A New Coverglass Support.—A convenient coverglass support, which is also adapted to many other uses, is made as follows:

Three glass rods of equal size and length are held firmly in a bundle while being melted together at one end in a small blowpipe flame. This union is then drawn to a point by touching with a piece of glass, and the rods immediately bent apart at equal angles and to any depth desired. The now central joint should be reheated and annealed, but this does not require a temperature sufficient to deform the triangle. The ends are bent downward at a convenient angle. ROSS ALLEN BAKER.

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TRIPHENYLMETHYL. XXII. ETHERS OR OXIDES IN THE TRIPHENYLMETHANE SERIES.[1]

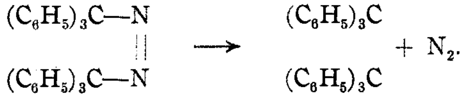
BY M. GOMBERG.

Received December 28, 1912.

It is now generally accepted that the compounds of the supposedly hexaarylethane type tend to dissociate while in solution into two free triarylmethyl radicles, this spontaneous dissociation being complete in some individual instances. Moreover, accumulated experience shows that such a tendency towards dissociation with the production of triarylmethyl radicles exists even in compounds where the two triarylmethyl groups are not linked directly to each other, but through the medium of some other simple group. Thus Anschütz[2] found that the triphenylmethyl ester of triphenylacetic acid loses carbon dioxide on heating to its melting point, and that the resulting product is not hexaphenylethane but triphenylmethyl, or rather the decomposition products thereof:

$$(C_6H_5)_3C.CO.OC(C_6H_5)_3 \longrightarrow CO_2 + (C_6H_5)_3C + C(C_6H_5)_3.$$

Wieland[3] attempted to prepare azotriphenylmethane by the oxidation of the fairly stable corresponding hydrazo derivative. While triphenylmethyl-azo-benzene was found by Gomberg[4] to decompose at 100°, Wieland's azo-body was found by him to break down spontaneously even at 0° into triphenylmethyl and nitrogen:



$$\begin{array}{l} (C_6H_5)_3C\text{—}N \\ \qquad\qquad\ \ \| \\ (C_6H_5)_3C\text{—}N \end{array} \longrightarrow \begin{array}{l} (C_6H_5)_3C \\ \\ (C_6H_5)_3C \end{array} + N_2.$$

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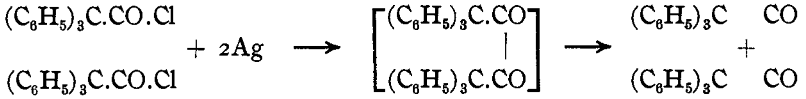
[1] This communication constitutes the larger part of a paper read at the Eighth International Congress of Applied Chemistry, New York, September, 1912. The remaining portion not published at this time dealt with the unsuccessful "Attempts to Prepare *p*-Hydroxytriphenylmethyl Oxide."

[2] *Ann.*, 359, 196 (1908).

[3] *Ber.*, 42, 3020 (1909).

[4] *Ibid.*, 30, 2043 (1897).

Schmidlin[1] found that when triphenylmethylacetyl chloride is treated with molecular silver, there is formed not an orthodiketo derivative, but triphenylmethyl and carbon monoxide:

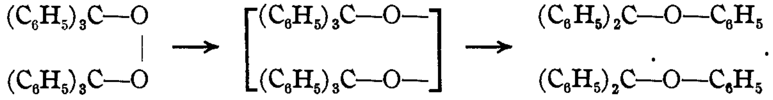


$$\begin{array}{l}(C_6H_5)_3C.CO.Cl\\ \\(C_6H_5)_3C.CO.Cl\end{array} + 2Ag \longrightarrow \left[\begin{array}{c}(C_6H_5)_3C.CO\\ |\\(C_6H_5)_3C.CO\end{array}\right] \longrightarrow \begin{array}{cc}(C_6H_5)_3C & CO\\ & +\\ (C_6H_5)_3C & CO\end{array}$$

Gomberg[2] found that triphenylmethyl does not unite with carbon monoxide. Schlenk[3] allowed nickel carbonyl to act upon triphenylchloromethane, but instead of the carbonyl derivative he also obtained triphenylmethyl:

$$(C_6H_5)_3C.Cl + Ni(CO)_4 \longrightarrow [(C_6H_5)_3C.CO.C(C_6H_5)_3] \longrightarrow 2(C_6H_5)_3C + CO.$$

