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.

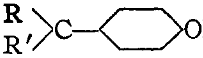
ANN ARBOR, MICHIGAN

[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

Received October 9, 1922

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).

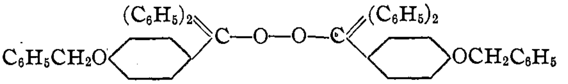
[6] Gomberg and Nishida, THIS JOURNAL, **45**, 190 (1923).

We now decided to block the *p*-hydroxyl group by a radical heavier than the methyl, namely, by the benzyl, in the hope that this would lend greater stability to the free radical and thereby permit more readily the isolation of such triarylmethyls in the solid state. This proved to be the case. A detailed study was then made of this free radical in respect to its behavior toward oxygen, iodine, hydrogen chloride, light; its capacity to form additive compounds, and the degree of dissociation of the hexaarylethanes.

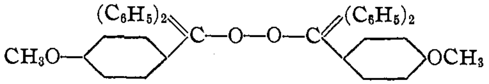
We next attempted the isolation of the *p*-methoxy-triphenylmethyl, notwithstanding the negative results previously obtained in this Laboratory and elsewhere, as mentioned above. The attempt to isolate this radical also was successful.

Discussion of Results

Both *p*-benzyloxy- and *p*-methoxy-triphenylmethyl are practically colorless, or light yellow, when freshly prepared, yet their solutions in organic solvents are always orange-yellow, slightly deeper in color than those of triphenylmethyl. On exposure to air, the solutions decolorize rapidly with the absorption of the quantity of oxygen which is necessary to form the corresponding peroxides.



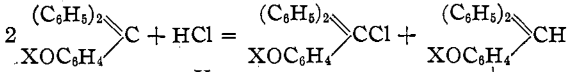
I



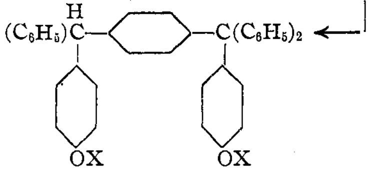
II

Benzene solutions of the free radicals absorb iodine rapidly, and the corresponding triarylmethyl iodides result. The equilibrium is reached when 55 to 60% of the calculated quantity of iodine has been added.

The free radicals in benzene react with hydrogen chloride with the formation of the corresponding carbinol chloride and the triarylmethane (Equation 1), and these only partially interact according to Equation 2, forming a stable polymer of the free radical, that is, a dialkoxy-*p*-benzhydryl-tetraphenylmethane, (III):



$$2\,\begin{matrix}(C_6H_5)_2\\ XOC_6H_4\end{matrix}\!>C + HCl = \begin{matrix}(C_6H_5)_2\\ XOC_6H_4\end{matrix}\!>CCl + \begin{matrix}(C_6H_5)_2\\ XOC_6H_4\end{matrix}\!>CH \qquad (1)$$

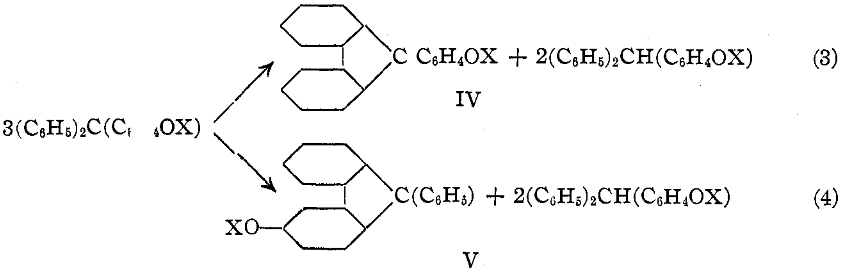


(2)

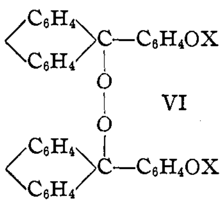
III

With triphenylmethyl itself the reaction proceeds largely according to the combined scheme in Equations 1 and 2, whereby over 90% is transformed into *p*-benzhydryl-tetraphenylmethane, and only 6% remains as chloride and methane. *p*-Benzyloxy- and *p*-methoxy-triphenylmethyl, however, react in accordance solely with Equation 1 to the extent of 80 to 85%; thereby they resemble diphenyl-α-naphthylmethyl, which forms chloride and methane[7] to the extent of 80%, without subsequent condensation of these two products.

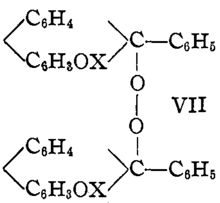
Benzene solutions of the free radicals in quartz test-tubes, placed in direct sunlight, decolorize after several hours' exposure, undergoing auto-oxidation and reduction. In other words, $^1/_3$ of the original free radical is transformed into a dehydrogenated triarylmethyl, while $^2/_3$ becomes reduced to the triarylmethane. Such a reaction might proceed according to either Equation 3 or 4.



On exposure to the air, the solution absorbs oxygen and forms the peroxide of the corresponding biphenylene free radical. This peroxide should have the constitution either VI or VII according as to whether the photochemical reaction has proceeded in the sense of Equation 3 or of Equation 4.



