The solubility characteristics and general behavior of the enzyme point strongly toward its being essentially a globulin.

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The Reaction of a Free Radical, Triphenylmethyl, with Ethers, Esters and Acetone[1]

BY AVERY A. MORTON AND LAWSON V. PEAKES, JR.

This paper will present work showing that under certain conditions triphenylmethyl reacted with ether, ethyl acetate, and acetone, forming triphenylcarbinol in yields of 44, 31 and 14%, respectively, together with smaller amounts of other substances. During the course of some experiments on triphenylmethyl an ethereal solution of the compound, prepared *in situ* from triphenylchloromethane and copper, was decolorized when heated overnight in a sealed tube at 80°. Upon opening the tube a considerable pressure of gas, later identified as carbon monoxide and methane, was revealed. Acetaldehyde, triphenylcarbinol, triphenylmethane, and an uncrystallizable oil were found in the solution. In the absence of copper or cuprous chloride the decolorization of a solution of the free radical required heating to 110° for a longer time. Gases were still found in the tube after the reaction and the aldehyde was detected but the solid products could not be identified. With ethyl acetate the behavior in general was similar to that with ether except that no gaseous nor aldehyde products were found. A reaction with acetone was not as smooth as that with ether or with ethyl acetate.

This interesting discovery extends the list of substances with which a free radical, triphenylmethyl, reacts to include some of the most common solvents[2] used. It is also another illustration of the great tendency of triphenylmethyl to saturate itself at the expense of other molecules which are relatively stable compounds.[3]

The mechanism of the reaction is not known but a likely inference, in the cases of ether and ethyl acetate, at least, is that triphenylmethyl ethyl ether is formed as an intermediate which then breaks[4] down into triphenylcarbinol and triphenylmethane.

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(1) From a portion of the thesis of Lawson V. Peakes, Jr., presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

(2) Schmidlin [*Ber.*, **39**, 632, 4189 (1906); **40**, 2316 (1907)] observed that the yield of triphenylmethyl from triphenylchloromethane and magnesium in ether was less when the solution was heated for a long time. He attributes his results to an alpha and beta form of triphenylmethylmagnesium chloride. He also found considerable quantities of triphenylcarbinol in his product at times, a fact which he believes was due to the least trace of moisture.

(3) As another example of this type the reaction with *o*- and *p*-xylene may be cited, Wieland and Müller, *Ann.*, **401**, 236 (1913).

(4) Norris and Young, THIS JOURNAL, **52**, 753 (1930).

Experiments

Procedure.—In each case the reaction was carried out by sealing the reagents, previously dried, in a tube and heating in the dark. The solution at first changed to a reddish-orange color due to the dissociation of hexaphenylethane into the free radical. The color gradually faded to a greenish-yellow. At the higher temperatures of 110° a strong fluorescence developed. At the end of the reaction the tube was opened, the solvent removed by evaporation, and the gummy product separated as well as possible into its components by crystallization. All products were identified by mixed melting points.

Preliminary runs with ether and ethyl acetate were made by sealing triphenylchloromethane, dissolved in the compound as a solvent, with copper (antique copper bronze) or with silver powder and heating until the color of the free radical was discharged. In the case of copper the temperature was 80° and the time forty-eight hours. The products were easier to identify from the reaction with copper. Not only were triphenylcarbinol and triphenylmethane found but also a little triphenylmethyl ethyl ether. In the absence of any metal triphenylchloromethane did not react with ether during two days of heating at 110°.

The reactions with triphenylmethyl were carried out to ensure beyond any question of reasonable doubt that the reaction was that of the free radical. Triphenylmethyl was prepared by shaking 10 g. of triphenylchloromethane in 50 cc. of benzene with 25 g. of mercury in a pendulum shaker under an atmosphere of dry oxygen-free nitrogen. An analysis of the chloride content of the solution showed that 92% of the triphenylchloromethane originally present was converted within three hours. The solutions for the experiments recorded in the table below were taken after three and one-half hours of shaking. In this table the columns marked C and M refer to the quantities of triphenylcarbinol and triphenylmethane recovered, respectively.

