[Contribution from the Department of Chemistry of the Massachusetts Institute of Technology]

THE PREPARATION OF TRIPHENYLMETHANE AND THE ACTION OF HEAT ON THE ETHERS AND ESTERS DERIVED FROM TRIPHENYL CARBINOL

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In connection with the study of the chemical properties of certain organic molecular compounds containing aluminum chloride, an account of which will be published later, the behavior of the compound[1] $(C_6H_5)_3CCl.AlCl_3$ with a number of substances has been investigated. When equal molecular quantities of triphenyl-chloromethane and aluminum chloride are dissolved in ether and the solution is allowed to stand for several hours, a reaction takes place as the result of which there is formed a mixture of triphenylmethane and a product that could not be crystallized or distilled without decomposition. This reaction has been studied with the object of developing an improved method for the preparation of triphenylmethane and with the view of elucidating its mechanism.[2] Detailed directions are given in the experimental part of the paper for the preparation in a high state of purity of triphenylmethane from carbon tetrachloride, benzene, ether and aluminum chloride. The procedure does not involve the isolation of triphenyl-chloromethane, and can be carried out readily. The yield of pure hydrocarbon after a single crystallization was 64% of that calculated based on the aluminum chloride used.

The compound of benzoyl chloride and aluminum chloride reacts with ether to form ethyl benzoate. In the presence of zinc chloride, benzoyl chloride and ether yield ethyl benzoate and ethyl chloride. It seemed probable that a similar reaction would take place in the case of triphenylchloromethane. The first step in the reaction would be the formation of triphenylmethyl ethyl ether and ethyl chloride. In this case the ultimate formation of triphenylmethane would result from the decomposition of the triphenylmethyl ethyl ether first produced. To test this view the ether was dissolved in ethyl ether containing aluminum chloride. The products of the reaction were as before, triphenylmethane and a gummy substance. When triphenyl-chloromethane and aluminum chloride were dissolved in normal butyl ether the transformation to triphenylmethane took place.

The first step in the reaction appeared to be that stated above, but neither ethyl chloride nor butyl chloride could be identified as products of the reaction. To determine whether ethyl chloride was stable under the con-

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[1] Norris and Sanders, *Am. Chem. J.*, **25**, 54 (1908).

[2] Gomberg [This Journal, **35**, 204 (1913)] has shown that when triphenyl-chloromethane is treated with ether and zinc chloride, triphenylmethane is formed.

ditions of the experiment a known weight of the chloride was added to a solution of aluminum chloride in ether, and to aluminum chloride alone. In both cases the ethyl chloride was recovered. When, however, triphenylchloromethane was present in the ethereal solution of aluminum chloride the added ethyl chloride could not be recovered. It is evident that it reacted with the triphenylmethane derivative present, and the fact that it was not isolated as a product of the original reaction is not evidence against the mechanism suggested.

The study of the mechanism of the conversion of the triphenylmethyl ethers into trimethylmethane led to the view that under the influence of aluminum chloride the carbon oxygen bond was first broken, the radical OC_2H_5 then lost a hydrogen atom which converted the triphenylmethyl to triphenylmethane, and the resulting radical rearranged to acetaldehyde. The latter was then polymerized by the aluminum chloride present. When the reaction between triphenyl-chloromethane, ether and zinc chloride is carried out in the presence of metallic zinc, an appreciable amount of aldehyde is formed and escapes from the solution.

Since the carbon-oxygen bond in triphenylmethyl carbinol and its derivatives is a very labile one, experiments were made to determine whether the decomposition of the ethers could be effected by heat alone. It was found that the ethyl ether yielded triphenylmethane and acetaldehyde. The normal butyl ether gave the hydrocarbon and butyric aldehyde and the *iso*propyl ether, the hydrocarbon and acetone. The esters of triphenyl carbinol behave in a similar manner. The acetate and the benzoate are converted into triphenylmethane when heated. These reactions are now being studied.

Diphenyl-dichloromethane is converted by ether in the presence of aluminum chloride into benzophenone.

Experimental Part

Preparation of Triphenylmethane.—A 1-liter flask is provided with a return condenser to which is fitted a drying tube. The apparatus is so arranged that the flask can be immersed in ice water to within 5 cm. of the top. A mixture of 292 g. of benzene and 115 g. of carbon tetrachloride is added to the flask, which is then immersed in the ice water. One hundred g. of anhydrous aluminum chloride in the form of lumps is added, the condenser is attached, and the mixture allowed to stand for 48 hours. If powdered aluminum chloride only is available, it must be added in small portions in order to reduce the violence of the reaction. One hundred and ten g. of ether is then added slowly through the condenser, the flasks being shaken occasionally during 20 minutes. After the mixture has stood for about 24 hours it is poured slowly onto 650 g. of ice and 25 cc. of concd. hydrochloric acid. About 400 cc. of carbon disulfide is added, and the solution is separated and dried over calcium chloride. The solvent is distilled until the temperature of the vapor reaches 100°. The product is transferred to a 300cc. flask and distilled. The fraction boiling between 330° and 356° is collected and dissolved in 540 cc. of boiling alcohol. On cooling, the solution deposits crystals of triphenylmethane which melt sharply at 92°. The crystals are filtered off and washed twice with 30cc. portions of cold alcohol. The yield is about 120 g. An additional amount of the hydrocarbon can be recovered from the mother liquor.

The Reactions of Triphenylmethyl Derivatives.—Triphenyl-chloromethane is converted into triphenylmethane under the influence of aluminum chloride by normal butyl ether and by alcohol. It is not affected when the solvent is ethyl acetate.