VI



VII

The peroxide VI, where X = CH_3, was synthesized according to Schlenk and Mair,[8] and it proved different from the peroxide actually obtained in our photochemical reaction. The peroxide of the constitution VII was then synthesized as follows. 3-Methoxy-9-fluorenone (VIII) was made according to Ullmann and Bleir[9] from anthranilic acid. The carbinol (IX), prepared through the Grignard reaction, was then converted

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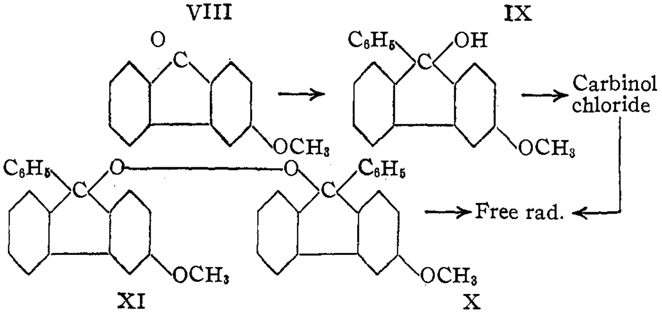
[7] Gomberg and Schoepfle, THIS JOURNAL, **41**, 1663 (1919).

[8] Ref. 5, p. 198.

[9] Ullmann and Bleir, *Ber.*, **35**, 4273 (1902).

into the chloride in the usual manner. Exposure to the air of a solution of the chloride previously shaken with molecular silver gave a peroxide, the constitution of which could be no other than XI. It proved identical with the peroxide obtained from the *p*-methoxy-triphenylmethyl by action of light and subsequent oxidation.



p-Benzyloxy- and *p*-methoxy-triphenylmethyl were crystallized from a large number of solvents representing esters, ethers, ketones, and hydrocarbons, but in only one case was an additive compound formed, namely, between ether and *p*-benzyloxy-triphenylmethyl, and here only partially. The isolated free radical never contained over 50% of the additive compound. This negative behavior is quite in contrast to that of triphenylmethyl, which forms additive compounds readily with all classes of solvents. It furnishes further experimental evidence in support of the hypothesis[10] which attempts to relate capacity of the hexa-arylethanes to form additive compounds and their degree of dissociation into free triarylmethyls.

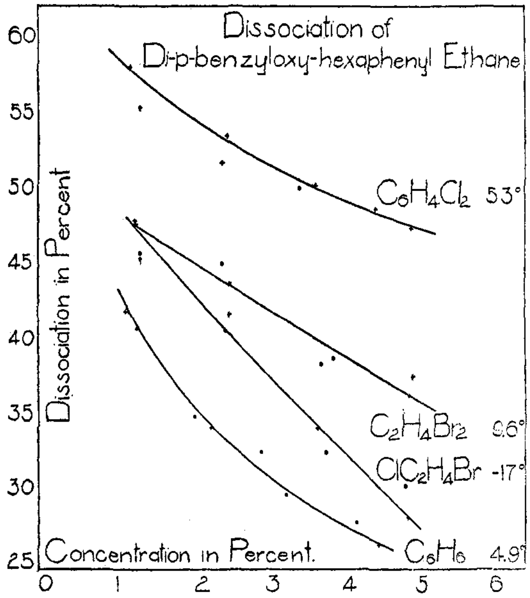


Fig. 1.

The degrees of dissociation of the two dialkoxy-hexa-arylethanes, that is, the molecular weight of the *p*-benzyloxy- and *p*-methoxy free radicals, were carefully determined in a number of solvents over a wide range of temperature and concentration. The molecular state

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[10] Ref. 7, p. 1672.

of the triarylmethyls is undoubtedly best represented by the formulation which involves simultaneously both dissociation of the hexa-artylethane and subsequent tautomerization of the triarylmethyl to the quinonoid state.[11] However, since the question of tautomerism is not involved in the discussion in this paper, the dissociation of di-*p*-benzyloxy- and di-*p*-methoxy-hexaphenylethane into the corresponding triarylmethyls may be formulated for this discussion by the simple system: $R_3C—CR_3 \rightleftharpoons 2\ R_3C$.

As was to be expected, this equilibrium was influenced by the concentration of the solute, the temperature and nature of the solvent. The degree of dissociation was found to decrease with increase in concentration, and increase with temperature, while the nature of the solvent also seemed to exert an influence. (Figs. 1 and 2.) With di-*p*-benzyloxy-hexaphenylethane at the freezing point of benzene for a 2% concentration, the equilibrium is reached between 36% of the triarylmethyl and 64% of the ethane; while for di-*p*-methoxy-hexaphenylethane under the same conditions the equilibrium is between 25% of the triarylmethyl and 75% of the ethane. Thus, these 2 free radicals exist to a much greater extent in the monomolecular form than does hexaphenylethane, which is dissociated to the extent of 2 to 5% under these conditions. It would seem that the heavier benzyl group induces greater dissociation tendency than the lighter methyl group. As regards the relative influence of the orientation, the methoxy group in either *ortho*[6] or *para* position exerts about the same influence.

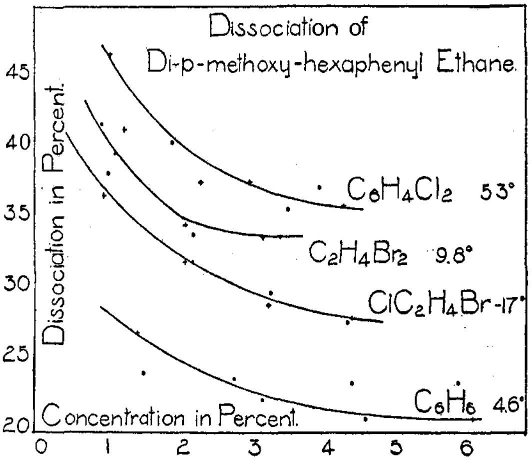

Fig. 2.

