was hydrolyzed by refluxing for 2 hours with 10% of hydrochloric acid. The levulose was determined by Benedict's method.[13] Fifty mg. of dextrose is equivalent to 52 mg. of levulose. The carbohydrate content was found to be 15.5%.

The nitrogen determination of the extract made as described above shows that of the nitrogen listed as "protein" 71.5% is readily water-soluble and hence not protein. The amino acid nitrogen determined by Van Slyke's method[14] is 27.5% of the water-soluble nitrogen.

Summary

Analysis of the Jerusalem artichoke shows that it contains 15.5% of inulin. Of the total nitrogen, 71.5% is water-soluble. It contains but small amounts of water-soluble B vitamin. Its use in the treatment of diabetes should be reinvestigated. Analysis, clinical experience and a single experiment in metabolism indicate that the Jerusalem artichoke is a valuable adjunct in the dietetic treatment of diabetes.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, NO. I, 31]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION.
IV. ACTION OF THE ALKALI METALS ON TRIPHENYLMETHYL AND ITS COMPOUNDS

BY CHARLES A. KRAUS AND T. KAWAMURA

RECEIVED SEPTEMBER 6, 1923

The triphenylmethyl group is the first example discovered of a class of compounds exhibiting certain characteristic properties. What attracted particular notice in the first instance was the fact that these compounds appeared to form an exception to the quadrivalence of the carbon atom. These groups, however, possess many other properties which serve to distinguish them, as well as their compounds, from other organic compounds. Thus, compounds of the triphenylmethyl group with the halogens exhibit electrolytic properties in solutions in certain solvents, while the groups also yield compounds with strongly electropositive metals, such as sodium, the properties of which characterize them as exceptional. We now know that many other elements yield compounds resembling the triphenylmethyl group as, for example, lead,[1] tin,[2] mercury[3] and nitrogen,[4] although the properties of these groups have not been extensively investigated.

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[13] Benedict, *J. Am. Med. Assoc.*, **57**, 1193 (1911).

[14] Van Slyke, *J. Biol. Chem.*, **12**, 275 (1912).

[1] Rügheimer, *Ann.*, **364**, 53 (1909).

[2] E. Krause, *Ber.*, **54**, 2060 (1921); **55**, 888 (1922).

[3] Kraus, THIS JOURNAL, **35**, 1732 (1913).

[4] H. Weiland, *Ber.*, **48**, 1078, 1098, 1112 (1915).

Some years ago one of the present authors[5] made the observation that the triphenylmethyl halides, when treated with alkali metals in liquid ammonia solution, yield a compound highly soluble in liquid ammonia, exhibiting a strong red color by transmitted light and a greenish-violet color by reflected light in concentrated solution. In view of the strongly electropositive nature of sodium and the electronegative nature of chlorine, it appeared probable that a reaction occurred in which sodium chloride was formed, leaving behind either the free group or a compound between this group and sodium. This reaction has accordingly been studied further.

Experimental Part

Action of Sodium on Triphenylmethyl Chloride.—The reactions were carried out in an apparatus similar to that which has already been described in an earlier number of this series.[6]

As stated, metallic sodium reacts with the triphenylmethyl halides in liquid ammonia solution. Because of the low solubility of the halides, reaction takes place somewhat slowly; this difficulty may, however, be overcome by stirring the reaction mixture by means of a stream of ammonia vapor passed through the solution. The compound formed is very soluble. Under favorable conditions it may be obtained in the form of reddish needles. No gas is evolved in the reaction with triphenylmethyl chloride.

Five g. of triphenylmethyl chloride was treated with 0.825 g. of metallic sodium in liquid ammonia. At the end of the reaction about 50 cc. of pure toluene was added, after which the bath of ammonia surrounding the reaction chamber was removed. The compound is soluble in toluene and separation was effected from the sodium chloride by filtering through a Gooch crucible in an apparatus in which the air was displaced by means of ammonia vapor. The residue on the filter consisted of sodium chloride with a small amount of sodium hydroxide, due presumably to the presence of a slight amount of moisture. The sodium chloride obtained weighed 0.98 g., corresponding approximately to one-half the sodium originally introduced.