When a solution of aluminum chloride and triphenyl carbinol or triphenylmethyl ethyl ether in ethyl ether is allowed to stand for several hours triphenylmethane is formed in nearly the calculated quantity.

Triphenylmethyl ethyl ether is converted in carbon disulfide solution by aluminum chloride into triphenyl-chloromethane. To determine whether the change is due to the presence of adsorbed hydrogen chloride in the aluminum chloride an experiment was carried out with a sample of the aluminum salt which had been melted under pressure; the result was the same as in the previous experiment.

It seemed possible that the chloride may have been formed by the action of hydrochloric acid set free when the product was decomposed by water. To test this view a sample of triphenylmethyl ethyl ether was added to carbon disulfide containing an amount of aluminum chloride equivalent to the weight of ether used. After some time a molecular compound separated. An equivalent amount of ethyl malonate was next added. It was found that this ester has a great affinity for aluminum chloride and withdraws it from such molecular compounds of the chloride as the one with benzoyl chloride. In a short time, reaction was evident and the molecular compound changed in appearance. After several hours the solution was decanted and yielded on evaporation triphenyl-chloromethane.

It was evident from the above that aluminum chloride converts triphenylmethyl ethyl ether into triphenyl-chloromethane; if ether is present, however, the hydrocarbon is the product of the reaction.

The Action of Heat on the Ethers Derived from Triphenyl Carbinol.—Triphenyl-chloromethane reacts with ethyl alcohol and forms the ethyl ether, but since the reaction is reversible the ether is best prepared by dissolving in the alcohol sodium equivalent to the chloride used. The ether was prepared by dissolving 2.5 g. of sodium in 80 g. of anhydrous ethyl alcohol and then adding 27.8 g. of triphenyl-chloromethane. The mixture was refluxed for three hours. The solvent was then distilled and the product treated with water, dried and crystallized from petroleum ether. The compound used was pure and melted at 81.3°.

When the ether was heated in a melting-point tube it began to give off a gas at 300°. When it was slowly distilled it was converted into triphenylmethane and acetaldehyde. The latter was absorbed in water and was identified by its odor and by the usual tests for aldehyde.

Triphenyl-chloromethane reacts so slowly with *iso*propyl alcohol, that it can be recrystallized from the alcohol with only a slight change. The ether was prepared in the way described above in the case of the ethyl ether.

Triphenylmethyl *iso*propyl ether melts at 111.7° and begins to decompose at 270°. When 8.5 g. of the ether was heated, 1.6 g. of a low-boiling distillate was obtained. The product had the characteristic odor of acetone and was converted into dibenzalacetone. The high-boiling distillate was a solid, weighed 5 g., after crystallization from alcohol melted at 92°, and had the characteristic properties of triphenylmethane.

The normal butyl ether behaved in a similar way. The butyric aldehyde formed was identified by its boiling-point.

The Action of Ether and Aluminum Chloride on Diphenyl-dichloromethane.—A mixture of 10 g. of the chloride, 10.5 g. of aluminum chloride and 49 g. of ether was allowed to stand in cold water for one night. The mixture was then poured onto ice and the solution separated, dried over calcium chloride, and distilled. The yield of benzophenone was 4.6 g.; the substance melted at 48° after recrystallization from ether.

Summary

1. Triphenyl-chloromethane is converted by ethers in the presence of aluminum chloride into triphenylmethane.

2. The reaction has been utilized to develop a convenient method of preparation of triphenylmethane from carbon tetrachloride, benzene, aluminum chloride and ether.

3. When the alkyl ethers or esters derived from triphenyl carbinol are heated an excellent yield of triphenylmethane is obtained.

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THE STRENGTH OF TRIMETHYLAMINE OXIDE AND TRIMETHYL ALKOXYL AMMONIUM HYDROXIDES AS BASES. THE STRUCTURE OF AMMONIUM COMPOUNDS

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The real basicity of trimethylamine oxide hydrate, $(CH_3)_3NO.2H_2O$, and the basicity of alkoxyl derivatives formed from it by the reaction, $(CH_3)_3NO \xrightarrow{RI} [(CH_3)_3NOR]\,I \xrightarrow{AgOH} [(CH_3)_3NOR]\,OH$, have long been in question. Dunstan and Goulding[1] state that the properties of the aqueous solutions of the free alkoxyl ammonium bases show them to be "strongly basic substances." Meisenheimer[2] describes the amine oxides as "very weak bases, much weaker than ammonia" and the alkoxyl ammonium salts as "colorless, strongly acid reacting substances . . . ." Hantsch and Graf[3] deduced from the conductivity of the salts of the amine oxide that only very slight hydrolysis takes place in solution. Noyes and Hibben[4] found qualitatively that the conductivities of solutions of the free bases were much less than the conductivities of the respective salts.

Much speculation has been based on the assumption of weak basicity in these compounds. Michael[5] has represented the structure of the

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[1] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 792 (1899).

[2] Meisenheimer, *Ann.*, **397**, 284 (1910).

[3] Hantsch and Graf, *Ber.*, **38**, 2156 (1905).

[4] Noyes and Hibben, THIS JOURNAL, **45**, 355 (1923).

[5] Michael, *ibid.*, **42**, 1238 (1920). A complete discussion of previous work, with references, is given in this paper. No attempt is to be made here to fix completely the structure of the ammonium ion portion of these salts. Michael assumed that the mechanism by which aldehydes are formed on decomposition involved hydrolysis, and since an alkoxyl group must hydrolyze to an alcohol, the structure should not be represented as containing an alkoxyl group. However, chlorine attached to nitrogen