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

The Reaction of Sodium with Triphenylchloromethane and with Triphenylmethyl in Organic Solvents

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From the results that have been reported by a number of investigators,[1] it has been concluded that sodium does not react with triphenylchloromethane or triphenylbromomethane in ether or in benzene solution. This result is strange in view of the ease with which the halogen atom of triphenylchloromethane can be removed by other metals as silver, mercury and copper and especially by sodium amalgam. In order to account for the formation of triphenylmethyl from sodium and triphenylchloromethane in the presence of bromobenzene, Morton and Stevens[1d] postulated the intermediate formation of an active "metal halyl" from sodium and bromobenzene, followed by interaction of this "sodium carrier" and the triphenylchloromethane.

During the past four years a number of us in this Laboratory, including Professor M. Gomberg, have utilized the reaction between sodium and triphenylchloromethane in ether to prepare triphenylmethyl, for we found that the reaction proceeds *rapidly* provided that fresh surfaces of the metal are exposed throughout the reaction. Indeed, the reaction is so rapid under certain conditions that it is necessary to cool the mixture. Thus, 5 g. of triphenylchloromethane can be converted completely to triphenylmethyl in ten minutes. In our opinion the reaction is ordinarily prevented or retarded by the formation of an insoluble coating of sodium chloride on the surface of the metallic sodium. If the coating is continually scraped off or if fresh surfaces of the metal are exposed in some other manner as by pressing the metal with a glass rod, then the reaction is able to proceed at a rapid rate. It is easy to understand why liquid sodium amalgam (1 or 40%) is capable of reacting rapidly with triphenylchloromethane.

It is not unlikely that as soon as some triphenylmethyl is formed part of the reaction leading to the further formation of triphenylmethyl takes place through the intermediate formation of triphenylmethyl-sodium, which then reacts with the triphenylchloromethane.

$$(C_6H_5)_3C + Na \longrightarrow (C_6H_5)_3CNa$$
$$(C_6H_5)_3CNa + ClC(C_6H_5)_3 \longrightarrow (2C_6H_5)_3C + NaCl$$

In this way a direct reaction between the sodium and the triphenylchloromethane is not involved. Whatever the mechanism, the reaction between sodium and triphenylchloromethane in ether can be made to proceed rapidly.

According to Schlenk and Marcus[1c] sodium does not add to triphenylmethyl in ether except in the form of sodium amalgam; instead, the radical is polymerized to *p*-benzohydryltetraphenylmethane under the influence of the sodium metal. Under the conditions employed by us triphenylmethyl and sodium powder reacted rapidly in ether to give triphenylmethyl-sodium in practically quantitative yield, only traces of the dimer being formed. The same authors reported that triphenylmethyl-sodium reacts with air to form triphenylmethyl, which oxidizes further to triphenylmethyl peroxide, but they give no experimental details. Inasmuch as interaction of triphenylmethyl-magnesium bromide and air gives triphenylcarbinol (in the form of its bromomagnesium salt) as the chief product,[2] we have investigated the behavior of the corresponding sodium derivative. Here, too, by passing air through a solution of triphenylmethyl-sodium we obtained triphenylcarbinol as the principal product and only a small amount of triphenylmethyl peroxide.

Although Morton and Stevens observed no reaction between sodium and triphenylchloromethane in benzene in sixty days, the reaction can be made to take place in this solvent also. The rate of the reaction in benzene is very much slower than the rate in ether and for this reason the reagents must be extremely pure if by-products are to be avoided. Thus, in two hours, by pressing the sodium with a glass rod, a 10% yield of triphenylmethyl was obtained. Triphenylmethyl-sodium can also be prepared in benzene from triphenylchloromethane and sodium provided the mixture is shaken with glass beads.

(1) (a) Elbs, *Ber.*, **17**, 700 (1884); (b) Gomberg, *ibid.*, **33**, 3150 (1900); (c) Schlenk and Marcus, *ibid.*, **47**, 1664 (1914); (d) Morton and Stevens, THIS JOURNAL, **54**, 1919 (1932).

(2) Bachmann and Cockerill, *ibid.*, **55**, 2932 (1933).

