

The solution was finally heated to boiling, then cooled and acidified with dilute hydrochloric acid. The precipitated acid was filtered off and recrystallized from water. It melted at 145°. When mixed with an equal quantity of asaronic acid there was no depression of the melting point.

Summary

The reaction of 3,4-dimethoxyphenyldiazonium

borofluoride with acetic acid gives 2-hydroxy-4,5-dimethoxyacetophenone.

Oxidation of 2,4,5-trimethoxyacetophenone by aqueous potassium permanganate yields 2,4,5-trimethoxyphenylglyoxylic acid, which is oxidized to asaronic acid with hydrogen peroxide.

WASHINGTON, D. C.

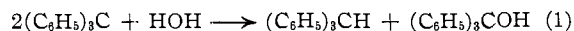
RECEIVED OCTOBER 17, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Indirect Hydrolysis of Hexaphenylethane

BY W. E. BACHMANN

We have observed that when a solution of triphenylmethyl and magnesium iodide in a mixture of ether and benzene is poured into water, triphenylmethane and triphenylcarbinol are formed in equivalent amounts. The reaction corresponds to the addition of the elements of water to the radical.

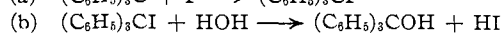
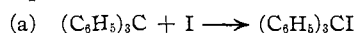


However, it is well known that triphenylmethyl in spite of its great reactivity does not react with water.

An explanation for the products seemed to be provided by the reaction reported by Gorski¹ to take place between triphenylmethyl and magnesium iodide; according to him interaction of the two compounds gives a Grignard reagent and iodine. Since the latter would react with triphenylmethyl and give triphenylmethyl iodide, one should expect to get a mixture of carbinol and methane on hydrolysis. In support of his formulation Gorski reported that an excellent yield of triphenylacetic acid is obtained when carbon dioxide is passed through a mixture of magnesium iodide and triphenylmethyl in ether and benzene.² We have repeated the reaction of Gorski and we have found that the reported reaction does not take place. We passed carbon dioxide through a solution of magnesium iodide and triphenylmethyl in ether and benzene at room temperature and at the boiling point of the mixture, for short and for long periods of time; in no case was triphenylacetic acid formed. A reading of the experimental details in Gorski's article showed that he allowed metallic magnesium to remain in the mixture in order to take

up the iodine which he wrongly believed was liberated in the reaction. Actually, then, the formation of the Grignard reagent which took place in his experiments was due to the action of the binary system $\text{Mg} + \text{MgI}_2^3$ on the triphenylmethyl. Indeed, the absence of reaction between triphenylmethyl, magnesium iodide and carbon dioxide confirms the view of Gomberg and Bachmann that the formation of the Grignard reagent from triphenylmethyl takes place by direct addition of MgI to the radical.

The true explanation for the conversion of triphenylmethyl to the corresponding methane and carbinol was found in an observation made during the process of hydrolysis. It was noticed that when the mixture of triphenylmethyl and magnesium iodide comes in contact with the oxygen of the air a deep red-brown color develops and when this mixture is poured into water iodine is liberated. It occurred to us that part of this iodine is taken up by the triphenylmethyl; the triphenylmethyl iodide thus formed is then rapidly hydrolyzed to triphenylcarbinol with liberation of hydrogen iodide. The latter then reacts with triphenylmethyl and gives a mixture of triphenylmethane and triphenylmethyl iodide; hydrolysis of the latter to the carbinol regenerates the hydrogen iodide and the chain reaction continues until all of the radical has been converted to equivalent amounts of the methane and carbinol.



If this hypothesis is correct, then it should be possible to convert triphenylmethyl into a mixture of equivalent parts of triphenylmethane and triphenylcarbinol by means of water and a small

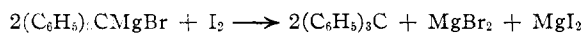
(1) Gorski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1454 (1913).

(2) See Beilstein, fourth ed., Supplement, Vol. IX, p. 309; also *C. A.*, **8**, 325 (1914).