The triarylmethyls, on exposure to air, take up oxygen and form peroxides which are not explosive, are fairly stable but decompose to some extent on recrystallization as was shown by Gomberg in the first paper on triphenylmethyl. Wieland,[4] in studying this decomposition at a somewhat higher temperature, 140°, came to the conclusion that it is due again to the tendency of the peroxide towards dissociation, whereby a new triarylmethyl is formed:



$$\begin{array}{l}(C_6H_5)_3C—O\\ \quad\quad\quad\ |\\(C_6H_5)_3C—O\end{array} \longrightarrow \left[\begin{array}{l}(C_6H_5)_3C—O—\\ \\(C_6H_5)_3C—O—\end{array}\right] \longrightarrow \begin{array}{l}(C_6H_5)_2C—O—C_6H_5\\ \\(C_6H_5)_2\dot{C}—O—C_6H_5\end{array}.$$

In view of all that has been said above, the question as to the existence of triarylmethyl oxides assumes considerable interest and importance, for such oxides are nearer to hexaarylethanes in structure than any of the readily decomposable compounds mentioned above. In such oxides the two triarylmethyl groups would be separated from each other only by one oxygen atom. To what extent would such ethers prove stable? How far would they resemble the hexaarylethanes?

It is well known that the diarylcarbinols give rise quite readily to the corresponding oxides or ethers. Benzhydrol-ether,[5] fluorenol-ether,[6] xanthydrol-ether,[7] dinaphthydrol-ether,[8] are produced from their alcohols when the latter are heated alone or in the presence of some dehydrating agent. Indeed, a few oxides of the triarylcarbinols have also been re-

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[1] *Ber.*, 43, 1140 (1910).

[2] *Ibid.*, 33, 3154 (1900).

[3] *Ibid.*, 44, 1176 (1911).

[4] *Ibid.*, 44, 2550 (1911).

[5] Linnemann, *Ann.*, 133, 6 (1865).

[6] Barbier, *Ber.*, 8, 829 (1875).

[7] Meyer, *Ibid.*, 26, 1276 (1893).

[8] Fosse, *Ann. chim. phys.*, 2, 279 (1904).

ported in the literature, by Werner,[1] Bistrzycki,[2] Kliegel,[3] Decker,[4] etc. But an examination of the methods employed for their preparation and the properties ascribed to these supposed oxides, as well as the complete lack of data as regards their molecular weights, made it appear to the author very doubtful whether the compounds so designated and described were in reality triarylmethyl oxides. The results presented in this paper show that, in most instances, they are not, and a general reaction is here described whereby such oxides can be readily obtained.

As regards their general properties, these oxides are far more stable than might have been anticipated. They are as stable as the peroxides, if not more so. The oxides are unaffected by exposure to air, or by heating to temperatures below their melting points, which usually lie above 200°. Water and dilute alkalies, even at 100°, do not decompose them. They are hydrolyzed on boiling with dilute acids, by alcohol, by acetic acid, acetyl chloride, and by dry hydrochloric acid in benzene. But in all these decompositions, the hydrolysis results in the formation of the corresponding carbinols, and in no case has the occurrence of the free triarylmethyl radicles been observed. The oxides decompose when heated to the temperature of their melting point, but whether in this manner of decomposition the oxides, like the peroxides, give rise to triarylmethyls, has not yet been established.

Action of Silver Oxide upon Triphenylchloromethane.—In looking for a general reaction for the synthesis of the oxides under consideration one would naturally think first of the action of silver oxide upon triarylmethylhalides,

$$2(C_6H_5)_3C.Cl + Ag_2O = (C_6H_5)_3C.O.C(C_6H_5)_3 + 2AgCl.$$

Triphenylchloromethane is indeed readily acted on by silver oxide in various inert organic solvents, as benzene, ether, etc. The reaction, however, does not lead to the formation of the ether. There is produced some compound of marked susceptibility towards acids, alkalies, and other reagents. With the exception of a small amount of diphenylquinomethane,[5] $(C_6H_5)_2C : C_6H_4 : O$, all the other products isolated are amorphous and apparently difficult to purify. Nor can it be said with certainty at present whether the diphenyl-quinomethane itself is the primary result of the action of silver oxide upon the chloro compound, or is formed rather as the result of the action of the air upon the sensitiv compound mentioned above. Later, when the triphenylmethyl ether was obtained by the method described below, it was possible to prove

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[1] *Ber.*, 34, 3305 (1901).