Experimental

p-Benzyloxy-triphenylmethyl

p-Benzyloxy-triphenyl **Carbinol,** $(C_7H_7OC_6H_4).(C_6H_5)_2COH$.—The *p*-hydroxy-triphenyl carbinol was prepared by the condensation of benzophenone chloride and phenol;[12] 40 g. (1 mole) of *p*-hydroxy-triphenyl carbinol was dissolved in a solution containing 14 g. (2.4 mole) of sodium hydroxide in 150 cc. of water in a flask provided with a reflux condenser and an efficient stirrer. To this was added 22 g. (1.2 mole) of benzyl chloride and the reaction mixture was heated for 4 hours in an oil-bath at 50°,

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[11] Gomberg and Sullivan, THIS JOURNAL, **44**, 1811, 1832 (1922).

[12] Gomberg and Jickling, *ibid.*, **38**, 3578 (1915).

with rapid stirring. After it had cooled, the alkaline supernatant liquid was decanted, and the solid product digested with warm 5% alkali solution, in order to remove any unchanged *p*-hydroxy-triphenyl carbinol. After the product had been filtered and washed thoroughly with water it was, while still moist, digested with 25 cc. of alcohol to remove any occluded benzyl alcohol or chloride. By following this procedure, yields of 90% were obtained. After several recrystallizations from benzene, *p*-benzyloxy-triphenyl carbinol was obtained in pure white crystals; m. p., 94°.

Analyses. Calc. for $C_{26}H_{22}O_2$: C, 85.34; H, 6.01. Found: C, 85.34; H, 5.97.

p-Benzyloxy-triphenylmethane.—Ten g. of the carbinol was dissolved in 50 cc. of glacial acetic acid and, after the addition of 15 g. of zinc dust, the solution was gently boiled under a reflux condenser until it became colorless. While the mixture cooled, *p*-benzyloxy-triphenylmethane crystallized, the yield being practically quantitative. Upon recrystallization from alcohol the substance separated in white needles which melted at 116.5°.

Analyses. Calc. for $C_{26}H_{22}O$: C, 89.14; H, 6.28. Found: C, 89.26; H, 6.31.

p-Benzyloxy-triphenylmethyl Chloride, $(C_7H_7OC_6H_4).(C_6H_5)_2CCl$.—The chloride was prepared by saturating a benzene solution of the carbinol with dry hydrogen chloride in the presence of anhydrous calcium chloride. After the solution had stood overnight and become concentrated, the chloride crystallized. For all further work the chloride was always recrystallized from absolute ether; m. p., 77°.

Analysis. Calc. for $C_{26}H_{21}OCl$: Cl, 9.22. Found: 9.20.

Upon addition of the theoretical quantities of ferric chloride, zinc chloride, mercuric chloride, or stannic chloride in ethyl acetate, to a benzene solution of the triarylmethyl chloride, the corresponding red double salts immediately separated as an oil. Later these salts became crystalline, with the exception of the zinc salt.

Analyses. Calc. for $C_{26}H_{21}OCl.FeCl_3$: Cl, 25.94. Found: 26.20. Calc. for $C_{26}H_{21}OCl.SnCl_4$: Cl, 27.49. Found: 27.92.

p-Benzyloxy-triphenylmethyl-ethyl Ether, $(C_7H_7OC_6H_4).(C_6H_5)_2COC_2H_5$.—This ether was prepared by the addition of benzyloxy-triphenylmethyl chloride to a solution of sodium ethylate. On crystallization from alcohol it separated in fine needles; m. p., 89°.

p-Benzyloxy-triphenylmethyl Bromide, $(C_7H_7OC_6H_4).(C_6H_5)_2CBr$.—In order to prepare the bromide, slightly more than the calculated amount of acetyl bromide was added to the carbinol dissolved in benzene. The solution was warmed, and after concentration and the addition of petroleum ether to it, the bromide crystallized. From absolute ether the bromide crystallizes in white needles which melt at 90°.

Analysis. Calc. for $C_{26}H_{21}OBr$: Br, 18.63. Found: 18.58.

Preparation of *p*-Benzyloxy-triphenylmethyl.—Three g. of benzyloxy-triphenylmethyl chloride together with 3 g. of molecular silver was introduced into a glass tube of 30 cc. capacity, the latter completely filled with dry thiophene-free benzene, and quickly stoppered, so as to be absolutely air-tight. After having been shaken for 8 hours, the solution of the free radical was siphoned into the apparatus especially designed for work with free radicals, and described in previous papers. The apparatus was immersed in a jar of warm water, at 45–50°, and the benzene removed under reduced pressure; then 10 cc. of warm acetone was added to dissolve the oily residue. The apparatus, filled with carbon dioxide under slight pressure, was allowed to remain in a cool place overnight, whereupon *p*-benzyloxy-triphenylmethyl crystallized. The supernatant liquid was drawn off, and after the substance had been washed several times with acetone, it was thoroughly dried in a slow stream of dry carbon dioxide under reduced pressure. Of the different solvents, acetone, ether, ethyl acetate, carbon disulfide, and methylethyl ketone, the first was found to be the most suitable, giving the purest product and the best yield, usually about 1.5 g. In an atmosphere of carbon dioxide the free radical begins to darken at about 125° and melts at 142–145°.

Analyses. Calc. for $C_{26}H_{21}O$: C, 89.40; H, 6.02. Found: C, 89.33, 89.50; H, 6.36, 6.15.