It follows that one molecule of triphenylchloromethane reacts with two atoms of sodium to form one molecule each of sodium chloride and a compound of sodium with the triphenylmethyl group.[7] Reaction takes place according to the equation

$$(C_6H_5)_3CCl + 2Na = (C_6H_5)_3CNa + NaCl \qquad (1)$$

The compound formed between sodium and the triphenylmethyl group is very reactive, even at the temperatures of liquid ammonia. With water

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[5] Kraus, unpublished observations.

[6] White, THIS JOURNAL, **45**, 779 (1923).

[7] This same compound had previously been described by Schlenk and Ochs [*Ber.*, **49**, 608 (1916)], although this publication was not available when the present investigation was carried out. It may be noted that, as here prepared, the sodium triphenylmethyl compound contains one molecule of ammonia, as has since been shown by Dr. R. Rosen in this Laboratory.

it reacts to form sodium hydroxide and triphenylmethane, as was shown by characterizing the products of the reaction. Thus

$$(C_6H_5)_3CNa + H_2O = (C_6H_5)_3CH + NaOH. \qquad (2)$$

The compound combines readily with oxygen to form a white product, the nature of which was not determined at the time.[8]

With ammonium chloride in liquid ammonia, sodium triphenylmethyl yields an immediate pinkish precipitate and the red color disappears. This compound, however, is unstable, since it turns white slowly on standing at the temperature of boiling ammonia. Apparently the initial reaction consists in a replacement of the sodium by the ammonium group to form an ammonium triphenylmethyl, which subsequently decomposes according to the equation

$$(C_6H_5)_3CNH_4 = (C_6H_5)_3CH + NH_3. \qquad (3)$$

Triphenylmethane was characterized as an end-product in this reaction. Sodium triphenylmethyl reacts with bromobenzene and triphenylchloromethane to form tetraphenylmethane and triphenylmethyl, respectively, as will be described below. Sodium triphenylmethyl is moderately soluble in toluene and benzene, but is insoluble in petroleum ether and ligroin.

Action of Metallic Sodium on Triphenylmethane.—The nature of the compound formed between sodium and the triphenylmethyl group was further elucidated by the action of sodium on triphenylmethane in liquid ammonia solution. When triphenylmethane is treated with metallic sodium in equivalent amount in liquid ammonia, reaction takes place somewhat slowly with the formation of sodium triphenylmethyl and the evolution of hydrogen. The compound formed, as was shown by its properties at the end of the reaction, is the same as that formed by the action of sodium on triphenylmethyl chloride. This method of preparing sodium triphenylmethyl has the advantage that the solutions of the compound in ammonia may be obtained without the presence of sodium chloride. Three g. of triphenylmethane reacted completely with 0.2829 g. of sodium in the course of about an hour. Reaction takes place according to the equation

$$(C_6H_5)_3CH + Na = (C_6H_5)_3CNa + {}^1/_2H_2. \qquad (4)$$

What is perhaps most striking in the case of this reaction is the fact that hydrogen attached to a saturated carbon atom is replaced by sodium. Evidently, triphenylmethane is to be looked upon as a very weak monobasic acid. Further evidence to this effect will be adduced in a subsequent article.

Synthesis of Triphenylmethyl in Liquid Ammonia.—If sodium triphenylmethyl is present in liquid ammonia solution, we should expect it to be a comparatively weak electrolyte because of the weakly electronegative

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[8] This reaction has subsequently been studied by Dr. R. Rosen in this Laboratory. The results will appear later.

properties of the triphenylmethyl group. If, therefore, we were to treat sodium triphenylmethyl with triphenylmethyl chloride, we should expect the following reaction to take place

$$(C_6H_5)_3CNa + (C_6H_5)_3CCl = 2(C_6H_5)_3C + NaCl \quad (5)$$

The sodium compound was prepared from equivalent amounts of sodium and triphenylchloromethane in liquid ammonia according to the method previously described. An equivalent amount of triphenylchloromethane was then added to the solution. In liquid ammonia, the reaction between triphenylchloromethane and sodium triphenylmethyl takes place only very slowly because of the low solubility of the former substance. When toluene is added to the mixture, both compounds are dissolved and reaction takes place immediately. The red color due to the sodium compound disappears, while the yellow color which is characteristic of triphenylmethyl makes its appearance. By stirring the solution with a stream of ammonia vapor the rate of the reaction is greatly accelerated.

