2. The nitro ketone is easily brominated in the gamma position; the bromo ketone is unstable to heat. Hydrogen bromide is eliminated by the use of potassium acetate, and the product is a tertiary nitrocyclopropanone.

3. Sodium methylate reacts with this cyclic nitro compound in such a way that the ultimate product is dibenzoylethane.

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TRIARYLMETHYL CARBONATES. CATALYTIC DECOMPOSITION IN THE PRESENCE OF COPPER

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Triphenylmethyl carbonate has been recorded by Gomberg[1] as an intermediate in the preparation of triphenylmethyl oxide. The carbonate was formed by the action of silver carbonate on triphenylchloromethane in benzene

$$2(C_6H_5)_3CCl + Ag_2CO_3 = [(C_6H_5)_3C]_2CO_3 + 2AgCl \qquad (1)$$

A solution of triphenylmethyl carbonate in boiling xylene produced triphenylmethyl oxide and carbon dioxide under the catalytic influence of finely-divided copper.

$$[(C_6H_5)_3C]_2CO_3 \longrightarrow CO_2 + [(C_6H_5)_3C]_2O \qquad (2)$$

This reaction, similar to the thermal decomposition of metallic carbonates, is consistent with the general properties of the triarylmethyls, whose salts with strong acids, particularly the halides, show many of the reactions of metallic salts. If the analogy is complete, Equation 2 should represent a general reaction of the triarylmethyl carbonates and should be reversible.

With this in mind, three other carbonates, those of diphenyl-α-naphthylmethyl, *p*-tolyldiphenylmethyl and phenylbiphenylenemethyl, have been prepared and their behavior in the presence of copper powder studied. Although *p*-tolyldiphenylmethyl carbonate and diphenyl-α-naphthylmethyl carbonate are decomposed catalytically by copper, the oxides have not been obtained in appreciable quantity and it must be concluded that Reaction 2 is not general, but that the catalytic effect of copper is common to the triarylmethyl carbonates. The decomposition of triphenylmethyl carbonate has not been reversed.

Further, the occurrence of a slow catalytic decomposition presents an opportunity to study the mechanism through the interpretation of the rate of reaction. This has been done for the decomposition of triphenylmethyl carbonate.

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[1] Gomberg, This Journal, **35**, 200 (1913).

Triphenylmethyl Carbonate.—Ten grams of triphenylchloromethane in 50 cc. of dry benzene was shaken with two to three times the theoretical amount of silver carbonate for twenty-four hours. The silver carbonate had been dried at 140° in a stream of carbon dioxide and analyzed as 99.7% pure. The benzene solution was heated to boiling, filtered and the residue extracted with 50 cc. of boiling benzene. The volume was reduced to 30 cc. at low pressure on the steam-bath. The carbonate crystallized rapidly and was light yellow in color. One recrystallization produced white crystals containing one molecule of benzene of crystallization. The yield is 60–80%; m. p. 200–201° with carbon dioxide evolution.

Anal. The carbon dioxide evolved by heating to 200° was weighed. Calcd. for $C_{45}H_{36}O_3$: CO_2, 7.05. Found: CO_2, 7.00, 7.03.

Part of the benzene was removed by heating for several hours in a vacuum at 90°, the rest by recrystallization from xylene and washing with dry ether; m. p. 208–209° with carbon dioxide evolution.

Anal. Calcd. for $C_{39}H_{30}O_3$: CO_2, 8.06. Found: CO_2, 7.98, 8.12. The first measurement (7.98) was obtained by heating the dry solid, the second (8.12) by titrating the carbonate produced by alkaline hydrolysis. *Mol. wt.* in benzene, calcd., 546. Found: 523, 560, 531, 531; average 536. The solubility in hot benzene is about 55 g. per 100 cc.; in cold benzene, 2 g. per 100 cc.; in hot acetone, 5 g. per 100 cc.; in hot ethyl acetate, 20 g. per 100 cc. Long standing in ethyl acetate slowly produces triphenylcarbinol.