Reaction of *p*-Benzyloxy-triphenylmethyl with Oxygen.—Although *p*-benzyloxy-triphenylmethyl when perfectly dry may be exposed to the air for short periods of time without harm, it is much more susceptible to oxidation than is triphenylmethyl. Its solutions on exposure to the air decolorize rapidly with the absorption of oxygen, and this reaction may be used as a check on the purity of samples of the free radical. The absorption is very rapid, reaching the limit in less than 5 minutes. In the following table are given the results of some typical experiments on the absorption of oxygen based on weighed samples of the crystalline free radical in bromobenzene as a solvent, and also on the free radical in solution prepared directly from a definite quantity of the chloride.[13]

TABLE I

ABSORPTION OF OXYGEN BY BENZYLOXY-TRIPHENYLMETHYL

Wt. of Sample		Oxygen Absorbed	
Chloride G.	Free radical G.	Cc. (N. T. P.)	% of calc.
1	....	29.43	101.0
1	....	28.90	99.2
1	....	29.03	99.7
..	1.0302	33.52	101.4
..	1.2800	41.53	101.1

Although practically the calculated quantity of oxygen is absorbed, yet the amount of peroxide isolated from the reaction is usually only about 90%.

In order to determine the yield of peroxide, a weighed sample of the free radical was dissolved in benzene and the solution exposed to the air. After the benzene was allowed to evaporate, the residue was rubbed up several times with ether; the peroxide was then transferred to a weighed alundum crucible and thoroughly washed with ether; 1.432 g. of radical gave 1.352 g. of peroxide, which is 90.3% of the calculated amount. In two other experiments, yields of 91.2 and 90.8% were obtained. This is the largest yield obtained from any triarylmethyl so far reported. When the peroxide was recrystallized from hot benzene to which an equal amount of ether had been added, it was obtained in fine white crystals; m. p., 171°.

Analyses. Calc. for $C_{52}H_{42}O_4$: C, 85.48; H, 5.75. Found: C, 85.52; H, 5.89.

Reaction of *p*-Benzyloxy-triphenylmethyl with Iodine.—The amount of iodine that is absorbed by benzyloxy-triphenylmethyl was determined by titrating weighed samples, in absence of air, with a standard 0.1 *N* solution of iodine in benzene, the end-point being indicated by the first change in color due to excess of iodine. The equilibrium is reached when

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[13] Ref. 11, p. 1816.

approximately 60% of the calculated amount of iodine has been added; 1.351 g. required 23.0 cc. of 0.1 *N* iodine, which is 59.5% of the calculated amount. In two other experiments, 54.4 and 59.1% were obtained.

p-Benzyloxy-triphenylmethyl iodide was not isolated from the above reaction mixture. The iodide is very unstable and a benzene solution of it on exposure to the air immediately darkens, due to the liberation of free iodine. However, the presence of the iodide was proved by converting it into the anilide, and this proved identical with the compound obtained by the action of aniline directly upon the carbinol chloride.

Action of Hydrogen Chloride on *p*-Benzyloxy-triphenylmethyl.—A benzene solution of the free radical was treated with 20 cc. of benzene saturated with hydrogen chloride. After several hours the orange color of the solution of the free radical had gradually changed to reddish-yellow. The solution then failed to absorb oxygen.

In order to determine the extent to which the reaction proceeds according to Equation 1, the amount of *p*-benzyloxy-triphenylmethyl chloride was determined. The benzene solution containing a weighed sample of the free radical, after having been subjected to the action of hydrogen chloride, was concentrated under reduced pressure, in order to remove the excess of hydrogen chloride. To insure complete removal of the latter, the residue was again taken up in benzene and concentrated. From the chlorine content of the residue, the amount of *p*-benzyloxy-triphenylmethyl chloride was calculated; 2.019 g. of the radical gave 0.971 g. of the chloride, which is equivalent to 87.3% of the calculated amount, while another sample of 1.920 g. of the radical gave 0.976 g. of the chloride, which is 92.2% of the calculated amount.

Effect of Light on *p*-Benzyloxy-triphenylmethyl.—A benzene solution of the free radical was exposed in a quartz test-tube to the direct sunlight; the color of the free radical disappeared after several hours. On exposure to the air, the solution, which then contained a biphenylene free radical and *p*-benzyloxy-triphenylmethane (See Equation 4) absorbed oxygen in practically the calculated amount for the formation of the corresponding peroxide. Although the latter was not isolated in the pure state, the methane was isolated and identified as such.

Formation of Additive Compounds of *p*-Benzyloxy-triphenylmethyl.—In order to determine whether *p*-benzyloxy-triphenylmethyl possesses the property of forming additive compounds with different classes of solvents, the free radical was made as previously described, and for acetone were substituted the following solvents: Ethers: ethyl ether, *iso*-amylethyl ether, butylmethyl ether, butylethyl ether; Ketones: methyl-ethyl ketone, diethyl ketone; Esters: ethyl acetate, propyl acetate, propyl butyrate; Hydrocarbons: benzene, toluene, xylene; Acetonitrile; Carbon disulfide. The supernatant liquid was drawn off and the free radical thoroughly washed, first with mixtures of the respective solvent and petroleum ether, b. p. 50–60°, and finally with pure petroleum ether in order to insure complete removal of all adhering solvent. The free radical was transferred to a porcelain boat, weighed, and placed in a tube through which a slow stream of dry carbon dioxide was passed under reduced pressure. The tube was heated in an air-bath at 50–55° for 1 hour, and after the boat had cooled to room temperature it was reweighed.

With only one solvent, absolute ether, did the free radical combine, and always with less than required for 2 moles of triarylmethyl to 1 of ether. With 3 separate samples of about 1.5 g. each the loss was 4.03, 4.06, and 3.52%, respectively, against the calculated 9.60%.

Degree of Dissociation of Di-*p*-benzyloxy-hexaphenylethane.—For the determination of the molecular weight of *p*-benzyloxy-triphenylmethyl, the usual standard Beckmann apparatus was employed. The freezing-point tube was fitted with a rubber stopper, through which passed a small glass inlet tube for hydrogen, and a Beckmann thermometer. The side-arm was fitted with a rubber stopper through which passed an outlet tube for hydrogen, a glass tube in which the pellets were weighed, and a nickel wire flattened at one end so as to cover completely the outlet of the pellet-tube, thus protecting the pellets from the vapor of the solvent, for otherwise they became gummy. The apparatus was provided with a 2-ring electromagnetic stirrer.

