the stirrer brought into action through an electromagnet placed externally.[7]

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[7] Ref, 6, p. 1662.

During the operation a slow stream of dry and carefully purified hydrogen was allowed to pass through the apparatus. For the solvent, benzene, *p*-bromotoluene and *p*-dichlorobenzene were used, and the molecular depression constant of each solvent was determined under exactly the same conditions as were to be used afterwards with the triarylmethyl. As the solutes, benzophenone for benzene, triphenylmethane for *p*-bromotoluene and dichlorobenzene were used.

The material used for the molecular-weight determinations was carefully dried in the manner previously described, and quickly pressed into pellets. No sample was used which did not show an oxygen absorption above 92%. As a rule, three additions of the sample were made. No correction was made for the effect due to supercooling of the solvent.

The *per cent.* of dissociation (x) was calculated from the formula, $x = \frac{M_t - M_0}{M_0} \times 100$, where M_0 is the molecular weight calculated from the depression of the freezing point, and M_t is that from the formula, $C_{40}H_{34}O_2$, 546.5.

TABLE IX

MOLECULAR WEIGHT OF DI-*o*-METHOXY-HEXAPHENYLETHANE (546.5)
MOLECULAR WEIGHT OF *o*-METHOXY-TRIPHENYLMETHYL (273.3)

1. Solvent, Benzene, F. p., 5°, K, 52.6

Solvent G.	Sample G.	Conc. of solution %	Depression	Mol. wt.	Dissociation %
19.85	0.3381	1.70	0.208	431	26.8
19.85	0.6654	3.35	0.401	440	24.2
19.85	1.0331	5.20	0.616	444	22.9
21.87	0.3720	1.70	0.212	422	29.5
21.87	0.6585	3.01	0.364	435	25.6
21.87	0.9026	4.13	0.500	434	25.9
			Av.	434	25.8

2. Solvent, *p*-Bromotoluene, F. p., 27°, K, 84

27.22	0.2202	0.81	0.167	407	33.4
27.22	0.4497	1.65	0.337	412	32.7
27.22	0.7350	2.70	0.542	419	30.8
26.53	0.2581	0.97	0.202	405	34.9
26.53	0.6251	2.36	0.478	414	32.0
			Av.	411	32.4

3. Solvent, *p*-Dichlorobenzene, F. p., 53, K, 74

25.00	0.3800	1.12	0.309	364	50.1
25.00	0.6761	2.70	0.545	367	48.9
25.00	0.9353	3.74	0.743	373	46.5
24.70	0.2502	1.01	0.210	357	43.0
24.70	0.5747	2.33	0.468	368	51.2
24.70	0.8734	3.54	0.698	375	45.8
			Av.	367	49.3

The Number of Consecutive Decolorizations of the Triarylmethyl on Oxidation, and the Amount of Oxygen Absorbed in Connection with Each Decolorization.—A weighed amount of the material was placed in a small thin-walled test-tube, bromobenzene was added to fill the tube and the latter was sealed. The tube was then placed in the oxygen-absorption apparatus and the experiment was carried out in the same manner as described by Sullivan and Gomberg[8] in their work on diphenyl-β-naphthylmethyl. It required 16 to 18 successive oxidations, at intervals of 2 minutes each, before the solution remained permanently colorless. The results of two such experiments are given in Table X.

TABLE X

OXYGEN ABSORPTION IN EACH DECOLORIZATION

	1	2
Wt. of sample	0.9510	0.8353
Purity (by oxygen absorption)	92.3	92.%
Conc. of the solution	2.4	2.1%

Expt. 1				Expt. 2			
		Adsorption of oxygen in each interval				Adsorption of oxygen in each interval	
Interval	Reading of buret, Cc.	Found Cc.	Calc., assuming amt. of col. free rad. = 10% Cc.	Interval	Reading of buret, Cc.	Found Cc.	Calc., assuming amt. of col. free rad. = 10% Cc.
..	0.0	...	..	..	0.0	...	..
1	3.9	3.9	4.05	1	3.4	3.4	3.52
2	7.2	3.3	3.65	2	6.0	2.6	3.17
3	10.3	3.1	3.26	3	9.1	3.1	2.85
4	13.5	3.2	2.93	4	12.0	2.9	2.56
5	16.4	2.9	2.74	5	15.0	3.0	2.30
6	19.5	3.1	2.47	6	18.0	3.0	2.07
7	21.3	2.8	2.22	7	20.6	2.4	1.86
8	24.2	2.9	2.00	8	23.0	2.6	1.67
9	26.9	2.7	1.80	9	25.6	2.6	1.50
10	29.3	2.4	1.62	10	28.0	2.4	1.35
11	31.7	2.5	1.46	11	30.2	2.2	1.21
12	33.2	2.3	1.31	12	32.2	2.0	1.09
13	35.5	2.0	1.18	13	33.4	1.2	0.98
14	37.0	1.4	1.06	14	34.2	0.8	0.89
15	38.4	1.0	0.96	15	34.7	0.5	0.80
16	39.4	0.8	0.86	16	34.9	0.2	0.72
17	40.2	0.3	0.77	17	35.2	0.2	0.65
18	40.5	0.3	0.70				

The figures in the fourth and eighth columns were calculated upon the assumption that 10% of the substance in solution exists as the colored free radical; in Expt. 1, for instance, the total absorption is 40.5 cc., so the first absorption should be 4.05 cc., and in the second interval (40.5–4.05)/10 = 3.65 cc., and so on. Objection might be raised against the assumption that a 2-minute interval suffices to reëstablish the equilibrium between the colorless and the colored substance. Such objection, however, cannot hold in the case of the very first color-discharge, for the latter is executed long after the material has been in solution; and it is in the very first color-dis-

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[8] Ref. 2, p. 1823.

charge that the absorption of oxygen is almost exactly $^1/_{10}$ of the whole absorption finally reached.