[2] *Ibid.*, 34, 3073 (1901).

[3] *Ibid.*, 38, 291 (1905).

[4] *J. prakt. Chem.*, 84, 232 (1911).

[5] Bistrzycki and Herbst, *Ber.*, 36, 2333 (1903).

that silver oxide itself is totally without effect upon the ether. A mixture of silver oxide and the ether in benzene was shaken on the machine for three months, but the ether was recovered entirely unaltered. Consequently the formation of diphenyl-quinomethane and the other products, when silver oxide acts upon triphenylchloromethane, cannot be due to the oxidizing effect of silver oxide upon the ether, assuming the latter to be the first product of the reaction. We are therefore forced to infer that the reaction with silver oxide starts and proceeds along an entirely different line from what would be expected of such a reaction. Awaiting further experimental evidence the process may be surmized as proceeding something like this:

$$(C_6H_5)_3C.Cl + Ag_2O = (C_6H_5)_3\dot{C} + AgCl + Ag + O,$$

and the triphenylmethyl itself is then decomposed by the excess of silver oxide or by the liberated oxygen.

The statement by the author[1] some years ago, that silver oxide and triphenylchloromethane furnish the ether, must be considered therefore as incorrect.

Action of Zinc Oxide.—Freshly ignited zinc oxide and triphenylchloromethane were sealed with absolute ether in tubes and shaken on the machine at room temperature for varying lengths of time, from a few days to several months. The solutions as a rule soon turned dark, and a black viscous mass separated. Occasionally, when the temperature happened to be low and the ether unusually dry, the separation of the viscous mass was lacking. On opening the tubes the ether was distilled off and the residue extracted with dry benzene, leaving all the zinc chloride behind. The benzene solution was found to contain principally two products, in about equal proportions; namely, triphenylmethane and triphenylethoxymethane, with an occasional admixture of a small amount of triphenylcarbinol. Thus, while silver oxide acts apparently as an oxidizing agent, the results with zinc chloride point to a reducing action. Here, again, it was proven that whatever the products of the reaction be, they do not result from the subsequent action of the zinc oxide or the zinc chloride upon the triphenylmethyl oxide, if we should assume for the moment the latter to be the primary result of the action of zinc oxide upon triphenylchloromethane. Triphenylmethyl oxide remains entirely unaltered even after ten weeks' action of zinc oxide upon it. Zinc chloride, too, has but slight action upon triphenylmethyl oxide under the conditions of the above mentioned experiments, and decomposes it only after prolonged action.

In looking for a possible explanation to account for this abnormal reducing behavior of zinc oxide, the effect upon each other of all the reagents employed and produced in the experiment was tested. It was

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[1] *Am. Chem. J.*, **29**, 371 (1903).

found that *triphenylchloromethane itself, in absolute or in ordinary ether, is reduced by zinc chloride to triphenylmethane almost quantitatively.* On the basis of this fact the production of equal amounts of triphenylmethane and triphenylethoxymethane, when zinc oxide acts upon triphenylchloromethane, becomes intelligible. Just as soon as the zinc oxide begins to react with the chloro compound, zinc chloride, or something analogous to it (second equation), is formed and the latter then acts at once upon a second molecule of triphenylchloromethane, reducing it to triphenylmethane:

$$(C_6H_5)_3C.Cl + ZnO = (C_6H_5)_3C-O-Zn-Cl$$
$$(C_6H_5)_3C-O-Zn-Cl + (C_2H_5)_2O = (C_6H_5)_3C-O-C_2H_5 + Cl-Zn-OC_2H_5$$
$$(C_6H_5)_3C.Cl + Cl-Zn-OC_2H_5 = (C_6H_5)_3C.H + ZnCl_2 + C_2H_4O.$$

The presence of acetaldehyde, as indicated in the last equation, was often noticed, and the black viscous mass, formed as a by-product in this reaction, is not unlikely the polymerization product of the aldehyde.[1]

The effect of zinc oxide upon triphenylchloromethane in benzene and in chloroform was also tried. It was found to be without any appreciable action even after several months' shaking on the machine.