TABLE I

$(C_6H_5)_3C$, g.	Solvent	Cc.	Contact subs.	G.	*T*, °C.	Time in hours	*C*, g.	*M*, g.
4[a]	Ether	80	None		110	48		[b]
8.7	Ether	40	CuCl	3	80	24	4.1	0.2[c]
8.7	Ethyl acetate	40	CuCl	3	80	20	2.9	.65
8.7	Ethyl acetate	40	Cu	5	80	15	2.8	.9[d]
8.7	Acetone	40	CuCl	3	80	120	1.39	

[a] Prepared from triphenylchloromethane and copper in ether solution. [b] Material melting over a range of 125–130° was isolated but the quantity was too small to permit separation into its components. [c] *p*-Benzhydryltetraphenylmethane, 0.2 g., was also isolated. [d] A small amount of peroxide was found.

The reactions with ether always resulted in the formation of gaseous products and aldehyde, in which respect they differed from those in ethyl acetate and in acetone. The gases were at first supposed to be ethylene and ethane but no decrease in volume resulted on shaking with bromine water. An analysis[5] revealed that methane and carbon monoxide were the main constituents.

Experiments with Other Ethers and Esters.—Triphenylchloromethane, 10 g., was heated in a sealed tube at 80° with 28 g. of copper bronze and approximately 160 g. of diphenyl ether, phenetole, and anisole, respectively. In every case the solution turned very dark and yielded a tarry product.

When 5 g. of triphenylchloromethane was heated with 10 g. of silver and 75 cc. of isoamyl acetate at 80° for four and one-half days, 0.5 g. of triphenylcarbinol and 0.4 g. of triphenylmethane were isolated from the oily product. A similar run with ethyl

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[5] The analysis was made through the courtesy of Mr. George Standley.

acetate for seven days yielded only 0.35 g. of triphenylcarbinol and 2.6 g. of peroxide, showing that the latter ester did not react as readily as did isoamyl acetate. When phenyl benzoate and ethyl benzoate were used as the solvents and heated for seven days each, the products were chiefly tar and unchanged triphenylmethyl. The latter was shown by the separation of 0.75 and 0.5 g. of peroxide, respectively. From ethyl oxalate, heated for three and one-half days, an oil yielding a slight amount of *p*-benzhydryltetraphenylmethane was obtained. When a reaction with ethyl oxalate was stopped at the end of two and one-half days, 3.5 g. of peroxide, which required over two hours of standing in an open beaker to complete the precipitation, was obtained.

Summary

Triphenylmethyl has been shown to react with ether, ethyl acetate, and acetone. The major product is triphenylcarbinol. Copper and cuprous chloride catalyze the reaction. Silver has little, if any, effect.

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Studies in the Ketone Sugar Series. II. The Preparation and the Structure of the Heptaacetate and of the Methylglycosidic Derivatives of Turanose

BY EUGENE PACSU

It has been shown in Part I[1] that the stable crystalline halogeno-acetylturanoses differ profoundly from the common halogeno-acetyl sugars in that they are derivatives of the hypothetical orthoacetyl halides as represented in Formula I. In order to learn the general behavior in simple substitution reactions of this type of halogeno-acetyl sugars, it was considered desirable to study the replacement of the halogen atom in the stable bromoacetylturanose with such radicals as hydroxyl and methoxyl. The product of the replacement of halogen by hydroxyl was a crystalline heptaacetate. Simple as this transformation at first appears, it took on an added significance when it was found that the reactions carried out in order to determine the exact constitution of this heptaacetate led to contradictory results.

In the first of these reactions, the heptaacetate, on treatment with hydrobromic acid dissolved in glacial acetic acid, gave back the original bromo compound (I). From this result, in compliance with the principle of the least possible alteration in structure, it may be concluded that the heptaacetate possesses an ortho ester structure as represented by IV. If such be the case, then the exchange between OH and Br, and *vice versa*, would be a direct process, involving no tautomeric change. Such a simple procedure has been shown in Part I to occur between the acetoxyl residue and the bromine atom when the octaacetates II and III possessing an ortho ester structure were treated with hydrogen bromide dissolved in acetic acid.

(1) THIS JOURNAL, **54**, 3649 (1932).