In the earlier part of this investigation the free radical was crystallized from absolute ether and, in order to remove the ether, the substance was heated for 1 hour at 50–55° in a slow stream of dry carbon dioxide under reduced pressure. Even then the material apparently still retained some solvent, which made it impossible to obtain uniform product. It was, therefore, found necessary to use acetone as the solvent for the crystallization instead of ether. The substance was dried for 1 hour in a stream of carbon dioxide under reduced pressure, quickly powdered and made into pellets. The pellets were then weighed in the small glass tube and the apparatus assembled containing a weighed quantity of solvent.

For temperatures below 0°, a Dewar flask was used which was filled with ether and was connected to a suction pump. By the careful adjustment of the vacuum the bath could be maintained at a constant temperature within a degree, as shown by the thermometer in the ether.

In all, 6 solvents were used, ranging in temperature from —17° to +53°; all were very carefully purified by repeated distillation, and the *p*-dichlorobenzene in addition was recrystallized from alcohol. Usually the material was added in 4 lots, giving concentrations ranging from 1 to 5% Each set of determinations represents a separate preparation, the free radical having been allowed to crystallize overnight and used the next day.

The constant K was determined for each individual solvent under exactly the same conditions as prevailed in the molecular-weight determinations of the free radical, using triphenylmethane which had been very carefully purified by several vacuum distillations and recrystallizations. The quantity of free radical (Col. 2) is taken as hexa-arylethane in calculating the molecular weight and the degree of dissociation.

TABLE II

MOLECULAR WEIGHT OF DI-PARA-BENZYLOXY-HEXAPHENYLETHANE

Solvent G.	Solute G.	Conc. %	Depression ° C.	Mol. wt.	Dissociation %
SOLVENT: ETHYLENE CHLOROBROMIDE, F. P., —17° $K=83.4$					
24.70	0.3224	1.30	0.231	471.3	48.1
	0.8181	2.50	0.422	494.6	41.1
	0.9487	3.84	0.610	525.1	32.9
	1.2222	4.95	0.760	543.0	28.5
35.29	0.3455	1.36	0.338	478.7	45.8
	0.6458	2.55	0.434	490.7	42.2
	0.9433	3.73	0.600	518.5	34.6
	1.2510	4.94	0.772	534.4	30.6
SOLVENT: BENZENE, F. P., 4.9° $K=52.0$					
20.98	0.2753	1.31	0.138	494.4	41.2
	0.4852	2.31	0.232	518.4	34.6
	0.6949	3.31	0.321	536.5	30.1
	0.9513	4.53	0.428	550.9	26.7
21.15	0.2472	1.17	0.124	490.2	42.4
	0.4381	2.07	0.207	515.4	35.4
	0.6321	2.99	0.396	525.0	32.9
	0.8970	4.24	0.405	544.5	28.2
SOLVENT: NITROBENZENE, F. P., 5.8° $K=71.2$					
19.94	0.2234	1.12	0.155	514.6	35.6
	0.4397	2.20	0.299	525.1	32.9
	0.6212	3.11	0.409	542.3	28.7
	0.8764	4.39	0.570	549.0	27.1
20.12	0.2074	1.03	0.144	509.7	36.9
	0.4388	2.18	0.299	519.3	34.4
	0.6528	3.24	0.423	546.1	27.8
	0.8890	4.42	0.568	553.9	26.0
SOLVENT: ETHYLENE DIBROMIDE, F. P., 9.6° $K=114.9$					
26.04	0.3541	1.36	0.327	477.8	46.1
	0.6467	2.48	0.595	479.6	45.5
	0.9874	3.79	0.867	502.5	38.9
	1.2934	4.97	1.118	510.5	36.7
25.94	0.3347	1.29	0.315	470.7	48.3
	0.6630	2.55	0.607	483.8	44.2
	1.0223	3.94	0.904	500.9	39.3
	1.3000	5.01	1.139	505.6	38.0

SOLVENT: *p*-BROMOTOLUENE, F. P., 27° $K = 83.9$

25.24	0.2957	1.17	0.197	498,9	39.9
	0.6077	2.41	0.390	518.0	34.7
	0.9270	3.67	0.570	540.6	29.1
	1.2253	4.85	0.715	569.6	22.5
24.22	0.3251	1.34	0.224	503.8	38.8
	0.6432	2.65	0.424	525.5	32.8
	0.9676	3.99	0.607	552.2	26.4
	1.2499	5.16	0.779	555.8	25.6

SOLVENT: *p*-DICHLOROBENZENE, F. P., 53° $K = 75.4$

25.61	0.3498	1.36	0.230	447.8	55.9
	0.6467	2.52	0.420	453.3	54.0
	0.9518	3.72	0.605	463.2	50.7
	1.2853	5.02	0.801	472.4	47.7
26.24	0.3217	1.22	0.210	440.2	58.5
	0.6432	2.45	0.403	458.6	52.2
	0.9182	3.50	0.569	463.7	50.5
	1.1871	4.52	0.730	467.3	49.3