Dry air was passed through this solution, whereby the free group was oxidized, the yellow color disappearing and a white amorphous precipitate being formed. The contents of the tube were transferred to a small distilling flask and the toluene was distilled. Organic impurities were removed by extraction with ether, in which the peroxide, formed as a result of the process of oxidation, is insoluble. The residue was washed with water to remove sodium chloride, and the resulting compound, which remained behind on the filter paper, was recrystallized from hot benzene. The melting point was found to be 186° sharp, which corresponds to that of the peroxide of triphenylmethyl. Triphenylmethyl is evidently formed according to Equation 5.

Triphenylmethyl in liquid ammonia reacts at once with metallic sodium to form sodium triphenylmethyl, whose presence is made evident by its characteristic red color. The compound was further characterized by the formation of triphenylmethane when water was added to the solution, according to Equation 2.

No reaction appears to take place between ammonium chloride and the free triphenylmethyl group.

Sodium triphenylmethyl appears to be entirely stable in liquid ammonia solution and in the presence of ammonia vapor at low temperatures. At higher temperatures, however, the solid decomposes. Previous investigators have noted that sodium triphenylmethane is acted upon by ammonia vapor with the formation of sodium amide and triphenylmethane.[9] This reaction has since been studied more in detail and will be described in another paper.

Synthesis of Tetraphenylmethane.—Tetraphenylmethane may be readily synthesized through the action of bromobenzene on sodium triphenylmethyl. When the phenyl bromide is added directly to the solution of the sodium compound in liquid ammonia, reaction takes place slowly. The reaction is hastened if toluene is added to the liquid ammonia solution of triphenylmethyl. For this purpose the major portion of the ammonia is evaporated. The compound precipitated in this process must not be allowed to warm much above the boiling point of ammonia, as otherwise it is decomposed. When the excess ammonia has been evolved, phenyl bromide is added and the contents of the tube are allowed to warm slowly

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[9] Schlenk and Ochs, Ref. 7.

to room temperature. Tetraphenylmethane is formed according to the reaction

$$(C_6H_5)_3CNa + (C_6H_5)Br = (C_6H_5)_4C + NaBr \qquad (6)$$

Ten g. of triphenylchloromethane was treated with 1.65 g. of metallic sodium, the ammonia evaporated and toluene added as described; 55 cc. of pure dry bromobenzene was then added. The mixture was stirred by passing a stream of ammonia gas through the reaction tube at the temperature of liquid ammonia. At the end of about half an hour the bath of boiling ammonia was removed and the contents of the tube allowed to warm slowly to room temperature, after which the tube was placed in a water-bath and the contents brought to a temperature of 100°. As the temperature rises, the excess phenyl bromide dissolves the solid present, yielding a solution which is dark yellow in color. The insoluble residue consists chiefly of sodium bromide. On completion of the reaction, the contents of the tube were transferred to a small distilling flask and the excess of bromobenzene was evaporated. The residue of solid in the distilling flask was treated with ether and the mixture filtered. Any triphenylchloromethane which had not been acted upon was thus carried off with the ether. The residue on the filter consisted of tetraphenylmethane and sodium bromide, the latter being then removed with water. The residue was dried and recrystallized from hot benzene by slow cooling. From acetic anhydride the compound may be obtained in the form of long, silky needles; yield 4.35 g., or 37.8%. Tetraphenylmethane is practically insoluble in alcohol and ether, petroleum ether, ligroin, cold acetic acid and cold acetic anhydride; and is soluble in hot acetic acid, acetic anhydride, benzene, toluene and ethylene bromide. Recrystallization from hot acetic acid is recommended for the purpose of obtaining large crystals.