Electrolytic Conductivity of *o*-Methoxy-triphenylmethyl, of Its Chloride and Bromide in Liquid Sulfur Dioxide.—The cell used consisted of a uniform cylindrical vessel, 100 mm. high and 30 mm. in diameter.

The 2 platinum plates, 25 mm. in diameter, were fixed at a distance of 9 mm. from each other, and the lower plate was 5 mm. above the bottom of the vessel. The cell had a narrow mouth and could be made air-tight by a rubber stopper.

The cell constant was determined by 0.02 *N* potassium chloride solution at 25° in the usual way. Sulfur dioxide gas, which had been dried with phosphorus pentoxide, was condensed directly in the cell. Then the cell, supported on a spring, was placed in a Dewar bottle containing liquid sulfur dioxide, and in this manner the temperature of the cell was kept nearly constant at the boiling point of liquid sulfur dioxide, namely, about —10°. The liquid sulfur dioxide used in these experiments possessed uniformly the specific conductivity of 1×10^{-6} to 5×10^{-6}.

Table XI

Electrolytic Conductivity in Liquid Sulfur Dioxide

v = Volume of the solvent in liters, containing 1 g. mol. of solute.
μ = Molecular conductivity.

	v	μ	v	μ
o-Methoxy-triphenylchloromethane	991.5	102.7	1073.9	103.7
	319.5	99.8	264.8	95.1
	144.2	88.6	...	..
	43.5	73.4	61.7	79.8
	21.4	63.6	28.8	68.3
o-Methoxy-triphenylbromomethane	1196.0	153.8	950.2	137.8
	603.0	124.3	...	..
	...	...	283.0	115.3
	152.2	107.0	119.3	105.1
	65.5	87.1	72.2	99.0
	35.5	84.6	30.7	86.9
o-Methoxy-triphenylmethyl	1173.0	15.0	997.5	13.2
	544.1	12.2	635.2	12.0
	...	...	387.7	7.1
	189.9	7.3	125.9	5.7
	76.7	5.1	62.4	4.6

The solutions of the chloride and the bromide were red, the color of the latter being much deeper than that of the former in the same concentration. The solution of the free radical in liquid sulfur dioxide was dark brown.

Summary

1. It has been shown that when *o*-hydroxy-triphenyl carbinol is heated, it tautomerizes to the quinonoid modification. The change is reversible on cooling. At temperatures above 110° the carbinol loses 1 molecule of water, but the resulting fuchsone is isomerized at that temperature to

9-phenylxanthane. The carbinol chloride undergoes similar changes at much lower temperature, losing hydrogen chloride instead of water.

2. *o*-Hydroxy-*o*-benzyloxy- and *o*-methoxy-triphenyl carbinol chlorides have been prepared. It was found that they all give rise to the corresponding free radicals, the triarylmethyls. Because, of side reactions however, in the case of the first two chlorides, the isolation of the free radicals is not feasible; but *o*-methoxy-triphenylmethyl has been isolated and its principal physical and chemical properties have been determined.

3. *o*-Methoxy-triphenylmethyl has been found to exist in solution in the monomolecular state to the extent of 26 to 49%, depending upon the temperature. It has been proved that at room temperature only about $^1/_3$ of the total amount of the monomolecular triarylmethyl is colored—and hence quinonoid; the remaining $^2/_3$ is colorless, and consequently benzenoid.

Ann Arbor, Michigan

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

TRIPHENYLMETHYL. XXXII. PARA-BENZYLOXY- AND PARA-METHOXY-TRIPHENYLMETHYL[1]

By M. Gomberg and C. C. Buchler

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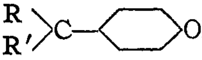
Numerous attempts have been made to prepare, in the solid state, triarylmethyls containing oxygen in the *para* position to the central carbon atom, but for the most part the results have proved negative. All attempts to isolate the free radical of the general formula,  in which R and R′ are similar or two different aromatic nuclei, and X = H, $COCH_3$, COC_6H_5, $CO.OC_2H_5$, CH_3, have failed, whether the hydroxyl group was protected through ester formation by the introduction of an acyl group[2] or through ether formation, by the introduction of the methyl group.[3] There is no doubt, however, that the respective triarylmethyls do exist, for the corresponding peroxides can generally be isolated.[4] Only one free radical containing *para* oxygen, *p*-anisyl-biphenylenemethyl,[5] has been successfully isolated; and recently, *o*-methoxy-triphenylmethyl[6] has been described.

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[1] The material here presented is from the thesis submitted by C. C. Buchler to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1922.**

[2] (a) Gomberg and Jickling, This Journal, **37,** 2575 (1915). (b) Gomberg and Van Stone, *ibid.*, **38,** 1577 (1916). (c) Gomberg and Johnson, *ibid.*, **39,** 1674 (1917).

[3] Schlenk and Herzenstein, *Ann.*, **394,** 187 (1912).

[4] Ref. 2. Gomberg and West, This Journal, **34,** 1529 (1912).

[5] Schlenk and Mair, *Ann.*, **394,** 196 (1912).

[6] Gomberg and Nishida, This Journal, **45,** 190 (1923).