Triphenylmethyl Oxide.—A sample of triphenylmethyl oxide was obtained by the action of mercuric oxide on triphenylchloromethane;[1] m. p. 232–233°. Five grams of triphenylmethyl carbonate was heated in boiling xylene for two hours. It crystallized unchanged. The experiment was repeated with the addition of a small quantity of copper powder. The resulting crystals melting at 235–236° were identified with triphenylmethyl oxide by a mixed melting point of 233–234°; yield, 95%. Recrystallization from xylene raised the melting point to 237–238°.

Diphenyl-α-naphthylmethyl Carbonate.—In the preparation of this substance, it is desirable, because of its low solubility, to use 10 cc. of benzene for each gram of diphenyl-α-naphthylchloromethane. The solution of the product in benzene was evaporated under reduced pressure to a thick sirup and crystallized by the addition of ether. Crystallization of the crude carbonate required twenty-four to forty-eight hours. The product at first obtained was dark yellow and contained 20 to 40% of impurities; yield 40–60%. Recrystallization from boiling xylene (20 cc. per gram) produced a white powder melting with carbon dioxide evolution at 228–230°.

Anal. Calcd. for $C_{47}H_{36}O_3$: CO_2, 6.8. Found: CO_2, 6.2, 6.6. *Mol. wt.* in benzene, calcd., 648. Found: 638, 639.

A solution of diphenyl-α-naphthylmethyl carbonate in xylene was boiled for an hour without appreciable carbon dioxide evolution. The addition of copper powder effected complete decomposition in thirty to forty-five minutes. However, no substance was successfully crystallized from the product, showing that diphenyl-α-naphthylmethyl oxide is probably unstable under the conditions of the experiment.

Diphenyl-α-naphthylchloromethane in benzene was kept in contact with mercuric oxide for several days. A 50% yield of diphenyl-α-naphthylcarbinol was obtained. The remainder was precipitated as a gum by petroleum ether and was not successfully crystallized. The occurrence of the carbinol in this quantity suggests the abstraction of hydrogen chloride and subsequent decomposition of half the material, accompanied by hydrolysis of the other half.

p-Tolyldiphenylmethyl Carbonate.—This compound is the most soluble in benzene and xylene of the carbonates prepared. It was obtained as a white powder by adding ether to the oily residue left after removal of the benzene used in the preparation. Four or five cc. of xylene per gram is sufficient for recrystallization; yield, 40–50%. The melting point is 193–195° with carbon dioxide evolution. For analysis the sample was refluxed in a solution of 0.1 *N* sodium hydroxide, barium chloride was added, and excess alkali titrated to phenolphthalein.

Anal. Calcd. for $C_{41}H_{34}O_3$: CO_2, 7.66. Found: CO_2, 7.40, 7.45. *Mol. wt.* in benzene, calcd., 574. Found: 556, 568.

p-Tolyldiphenylmethyl Oxide.—The use of xylene in recrystallizing *p*-tolyldiphenylmethyl carbonate shows its stability at 140°. The introduction of powdered copper into the solution in boiling xylene or toluene resulted in rapid carbon dioxide evolution. A small amount of white powder melting at 180–185° was separated. The reaction of *p*-tolyldiphenylchloromethane with mercuric oxide produced a 10% yield of white material melting at 205–207°. This latter must be the oxide since it has a high melting point and is readily converted to the carbinol by hydrochloric acid. One part of this substance was mixed with three parts of the material melting at 180–185° and a mixed melting point of 190–195° was obtained, showing that a small quantity of the oxide was produced by decomposition of the carbonate in the presence of copper. Evidently the *p*-tolyldiphenylmethyl compounds enter, to some extent, into the same reactions as the triphenylmethyl compounds.

The residue from the *p*-tolyldiphenylmethyl oxide preparation by the mercuric oxide method was a yellow oil from which nothing was crystallized. This result is similar to that of Schlenk and Meyer,[2] who attempted to prepare diphenylquinomethane from *p*-tolyldiphenylchloromethane and pyridine but obtained only a yellow oil from which nothing was crystallized. In this case mercuric oxide may have produced the same result as pyridine.