The quantitative reduction of triphenylchloromethane by zinc chloride and ethyl ether to triphenylmethane furnishes a good and rapid method for the preparation of this hydrocarbon. This is another illustration of how readily this hydrocarbon is formed. Gomberg has shown that triphenylcarbinol and tritolylcarbinol are reduced at room temperature by hydriodic acid to the corresponding hydrocarbons.[2] Chichibabin[3] noticed that dilute hydriodic acid reduces at low temperatures various triarylcarbinols to the corresponding hydrocarbons. Kaufmann and Pannwitz[4] showed that the reducing action of alcohol and hydrochloric acid is quite a general reaction for reducing triarylcarbinols to hydrocarbons. And recently, Guyot and Kovache[5] described a method for reducing the carbinols to the hydrocarbons by means of formic acid. To what extent the combined effect of zinc chloride and ether as a reducing agent is generally applicable to triarylcarbinol halides, will be further investigated.

Action of the Oxides of Cadmium, Lead, Nickel, Cobalt, Magnesium.—The triphenylchloromethane was dissolved in dry benzene, the powdered

[1] The results here described furnish the explanation why, in the reaction of metallic zinc upon triphenylchloromethane, there is produced, under certain circumstances, triphenylmethane. *Am. Chem. J.*, 25, 330 (1901).

[2] *Ber.*, 35, 1834, 1836 (1902); THIS JOURNAL, 26, 1520 (1904).

[3] *Ber.*, 44, 441 (1911). Chichibabin probably overlooked the fact that this reaction has been applied by the writer as mentioned above.

[4] *Ber.*, 45, 766 (1912).

[5] *Compt. rend.*, 154, 121 (1912).

dry metallic oxide added, some glass beads put in to aid in getting fine division of the oxide, and the tubes were shaken for from one to three months at room temperature. The oxides of all the above metals were found to be practically without action upon the chloro compound. In the case of lead oxide a small amount of triphenylmethyl peroxide was obtained. Its formation may have been caused by the presence of some lead peroxide.

Action of Mercuric Oxide.—Preliminary experiments showed that the same products result from the action of both mercurous and mercuric oxide upon triphenylchloromethane, namely, the desired triphenylmethyl oxide. Mercuric oxide, for obvious reasons, was used exclusively in all subsequent work. By means of this oxide various triaryl oxides can be obtained with ease and in good yield. The triarylchloromethane is dissolved in an absolutely dry solvent, preferably benzene, although ether, carbon disulfide or even chloroform can be employed. To this solution about two or three times the required amount of well dried mercuric oxide is added. The mixture, most carefully protected against the moisture of the air, may be heated on the water-bath for a few hours, or, still better, sealed in a large test tube and placed on the shaking machine for some hours or days at room temperature. When it is deemed that the chloro compound has been all converted into the triarylmethyl oxide the benzene solution is decanted, or siphoned off with a pipet from the solid metallic oxide. Filtration at this stage is inadvisable, for the moment the benzene solution comes in contact with the air a voluminous, gelatinous precipitate of colloidal mercuric oxide is formed. The decanted solution is therefore at once placed in a separating funnel and treated with very dilute hydrochloric acid which dissolves the gelatinous oxide and, at the same time, the water extracts the mercuric chloride from the benzene. Excess of acid or prolonged contact with acidulated water should be avoided, as the triarylmethyl ethers are hydrolyzed by it. After thorough drying over calcium chloride the benzene solution is completely evaporated and the crystallin residue washed with ordinary ethyl ether, in order to remove any triarylcarbinol which may possibly be present. The carbinols, as a rule, are soluble in ether, while the triaryl oxides are only slightly so. The oxides thus obtained are usually quite pure, and they can be further purified, if necessary, by recrystallization from a mixture of hot benzene and ether. Ether containing alcohol should be avoided, for the latter decomposes the oxides.

In the following are described a few ethers which have been prepared by the above method.

Triphenylmethyl Oxide.—The yield of this ether varies somewhat with the nature of the solvent employed in its preparation, but more so with the conditions of working up the reaction product. It has been obtained in yields varying from 50 to 85% of the calculated amount. It is a white, beautifully crystallin compound, not unlike the carbinol. When not quite pure it melts at about 195–210° with decomposition, but even when very pure the melting point is seldom sharp. It usually begins to melt at the top, the softening and melting then proceeds downwards, often through a range of 10°, and it finally melts at 235–237°, which is probably the correct melting point. The same general behavior characterizes all the ethers so far prepared.

Calculated for $C_{38}H_{30}O$: C, 90.80; H, 6.02.
Found: C, 90.85; H, 6.20.

Molecular weight determination in naphthalene as a solvent.