Experimental

Formation of Triphenylmethyl.—To a mixture of 2 g. of sodium powder in 80 cc. of anhydrous ether (or 40 cc. of ether and 40 cc. of benzene) in an Erlenmeyer flask was added 5 g. of triphenylchloromethane. Frequently the sodium immediately became colored with red triphenylmethyl-sodium and the solution became yellow. The flask was fitted with a stopper bearing a movable glass rod flattened at one end. By pressing the sodium against the bottom of the flask a rapid reaction was initiated and the solution became orange-yellow as the radical was formed. After ten minutes the color began to change to the red color of triphenylmethyl-sodium, an indication that all of the triphenylchloromethane had reacted. Oxidation of the triphenylmethyl gave an 80% yield of triphenylmethyl peroxide, m. p. 185–186°. A similar result was obtained by vigorously shaking a mixture of the metal and triphenylchloromethane in ether with sharp particles of glass for twenty minutes.

p-Benzohydryltetraphenylmethane is formed to a slight extent when the complete reaction between the sodium and triphenylchloromethane is slow. This is the case when only the theoretical amount of sodium (1 atom) is employed and the mixture is shaken for a day or two in order to allow time for the last traces of sodium to react. When the reaction proceeds rapidly as is the case when the sodium is pressed with a glass rod, the formation of the dimer is practically entirely suppressed.

Preparation of Triphenylmethyl-sodium.—After pressing the sodium (2 g.) contained in a solution of 5 g. of triphenylchloromethane in 40 cc. of anhydrous ether and 40 cc. of benzene with a glass rod for ten minutes, the rod was removed and the mixture was shaken for two hours. Hydrolysis of the deep-red triphenylmethyl-sodium solution gave a 96% yield of triphenylmethane and only a trace of *p*-benzohydryltetraphenylmethane. The excellent yield of triphenylmethane is an indication of the completeness of the two reactions: the reaction of sodium with triphenylchloromethane and the addition of sodium to triphenylmethyl. Even after one-half hour of shaking the solution contained only 2% of triphenylmethyl that had not been converted to triphenylmethyl-sodium. Similar results were obtained by simply shaking a mixture of triphenylchloromethane and sodium powder in ether–benzene with sharp particles of glass for several hours. In addition to hydrolysis the triphenylmethyl-sodium was also treated with benzyl chloride to give *unsym*-tetraphenylethane and with carbon dioxide to form triphenylacetic acid in excellent yields.

By shaking a mixture of 2.78 g. of triphenylchloromethane, 2 g. of sodium powder and two dozen glass beads in 40 cc. of benzene for one month, triphenylmethyl-sodium was formed as a red precipitate. Hydrolysis gave a 70% yield of triphenylmethane.

Oxidation of Triphenylmethyl-sodium.—Dry air was passed through a solution of triphenylmethyl-sodium that had been prepared from 5 g. of triphenylchloromethane for one hour. From the products of hydrolysis there were isolated 3.15 g. (67%) of triphenylcarbinol and 0.2 g. (4%) of triphenylmethyl peroxide. Although the oily residue liberated iodine from hydrogen iodide, a search for triphenylmethyl hydrogen peroxide was unsuccessful.

Summary

Sodium reacts rapidly with triphenylchloromethane in ether provided fresh surfaces of the metal are exposed throughout the reaction.

Sodium adds to triphenylmethyl in ether and in benzene to form triphenylmethyl-sodium.

Triphenylcarbinol is the principal product of the oxidation of triphenylmethyl-sodium.

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[CONTRIBUTION FROM THE GENERAL MOTORS CORPORATION, RESEARCH LABORATORIES SECTION]

The Action of Aluminum Halides on *n*-Pentane

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Recently, Nenitzescu[1] investigated the reactions of *n*-hexane and *n*-heptane in the presence of aluminum chloride and found isomerization to the 2- or 3-methyl isomer to be the main reaction. Dehydrogenation, condensation to higher paraffins, cyclization to mono and bicyclic cycloparaffins, hydrogenation and splitting of the chain to lower paraffins also occurred. Calingaert[2] repeated the work of Nenitzescu and found that only about 6% of the reacting *n*-heptane was isomerized.

We attempted to study the reported isomerization of *n*-heptane; however, preliminary experiments gave reaction products which were very difficult to analyze and we decided to use *n*-pentane as the starting material. The use of this hydrocarbon was expected substantially to reduce the number and complexity of reaction products, and, since Nenitzescu[3] had shown the reaction between *n*-pentane, acetyl chloride and aluminum chloride to lead to the formation of *unsym*-methyl isopropyl acetone, a result which can best be explained by the preliminary isomerization of *n*-

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(1) Nenitzescu and Dragan, *Ber.*, **66**, 1892 (1933).

(2) Calingaert and Beatty, THIS JOURNAL, **58**, 51 (1936).

(3) Nenitzescu and Chicos, *Ber.*, **68**, 1584 (1935).