p-Methoxy-triphenylmethyl

p-Methoxy-triphenyl Carbinol, $(CH_3O.C_6H_4).(C_6H_5)_2COH$.—This carbinol has previously been prepared by the action of phenylmagnesium bromide upon the methyl ester of *p*-anisic acid[14] and also by heating *p*-hydroxy-triphenyl carbinol with methyl iodide in the presence of sodium hydroxide in sealed tubes, using alcohol as a solvent.[15] However, a superior method, both with respect to yields and cheapness of materials, is that based on the action of dimethyl sulfate on an alkaline solution of *p*-hydroxy-triphenyl carbinol. To 10 g. (1.6 mole) of sodium hydroxide dissolved in 160 cc. of water was added 44 g. (1 mole) of *p*-hydroxy-triphenyl carbinol, and the mixture was warmed until a clear solution was obtained; 26.5 g. (1.3 mole) of dimethyl sulfate was added through a dropping funnel during the course of an hour, while the reaction mixture was constantly stirred and the stirring continued until the product which separated had solidified. The benzene solution of the methylated product was stirred with 5% sodium hydroxide solution to remove any occluded hydroxy-triphenyl carbinol and, after several washings with water, was dried over calcium chloride. The benzene was completely removed under reduced pressure, the viscous residue dissolved in 10 cc. of dry ether, and enough petroleum ether added to cause turbidity. When the solution was seeded, pure *p*-methoxy-triphenyl carbinol separated out, the yields ranging from 80 to 85%. After one recrystallization from equal parts of dry ether and petroleum ether (80–100°) the carbinol was obtained in white crystals which melted at 82°.

Analyses. Calc. for $C_{20}H_{18}O_2$: C, 82.76; H, 6.21. Found: C, 82.70; H, 6.30.

p-Methoxy-triphenylmethyl Chloride, $(CH_3OC_6H_4).(C_6H_5)_2CCl$.[16]—An ethereal solution of the carbinol was warmed with 2 to 3 times the calculated quantity of acetyl chloride; as the solution cooled, methoxy-triphenylmethyl chloride crystallized practically quantitatively. When the chloride was washed thoroughly upon the filter with ether and petroleum ether, and dried in a vacuum desiccator over sodalime, it melted at 122° and needed no further recrystallization. It may, however, be readily recrystallized from dry ether, in which it is quite insoluble in the cold.

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[14] Baeyer and Villiger, *Ber.*, **35**, 3027 (1902).

[15] Bistrzycki and Herbst, *ibid.*, **36**, 2334 (1903).

[16] Ref. 15, p. 2335. Baeyer and Villiger, *ibid.*, **36**, 2789 (1903).

Analysis. Calc. for $C_{20}H_{17}OCl$: Cl, 1150. Found: 11.42.

Methoxy-triphenylmethyl chloride gives crystalline red double salts with ferric chloride, zinc chloride, mercuric chloride or stannic chloride.

Analyses. Calc. for $C_{20}H_{17}OCl.FeCl_3$: Cl, 30.13. Found: 30.65. Calc. for $C_{20}H_{17}OCl.ZnCl_2$: Cl, 23.90. Found: 23.94.

***p*-Methoxy-triphenylmethyl Bromide.**—The bromide was prepared by exactly the same procedure as that used for the chloride, with the substitution of acetyl bromide for chloride. The bromide is best recrystallized from absolute ether; m. p., 143°.

Analysis. Calc. for $C_{20}H_{17}OBr$: Br, 22.64. Found: 22.87.

Preparation of *p*-Methoxy-triphenylmethyl.—The procedure used for the preparation of *p*-benzyloxy-triphenylmethyl served also for the preparation of this free radical; 4 g. of *p*-methoxy-triphenylmethyl chloride (in benzene) and 4 g. of molecular silver were shaken together for 6 hours. The orange-colored solution of the free radical was transferred to the usual form of apparatus and the benzene completely removed at 50–55°. The oily residue of the crude material, left upon evaporation of the benzene, was dissolved in 5 cc. of warm absolute ether, and the free radical allowed to crystallize. Four g. of the chloride usually gave about 2 g. of *p*-methoxy-triphenylmethyl. In an atmosphere of carbon dioxide, the substance begins to darken at 125° and melts at 145–150°, but not sharply. The free radical may also be crystallized from acetone, in which it is slightly more soluble than in ether.

Analyses. Calc. for $C_{20}H_{17}O$: C, 87.92; H, 6.23. Found: C, 88.14; H, 6.29.

Reaction of *p*-Methoxy-triphenylmethyl with Oxygen.—The free radical when perfectly dry may be exposed to the air without suffering appreciable oxidation. Its solutions, however, on exposure to the air decolorize rapidly, with the formation of the peroxide. The amount of oxygen which is taken up was measured quantitatively, using the same procedure as described for benzyloxy-triphenylmethyl.

TABLE III

ABSORPTION OF OXYGEN BY METHOXY-TRIPHENYLMETHYL

Wt. of Sample		Oxygen Absorbed	
Chloride G.	Free radical G.	Cc. (N. T. P.)	% of calc.
1	....	36.67	101.0
1	....	36.85	101.5
1	....	36.57	100.8
1	....	36.58	100.8
..	0.8000	33.04	100.6
..	1.1574	48.08	101.2

Although the quantity of oxygen absorbed is very nearly that calculated yet the amount of crystalline peroxide is, as in all other instances, less than this. With four separate samples of from 1 to 1.3 g. of the free radical, the yields were from 79.2 to 82.0% of the calculated amount.

The peroxide is quite soluble in benzene, chloroform or carbon tetrachloride, and practically insoluble in ether or petroleum ether. It can best be recrystallized by solution in hot benzene and the addition of an equal volume of ether. It crystallizes in fine white crystals; m. p., 157°.

Analyses. Calc. for $C_{40}H_{34}O_4$: C, 83.05; H, 5.88. Found: C, 83.36; H, 6.02.

Reaction of *p*-Methoxy-triphenylmethyl with Iodine.—The quantity of iodine absorbed was determined as described under benzyloxy-triphenylmethyl. The equilibrium was established when about 58% of the calculated quantity of iodine had been added. With three separate samples the yields were from 57 to 59.7%.