I. 0.4780 gram substance in 12.19 grams naphthalene caused a depression of 0.56° in the freezing point of the solvent.

II. 0.760 gram substance in 12.19 grams naphthalene caused a depression of 0.885° in the freezing point of the solvent.

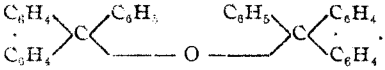
Calculated for $C_{38}H_{30}O$: Mol. wt., 502.2.
Found: I, 491; II, 495.

Solubility.—The ether is soluble in about 25 parts of benzene at room temperature and in about 5 parts of boiling benzene; about 1 gram in 11 cc. of carbon disulfide, and 1 gram in 325 cc. of ordinary ether. It is very little soluble in petroleum ether, and is decomposed by alcohol and by acetic acid.

Hydrolysis of the Ether.—(*a*) By *water* alone, or by water containing about 5% sodium hydroxide, the ether seems to be unaffected even when dissolved in benzene and shaken for several weeks, or when boiled for some hours on the water-bath. (*b*) But towards *acids* it is quite susceptible. 1 gram of the ether in 10 cc. of benzene was boiled with 100 cc. of 10% sulfuric acid for 2 hours and was found to be completely hydrolyzed to triphenylcarbinol. Concentrated sulfuric acid dissolves it readily and converts it at the same time into the carbinol. (*c*) *Acetic acid* also hydrolyzes the ether readily. 1 gram of the ether was boiled with 20 cc. of 90% acetic acid containing 2–3 drops of sulfuric acid for a few minutes. On the addition of water pure triphenylcarbinol precipitated out. (*d*) Two grams of the ether were suspended in 50 cc. of ordinary *alcohol* containing a few drops of acid. After two hours' boiling all went into solution. It was hydrolyzed to the carbinol.

Action of Hydrochloric Acid and Acetyl Chloride.—When suspended or dissolved in benzene, to which some solid calcium chloride has been added, and treated with dry hydrochloric acid gas, it is converted quantitatively, like triphenylcarbinol, into triphenylchloromethane. By acetyl chloride the ether is changed readily into triphenylchloromethane, and by the action of acetyl bromide the carbinol bromide is obtained.

Diphenylene-phenyl-methyl Oxide.—



$$\begin{matrix}C_6H_4\\ \cdot\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_5 & & C_6H_5\\ & -O- & \end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\\ \cdot\\ C_6H_4\end{matrix}.$$

A compound of the above constitution was described by Kliegel,[1] who

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[1] *Ber.*, 28, 201 (1895).

claims to have obtained it by the action of acetic and sulfuric acids upon the carbinol. The molecular weight was not determined and the melting point given is 100° higher than that of the true oxide which we obtained by the mercuric oxide method. Moreover, the solubilities as given by Kliegel are different from those we find for our oxide. We are forced to conclude that Kliegel's compound, while having the same composition as the oxide, is not the oxide.

We obtained the oxide, using benzene as a solvent, with a yield of 95% of the theory, and recrystallized it from a mixture of benzene and petroleum ether. The colorless, white crystals melt at 232–3°, accompanied by the same phenomena as described for the triphenylmethyl ether.

Calculated for $C_{38}H_{28}O$: C, 91.16; H, 5.64.
Found: C, 90.87; H, 5.23.

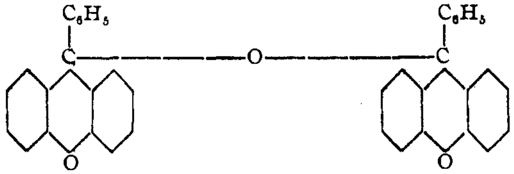
0.7812 gram substance in 12.1 grams naphthalene caused a depression of 0.934° in the freezing point of the solvent.

Calculated for $C_{38}H_{28}O$: Mol. wt., 500.2. Found: 477.

This oxide is more soluble in the organic solvents than the triphenylmethyl oxide. It is soluble in about 6.5 parts of benzene and in about 100 parts of ether. It is unaffected by water, dilute alkalies, or even dilute acids in the cold, but is hydrolyzed to the corresponding carbinol as the triphenylmethyl ether is, by boiling with acetic acid. On boiling with alcohol, with the addition of a drop or two of sulfuric acid, the ethoxy compound of the carbinol is formed.