Phenylbiphenylenemethyl Carbonate.—A solution of phenylbiphenylenechloromethane in benzene slowly turned dark red when kept in contact with silver carbonate. A 10% yield of pink crystalline material was obtained. White crystals melting with carbon dioxide evolution at 218–220° were separated by recrystallization from xylene. Heating in boiling xylene with or without copper for four to five hours failed to produce carbon dioxide evolution. The compound was decomposed by boiling in mesitylene over copper but phenylbiphenylenemethyl oxide was not obtained. This behavior is not surprising in view of the high stability and generally sluggish reactions of the phenylbiphenylenemethyl compounds.

Rate of Carbon Dioxide Evolution by Triphenylmethyl Carbonate

The mechanism of carbon dioxide evolution from triphenylmethyl carbonate in boiling xylene under the influence of powdered copper was studied through the rate of evolution of the gas. Rate measurements on the other carbonates were not made because their decomposition was complicated by side reactions. The triarylmethyl oxide was produced quantitatively only from triphenylmethyl carbonate.

The carbon dioxide evolved in the flask A was carried through the reflux condenser into the receiver B by a stream of dry nitrogen. The nitrogen was passed through soda lime and dried with phosphoric anhydride before entering the apparatus. Xylene was distilled in a small apparatus which

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[2] Schlenk and Meyer, *Ber.*, **52**, 16 (1919).

had been dried in an oven at 110°. The flask A and the reflux condenser were dried in the oven before use. Very small amounts of water interfered by hydrolysis of the carbonate. For example, calcium chloride instead of phosphoric anhydride let through enough water in an hour for complete hydrolysis of a gram of the carbonate. The receiver B contained a known amount of standard barium hydroxide whose concentration as a function of time was measured by means of the conductivity cell C. The pipet cell allowed sampling at definite time intervals with sufficient time for measurement. The outlets of the flask and cell were protected by soda lime tubes D. The temperature in the reaction flask was 139° during all the runs and the barium hydroxide in the receiving flask was kept at 25°. At the end of each run the triphenylmethyl oxide produced was separated and in each case was found to represent a 90–95% yield without taking into account the solubility in xylene. The xylene solution was made up each time in the same concentration and approximately the same quantity, 1 g. of carbonate to 24 g. of xylene. The resistance of the barium hydroxide as a function of concentration was found to be expressed accurately by the equation, log $CR^{1.0801} = 0.61584$. The

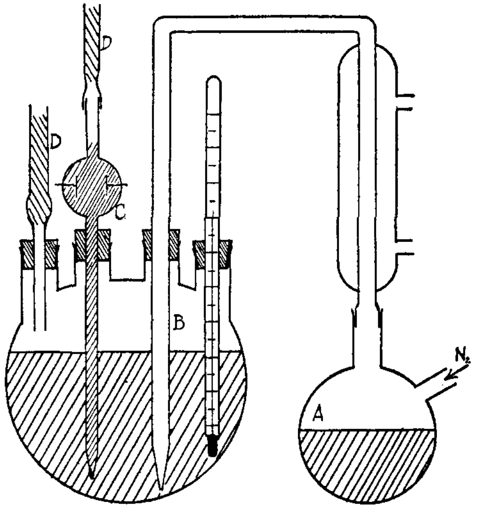

Fig. 1.

TABLE I

RATE OF EVOLUTION OF CARBON DIOXIDE AT 139° BY TRIPHENYLMETHYL CARBONATE IN XYLENE

Carbonate, 0.8827 g.; copper 1.1581 g.; xylene 22.0 g.

Time, minutes	R, ohms	Concn. $Ba(OH)_2$ $\times 10^2$ moles/liter	$CO_2 \times 10^6$, equivalents	K
0	57.6	5165	000	...
3	62.0	4778	387	0.092
6	62.3	4753	412	.046
9	62.8	4704	461	.038
14	66.0	4355	810	.050
20	69.4	4227	938	.044
25	72.6	4036	1129	.047
30	74.3	3945	1220	.047
40	76.2	2828	1337	.048
50	79.0	3681	1484	.050
60	79.9	3641	1524	.048
70	81.3	3573	1592	.060

range of concentration was 0.1 to 0.025 *M*. The results of a typical run are given in Table I. The last column gives the unimolecular rate constant in reciprocal minutes. The volume of barium hydroxide was 200 cc.