The presence of *p*-methoxy-triphenylmethyl iodide was proved by the formation of methoxy-triphenylmethyl anilide upon the addition of aniline to the above solution. The anilide was identical with that formed from the carbinol chloride and aniline according to Baeyer and Villiger.[17]

Action of Hydrogen Chloride on *p*-Methoxy-triphenylmethyl.—As in the case of benzyloxy-triphenylmethyl, when hydrogen chloride is allowed to react on a benzene solution of the free radical, the color disappears and the solution then fails to absorb oxygen. The amount of chloride formed according to Equation 4 was determined as previously described, and was found to be, with 2 separate samples, 80.5 and 88.9%, respectively.

Effect of Light on *p*-Methoxy-triphenylmethyl.—A benzene solution exposed to direct sunlight became decolorized after several hours. The resulting solution, containing now a biphenylene triarylmethyl, absorbed oxygen slowly with the formation of the corresponding peroxide. The amount of oxygen absorbed was determined quantitatively and was found to be practically $^1/_3$ of the amount calculated for the quantity of the original free radical used. This behavior is exactly that which would be expected from Equation 4, for the amount of 9-phenyl-3-methoxy-fluoryl (X).

TABLE IV

OXYGEN ABSORPTION BY 9-PHENYL-3-METHOXY-FLUORYL

Methyl-triphenylmethyl	Oxygen Absorbed		
G.	Cc. (N. T. P.)	Calc. for amount of original rad. %	Calc. for amount of compound V %
1.0000	13.8	33.6	100.8
1.0000	13.5	32.9	98.7
0.8929	13.0	35.5	106.5

The benzene solution was concentrated, and upon addition of petroleum ether the fine white crystalline peroxide separated, and after several recrystallizations from benzene and petroleum ether melted with decomposition at 200°, and proved to be 9-phenyl-3-methoxy-fluoryl peroxide.

Analyses. Calc. for $C_{40}H_{30}O_4$: C, 83.62; H, 5.23. Found: C, 83.86; H, 5.24.

***p*-Anisyl-biphenylenemethyl Peroxide (VI).**—*p*-Anisyl-biphenylene carbinol was made according to Schlenk and Mair,[5] by the action of *p*-methoxy-phenylmagnesium iodide on fluorenone. Although Schlenk obtained this carbinol only as an oil, it may be crystallized from petroleum ether as small transparent plates which melt at 87–88°.

Analyses. Calc. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 83.23; H, 5.46.

The chloride was prepared from the carbinol by using acetyl chloride rather than hydrogen chloride. It melted at 149°, as described. By the action of molecular silver, the chloride was converted into the corresponding free radical, and the latter on exposure

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[17] Baeyer and Villiger, *Ber.*, **37**, 608 (1904).

to air gave the peroxide; this was found to melt at 192°, as given by Schlenk and Mair. This peroxide differed from the peroxide isolated in the light experiment of our free radical, in respect to melting point, solubility in benzene, and color produced upon addition of sulfuric acid.

9-Phenyl-3-methoxy-fluoryl (X) and the Peroxide (XI).—3-Methoxy-fluorenone was made from anthranilic acid according to Ullmann and Bleir,[9] and was converted into the carbinol (IX) by the action of phenylmagnesium bromide. After several recrystallizations from benzene and petroleum ether, the carbinol melted at 84°. On treatment in benzene with hydrogen chloride, it gave the carbinol chloride; m. p., 119°.

Analysis. Calc. for $C_{20}H_{15}OCl$: Cl, 11.57. Found: 11.20.

The chloride when dissolved in bromobenzene, and shaken with molecular silver gave solutions of the free radical. These were purple; the color deepened markedly with slight increase of temperature and, with decrease, returned again to its former intensity.[18] The combination with oxygen is somewhat slow; 0.3883 g. of the chloride gave a solution of the radical which absorbed in several hours 14.6 cc. of oxygen (N. T. P.), which is equal to 102.8% of the calculated amount.

The *peroxide* was prepared by passing air through a benzene solution of the free radical. Upon addition of petroleum ether to the concentrated benzene solution, the peroxide crystallized. After several recrystallizations it melted with decomposition at 200° and proved in every respect identical with the peroxide obtained by the photochemical reaction.

Non-formation of Additive Compounds by *p*-Methoxy-triphenylmethyl.—The free radical was crystallized from the following solvents in order to determine whether it formed additive compounds: Ethers: ethyl ether, butylmethyl ether, butylethyl ether; Esters: ethyl acetate, propyl acetate; Ketones: acetone, methylethyl ketone, diethyl ketone; Carbon disulfide. Using the same procedure as described under *p*-benzyloxy-triphenylmethyl, it was found that the free radical formed no additive compounds, quite in contrast to triphenylmethyl.

Degree of Dissociation of Di-*p*-Methoxy-hexaphenylethane.—The molecular-weight determinations were made under exactly the same condi-

TABLE V

MOLECULAR WEIGHT OF DI-PARA-METHOXY-HEXAPHENYLETHANE

Solvent G.	Solute G.	Conc. %	Depression ° C.	Mol. wt.	Dissociation %
SOLVENT: ETHYLENE CHLOROBROMIDE, F. P., —17° $K=85.4$					
25.32	0.2524	0.99	0.213	399.8	36.6
	0.5417	2.14	0.442	413.4	32.0
	0.8393	3.31	0.669	433.1	39.0
	1.1435	4.51	0.906	435.7	28.2
25.22	0.2588	1.02	0.222	394.7	38.3
	0.5675	2.25	0.465	413.3	32.1
	0.8542	3.39	0.688	420.4	29.8
	1.1296	4.48	0.896	426.9	27.9

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[18] Gomberg and Cone, *Ber.*, **39**, 2968 (1906).