With *acetyl chloride*, on warming, it gives the carbinol chloride quantitatively. The latter was easily obtained pure on the addition of petroleum ether to the mixture, and was identified by its melting point (79°), and, furthermore, by its conversion into the characteristic peroxide by treating with metallic silver and subsequently exposing the triarylmethyl to the air. The peroxide melted exactly at 193°, as given by Gomberg and Cone,[1] and not at 204°, as recently claimed by Schmidlin.[2]

Phenyl-xanthenol Oxide.—



The phenylxanthenol chloride requisit for the preparation of the oxide was prepared from its colored hydrochloric acid addition compound according to the method of Gomberg and Cone.[3] The yield of the oxide,

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[1] *Ber.*, **39**, 2969 (1906); cf. Schlenk, *Ibid.*, **43**, 1755 (1910).

[2] *Ibid.*, **45**, 1348 (1912).

[3] *Ann.*, **370**, 155 (1909).

with benzene as a solvent, was 4.1 grams oxide from 5 grams of the chloride. The oxide retains a slightly yellowish pink color, even after several recrystallizations, and, like the carbinol, turns darker on exposure to laboratory air containing acid fumes. It melts at 250–252°.

Calculated for $C_{38}H_{28}O_3$: C, 85.68; H, 5.30.
Found: C, 85.91; H, 5.12.

0.3950 gram substance in 12 grams naphthalene caused a depression of 0.445° in the freezing point of the solvent.

Calculated for $C_{38}H_{28}O_3$: Mol. wt., 532.2. Found: 510.

The oxide is soluble to the extent of 1 gram substance in 12 cc. of cold, or 5 cc. of hot benzene; 1 gram in 160 cc. ethyl ether. It is hydrolyzed by dilute acids to the carbinol, and is converted by dry hydrochloric acid gas in benzene, or by acetyl chloride, into the quinocarbonium salt, chloride-hydrochloride.[1]

p-Methoxy-triphenylmethyl Oxide.—The *p*-methoxytriphenylcarbinol was prepared by Grignard's reaction from *p*-anisic ester and bromobenzene,[2] and was converted into the carbinol chloride by dry hydrochloric acid gas in benzene in the presence of fused calcium chloride. Treated with mercuric oxide the chloride gives the oxide. The isolation of this triarylmethyl oxide presents some difficulties, because of its marked tendency to form supersaturated solutions. It dissolves slowly in benzene, but once dissolved it may take several days before the oxide crystallizes out again, even on addition of absolute ethyl ether or petroleum ether. The yields of the oxide by the mercuric oxide method are good, about 80% of the calculated. It melts quite sharply at 212°.

Calculated for $C_{40}H_{34}O_3$: C, 85.36; H, 6.09.
Found: C, 85.30; H, 6.20.

0.4190 gram substance in 11.9 grams naphthalene caused a depression of 0.456° in the freezing point of the solvent.

Calculated for $C_{40}H_{34}O_3$: Mol. wt., 562.3. Found: 532.

The oxide is soluble to the extent of 1 gram substance in 25 cc. of cold benzene, and much more readily in hot benzene. It is very sparingly soluble in ether and even much less in petroleum ether. As regards susceptibility to hydrolyzing agents it resembles the other oxides described, being only slightly affected by water or dilute alkalies, but it is completely hydrolyzed to the carbinol on boiling a benzene solution of the oxide with 5% solution of sulfuric acid for 2–3 hours. The carbinol was identified by its own melting point, and also by its conversion into the chloride, and the conversion of the latter by silver and air into the peroxide, melting at 155° C.

p-Acetoxy-triphenylmethyl Oxide. Preparation of p-hydroxy-triphenyl

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[1] *Ann.*, 370, 154 (1909).

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

Carbinol.—This carbinol was made from the methoxy carbinol by adding to a warm benzene solution of the latter one and a half times its weight of aluminium chloride, and boiling on the water-bath for as hort time. There is formed at the same time a very small amount of diphenylmethane and more or less diphenyl quinomethane.[1] After decomposing the aluminium chloride in the usual way, the benzene solution is extracted with dilute (2%) sodium hydroxide, which dissolves the carbinol and leaves the other two products behind. The carbinol is precipitated on adding dilute acetic acid to the filtered sodium hydroxide solution and recrystallized according to Bistrzycki and Herbst[2] from dilute acetic acid. Twelve grams of the methoxy carbinol gave 8 grams of the hydroxy compound; in another instance 20 grams of methoxy carbinol gave 12 grams of the hydroxy compound and 5 grams of diphenyl-quinomethane.

p-Acetoxy-triphenylcarbinol Chloride.—The hydroxy carbinol was acetylated by acetic anhydride and sodium acetate according to Bistrzycki,[3] and the acetoxy carbinol obtained possesses the properties described for that compound. For the conversion into the carbinol chloride, the carbinol was dissolved in benzene, some fused calcium chloride added, and a stream of dry hydrochloric acid passed into the solution. After thorough drying, the benzene was distilled off and petroleum ether added. After a day's standing the oil changed to white crystals, melting at 85–86°.