With a rapidly boiling solution no interference by rate of diffusion was encountered. Some distortion of the rate curve might be expected during the first and more rapid part of the reaction due to lag in carrying over the carbon dioxide. This, however, was negligible since changes of the rate of flow of nitrogen during the reaction were without effect on the results.

In Table II the effect of the amount of copper surface is summarized. The first row gives the weight of copper per gram of triphenylmethyl carbonate; the second, the unimolecular rate constant. The solution in each case contained 1 g. of carbonate in 24 g. of xylene.

TABLE II

EFFECT OF THE EXTENT OF COPPER SURFACE ON THE RATE OF CARBON DIOXIDE EVOLUTION

Cu, grams	3.15	1.57	0.90	0.75	0.38
K	0.047	0.046	0.032	0.025	0.028

Although the fourth and fifth points are in reverse order, it is evident that doubling the copper surface produced only a small increase in the rate.

A series of qualitative experiments failed to discover any substance other than copper powder which would catalyze the reaction. Freshly reduced nickel, platinum and cadmium were without effect. With the possibility of intermediate metallic carbonate formation in mind, stannic oxide, mercuric oxide and cupric oxide were tried. The last two are significant, mercuric oxide because of its use in preparing the triarylmethyl oxides and cupric oxide because of the possibility of an oxide film on the surface of the catalyst. Although negative results are not necessarily significant in catalysis, the reaction is probably the result of a specific property of copper. The reaction was carried out with two samples of copper from different sources, although all rate measurements were made with the same sample to obtain a uniform surface.

Mechanism of the Reaction.—A catalytic reaction at a solid–liquid interface should be unimolecular[3] if it is governed by a rate of diffusion or by adsorption covering only a small fraction of the active surface at any time. In either case the amount reacting in unit time at a given concentration should be proportional to the surface, or nearly so, if the reaction causes adsorption to lag behind equilibrium. Since the rate constant is defined as the quantity reacting in unit time at unit concentration, it follows that the constant should increase in direct proportion to the surface. It must be concluded, then, that in the reaction studied the catalytic

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[3] Taylor, "Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1924, p. 953.

effect cannot be explained in terms of adsorption covering a small fraction of the active surface. However, if the catalyst is able to produce and maintain an equilibrium concentration of active molecules in the solution, rather than on the surface, the results are explained. If equilibrium were maintained by the catalyst, the constant would be independent of the extent of the surface; but if it is assumed that increasing the surface decreases the lag behind equilibrium, a large increase in the active surface should be attended by a small increase in the rate constant. The experimental results give no indication of the nature of such an intermediate but, since the yield of triphenylmethyl oxide is almost quantitative, it is probably a tautomer or active form of the carbonate itself.

Levi and Haardt[4] obtained a similar result in a measurement of the effect of the surface area of platinum on the rate of decomposition of hydrogen peroxide. Vavon[5] found that the rate of hydrogenation of nitrobenzene in alcohol increased rapidly with the weight of catalyst employed.

Summary

Triphenylmethyl carbonate, diphenyl-α-naphthylmethyl carbonate, *p*-tolyldiphenylmethyl carbonate and phenylbiphenylenemethyl carbonate have been prepared.

The evolution of carbon dioxide in boiling xylene from the first three of the carbonates mentioned has been shown to be catalyzed by copper powder. Phenylbiphenylenemethyl carbonate was not affected by copper, triphenylmethyl carbonate broke down quantitatively to triphenylmethyl oxide and carbon dioxide. Diphenyl-α-naphthylmethyl carbonate decomposed without producing the oxide, and a small quantity of *p*-tolyldiphenylmethyl oxide was obtained from *p*-tolyldiphenylmethyl carbonate.

p-Tolyldiphenylmethyl oxide was also prepared in small quantity from mercuric oxide and *p*-tolyldiphenylchloromethane.

The rate of evolution of carbon dioxide from triphenylmethyl carbonate catalyzed by copper in boiling xylene was measured as a function of the extent of copper surface. The rate constant was unimolecular and the effect of extent of surface precluded explanation in terms of adsorption. An alternative explanation has been given.

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[4] Levi and Haardt, *Gazz. chim. ital.*, **56**, 424 (1926).

[5] Vavon, *Bull. soc. chim.*, **41**, 1253 (1927).