SOLVENT: BENZENE, F. P., 4.6° $K=53.0$

20.31	0.2996	1.47	0.182	429.6	27.1
	0.6596	3.25	0.386	445.9	22.4
	0.9559	4.71	0.558	447.0	22.1
	1.2743	6.27	0.744	447.0	22.1
20.55	0.3220	1.56	0.189	439.4	24.2
	0.5934	2.89	0.347	441.0	23.8
	0.9875	4.51	0.541	442.1	23.5
	1.2363	6.01	0.721	442.2	23.4

SOLVENT: NITROBENZENE, F. P., 5.8° $K=70.2$

20.07	0.2654	1.32	0.222	418.2	30.5
	0.5782	2.88	0.480	421.4	29.5
	0.9011	4.49	0.742	424.8	28.5
	1.1824	5.89	0.980	422.0	29.4
20.03	0.2942	1.47	0.246	419.1	30.3
	0.5979	2.98	0.500	419.1	30.3
	0.9124	4.55	0.760	420.8	29.7
	1.2084	6.03	1.010	419.3	30.2

SOLVENT: ETHYLENE DIBROMIDE, F. P., 9.8° $K=116.1$

24.99	0.2306	0.92	0.278	385.4	41.7
	0.5383	2.15	0.617	405.3	34.7
	0.8216	3.28	0.936	407.8	33.9
25.41	0.2834	1.11	0.329	393.6	38.7
	0.5741	2.26	0.644	407.3	34.0
	0.8961	3.53	1.004	407.8	33.9

SOLVENT: *p*-BROMOTOLUENE, F. P., 26.6° $K=84.7$

24.96	0.3175	1.27	0.259	416.0	31.2
	0.6343	2.54	0.516	417.1	30.9
	0.9067	3.63	0.734	419.2	30.2
	1.2426	4.98	1.006	419.1	30.3
25.11	0.3032	1.21	0.246	415.7	31.3
	0.5529	2.20	0.445	419.1	30.3
	0.8654	3.44	0.695	420.0	30.0
	1.1944	4.75	0.961	419.2	30.2

SOLVENT: *p*-DICHLOROBENZENE, F. P., 53° $K=73.5$

25.06	0.2730	1.09	0.215	372.4	46.6
	0.4969	1.98	0.375	388.6	40.5
	0.7676	3.06	0.568	396.4	37.7
	1.0146	4.05	0.749	397.3	37.4
25.25	0.3223	1.27	0.243	386.1	41.4
	0.6040	2.39	0.443	396.9	37.6
	0.9124	3.61	0.660	402.4	35.7
	1.2134	4.80	0.864	408.8	36.0

tions as described for the benzyloxy radical. The substance was crystallized from absolute ether, and each set of determinations represents a separate preparation. The quantity of the free radical used in these experiments (Col. 2) is designated as the hexa-aryl ethane.

Summary

1. A number of derivatives of *p*-benzyloxy- and *p*-methoxy-triphenyl carbinol have been synthesized.
2. The 2 free radicals, *p*-benzyloxy- and *p*-methoxy-triphenylmethyl, have been prepared. A study has been made of the important reactions of these 2 radicals toward oxygen, iodine, hydrogen chloride and light, and of their capacity to form additive compounds.
3. The degree of dissociation of the 2 hexa-arylethanes into the corresponding triarylmethyls has been determined in 6 solvents over a range of temperature from —17° to +53°, and in concentrations from 1 to 6%. The degree of dissociation was found to be influenced by concentration of the free radical, temperature, and the nature of the solvent. The benzyloxy compound dissociates to the extent of from 26 to 56%, the methoxy, to the extent of from 22 to 42%.

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Ann Arbor, Michigan

[Contribution from the Chemical Laboratory of Barnard College]

THE ISOMERIC ESTERS OF BENZOYLACRYLIC ACID

By Grace Potter Rice

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Up to the time of this investigation the only ester of benzoylacrylic acid known was the yellow methyl ester described by Kozniewski and Marklewski[1] in their paper on this acid and its homologs.

In view of the many examples[2] of the transformation of unsaturated organic compounds into their geometrical isomers on exposure to light, it seemed of interest to study the action of light on this ester. Of the substances investigated, that which bears the closest resemblance to the esters of benzoylacrylic acid is dibenzoylethylene, $C_6H_5COCH{:}CHCOC_6H_5$; $C_6H_5COCH{:}CHCOOR$. Paal and Schulze[3] showed that the yellow *trans* form of this substance is changed completely in the light into the colorless *cis* form.

In the present investigation it has been found that the yellow methyl and ethyl esters of benzoylacrylic acid are transformed on exposure to sunlight into the corresponding stereo-isomeric colorless esters, which have higher melting points than the corresponding yellow substances. The reverse transformation of the colorless into the

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[1] Kozniewski and Marklewski, *Bull. Acad. Sci. Cracow*, **81** (1906).

[2] (a) Stoermer and Simon, *Ann.*, **342**, 1 (1905). (b) Stoermer and Friderici, *Ber.*, **41**, 324 (1908). (c) Stoermer, *ibid.*, **42**, 4865 (1909); **44**, 637 (1911). (d) Stoermer and Stockmann, *ibid.*, **47**, 1786, 1793 (1914). (e) Stoermer and Ladewig, *ibid.*, **47**, 1795 (1914). (f) Stoermer and Prigge, *Ann.*, **409**, 20 (1915). (g) Stoermer and Voht, *ibid.*, **409**, 36 (1915).

[3] Paal and Schulze, *ibid.*, **35**, 168 (1902).