Calculated for $C_{21}H_{17}O_2Cl$: Cl, 10.53.
Found: Cl, 9.97.

The Oxide.—An oxide of supposedly this composition and constitution has been described in detail by Bistrzycki and Herbst.[3] Auwers and Schröter[4] doubted the identity of this oxide, and on the basis of molecular weight determinations carried out by them, concluded that it must have been the carbinol. We are inclined to agree with Auwers and Schröter, for the very method of purifying the compound as employed by Bistrzycki, boiling with acetic acid, would destroy the oxide had he had it.

We obtained the acetoxy-triphenylmethyl oxide by treating the chloride with mercuric oxide in benzene at room temperature. This oxide comes down at times as a thick oil, and, like the methoxy-oxide, crystallizes from its solutions very slowly. Recrystallized from a mixture of benzene and absolute ether it was obtained as beautiful white needles, melting quite sharply at 123–124°, with evolution of gas.

Calculated for $C_{42}H_{34}O_5$: C, 81.53; H, 5.53.
Found: C, 81.03; H, 5.63.

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[1] Baeyer, *Ber.*, 36, 2792 (1903) demethylated the methoxytriphenylcarbinol by boiling a solution of it in a mixture of acetic and sulfuric acids for 12 hours.

[2] *Ber.*, 34, 3074 (1901).

[3] *Ibid.*, 34, 3077 (1901).

[4] *Ibid.*, 36, 3250 (1903).

0.6255 gram substance in 11.90 grams naphthalene caused a depression of 0.685° in the freezing point of the solvent.

Calculated for $C_{42}H_{34}O_5$: Mol. wt., 618.3. Found: 530.

This ether appears to be somewhat more readily hydrolyzed to the carbinol than the ethers previously described. But even so, it is not affected by water and only very slowly by dilute alkalies.

The facts presented above were withheld until now from publication in THIS JOURNAL, in the hope that the synthesis of the much disputed *p*-hydroxy-triphenyl-methyl oxide would also be realized.[1] The appearance, however, of the paper by Schlenk in the last number of Liebig's *Annalen*[2] makes it desirable that the results obtained in this laboratory thus far be published now. Schlenk, too, attempted to prepare triphenylmethyl oxide by the use of various reactions. His results proved entirely negativ, and he concluded that this oxide is in all likelihood incapable of existence.

We have recently worked out a still different method for the preparation of triarylmethyl oxides. When triphenylmethyl carbonate (m. p. 205–10°) is heated under definit conditions it loses carbon dioxide and yields almost quantitatively triphenylmethyl oxide. The details of this reaction and the work relative to the oxides described by Werner,[3] Decker,[4] and by Barbier[5] will be given in a subsequent paper.

In connection with the oxides the study of the triarylmethylsulfides has also been in progress. Here, apparently, lead sulfide promises to give the best results.

ANN ARBOR, MICHIGAN.

STUDIES ON ENZYME ACTION. III. THE ACTION OF MANGANOUS SULFATE ON CASTOR BEAN LIPASE.

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In the first paper[6] of this series an experiment was described in which it was shown that the continued passage of an electric current through a suspension in water of the castor bean lipase preparation resulted in the production of a lipolytically active substance at the anode. As stated there, this substance was probably formed by some oxidation reaction of the preparation. Hoyer[7] found that small amounts of man-

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[1] See footnote on title page of this paper.

[2] *Ann.*, 394, 178 (1912).

[3] *Ber.*, 34, 3305 (1901).

[4] *J. prakt. Chem.*, 84, 232 (1911).

[5] *Ann. chim.*, [5] 7, 507 (1876).

[6] THIS JOURNAL, 34, 735 (1912).

[7] *Z. physiol. Chem.*, 50, 414 (1907). Cf. also Tanaka, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 11, 37 (1912).