(3) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

amount of iodine. It was found by experiment that such is actually the case.

Similar results are obtained when the Grignard reagent triphenylmethylmagnesium bromide is treated with one atom equivalent of iodine. The Grignard reagent reacts rapidly with iodine and gives an orange-yellow solution of triphenylmethyl and magnesium halides.



When the mixture is poured into water triphenylmethane and triphenylcarbinol are the chief products. It has previously been shown³ that hydrolysis of a mixture of triphenylmethyl and magnesium bromide followed by treatment with air gives a quantitative yield of triphenylmethyl peroxide and no triphenylmethane or carbinol; if magnesium iodide or a small amount of iodine is added to the mixture prior to hydrolysis the products are triphenylmethane and triphenylcarbinol when water is added. In the literature a number of instances can be found in which triphenylmethane and triphenylcarbinol were obtained when water was added to solutions of triphenylmethyl which contained some magnesium iodide but the cause of the reaction was not known.

Of considerable interest is the reaction of oxygen with a solution of magnesium iodide and triphenylmethyl in ether and benzene to give a deeply colored product which liberates iodine on addition of water. A solution of magnesium iodide alone does not behave in this manner; nor does the product result from interaction of triphenylmethyl peroxide and magnesium iodide, for experiment showed that these two compounds do not react to any appreciable extent. We conclude that triphenylmethyl promotes the reaction between oxygen and magnesium iodide. Recently Ziegler and Ewald⁴ likewise observed that triphenylmethyl can aid in oxidation processes and we incline to their view that the active oxidizing agent is an intermediate radical $(\text{C}_6\text{H}_5)_3\text{-COO}$ formed from one molecule of triphenylmethyl and a molecule of oxygen.

(4) Ziegler and Ewald, *Ann.*, **504**, 162 (1933).

Experimental

Triphenylmethyl + Magnesium Iodide + Water.—

Twelve grams of solid triphenylmethyl was added to a filtered colorless solution of magnesium iodide which had been prepared from 8 g. of iodine in 30 cc. of ether and 120 cc. of benzene. When the orange-yellow solution was exposed to air it became dark red-brown in color. The solution was poured into water and treated with air; the products were triphenylmethyl peroxide (0.8 g.), triphenylcarbinol (5.0 g.) and triphenylmethane (4.5 g.). When dry air was passed through a similar mixture of radical and magnesium iodide a large amount of brown-black solid precipitated in a short time; when the solid was treated with water a large amount of iodine was liberated.

Triphenylmethyl + Iodine + Water.—Fifty cc. of water and 0.32 g. of iodine was added to a solution of 6 g. of triphenylmethyl in 50 cc. of benzene and the mixture was shaken for fifteen minutes. Oxidation gave no triphenylmethyl peroxide; a 48% yield of triphenylcarbinol and a 42% yield of triphenylmethane were isolated. Similar results were obtained with as little as 0.03 g. of iodine.

Triphenylmethylmagnesium Bromide + Iodine.—A solution of 6.4 g. of iodine in 60 cc. of benzene was added to the Grignard reagent from 16.2 g. of triphenylbromomethane in an atmosphere of nitrogen; the iodine color disappeared immediately; cooling was necessary. The solution was poured into water and treated with air; 0.55 g. of triphenylmethyl peroxide, 5.2 g. of triphenylcarbinol and 5.0 g. of triphenylmethane were obtained. The presence of triphenylmethyl in the mixture prior to hydrolysis was demonstrated by adding metallic magnesium to the reaction mixture; the triphenylmethyl was converted back to the Grignard reagent; no carbinol or methane was found.

Summary

Triphenylmethyl is converted to a mixture of equivalent amounts of triphenylmethane and triphenylcarbinol by a mixture of water and a small amount of iodine.

Triphenylmethyl does not react with magnesium iodide in ether and benzene solution to give a Grignard reagent as has been reported.

Triphenylmethyl promotes the oxidation of magnesium iodide by oxygen of the air.

The Grignard reagent triphenylmethylmagnesium bromide reacts rapidly with iodine and gives triphenylmethyl and magnesium halides.