The molecular weight of the compound was determined in benzene by the boiling-point method. Three determinations gave 310.3, 315.4, 317.5, which is in good agreement with the calculated value of 320.

Action of Potassium on Triphenylchloromethane.—The action of potassium on triphenylchloromethane is similar to that of sodium, two equivalents of potassium being required to complete the reaction. Potassium triphenylmethyl has the same appearance as sodium triphenylmethyl and exhibits very similar properties. It exhibits, however, this marked difference, namely, that while sodium triphenylmethyl is unstable in the presence of ammonia, potassium triphenylmethyl is stable even at a temperature of 100°. Another marked difference is that it has not been found possible to synthesize the triphenylmethyl group by the action of triphenylmethyl chloride on potassium triphenylmethyl, as will be shown below.

Action of Potassium Triphenylmethyl on Triphenylchloromethane.—The attempt was made to synthesize triphenylmethyl by the same procedure which was employed in the case of sodium triphenylmethyl. In no case, however, was any evidence of the formation of the free triphenylmethyl group obtained.

Reaction was found to take place on adding triphenylchloromethane to potassium triphenylmethyl in the presence of toluene, and was completed in the course of a few minutes, the red color of the potassium compound disappearing and a yellow color taking its place, while a small amount of solid impurity was left in the bottom of the reaction tube. The ammonia was evaporated, the residue heated to 70° and the toluene distilled under reduced pressure. The residue left in the reaction tube was treated with ligroin and then filtered. From the filtrate fine white crystals were obtained, m. p. 210°, and from the residue on the filter paper a powder was obtained, m. p. 235–236°. This experiment was repeated a number of times with practically the same results, the chief product of the reaction being the compound melting at 210°. From 50 to 60% of the original compound was obtained in this form.

Tests were made for the presence of free triphenylmethyl in the toluene solution, by passing air through this solution. No trace of peroxide could be obtained, the chief product again being a compound melting at 210°. The melting point of this compound agrees with that of the so-called stable hexaphenylethane obtained by Anschütz.[10] That this compound is actually hexaphenylethane may be doubted.

Action of Calcium on Triphenylchloromethane.—Metallic calcium reacts readily with triphenylchloromethane in ammonia solution to form a reddish-brown compound. From its appearance it may be inferred that the reaction is similar to that which takes place in the case of sodium The compound is much less stable than the corresponding sodium compound, since it decomposes almost at once at ordinary temperatures and slowly even at liquid ammonia temperatures. A white product results, the nature of which was not further studied.

Mechanism of the Reduction Process

The action of sodium on triphenylmethyl and its compounds is of interest, not only because of the light it throws on the nature of the triphenylmethyl group, but also because of the insight it yields into the mechanism of the reduction of organic compounds by means of electropositive metals. In the metal solutions, the active reducing agent is the free negative electron, and the process of reduction consists in the combination of the negative electron with the negative constituent of the carbon compound to form a negative ion. The carbon group, on the other hand, may be left in the free condition, may combine with the negative electron to form an anion, or may react with other substances present to form various compounds. In general, in the presence of excess of the free metal, that is, in the presence of excess negative electrons, the organic group will either form a stable negative ion or react with other substances, more particularly the solvent. The initial stage of the reaction, in any case, will take place as follows: $RX + 2e^- = Re^- + Xe^-$. Depending upon the strength of the acid RH and the strength of the base MNH_2, where M is the metallic element present in the solution, reaction may take place according to the equation, $Re^- + H^+ = RH$. In other words, if the hydrocarbon RH is a sufficiently weak acid and the base MNH_2 a sufficiently weak base, the salt RM will hydrolyze according to the equation, $RM + NH_3 = RH + MNH_2$.

In the case of triphenylmethyl chloride, the ionic reaction may be

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[10] Anschütz, *Ann.*, **395**, 196 (1908).

written thus: $(C_6H_5)_3CCl + 2e^- = (C_6H_5)_3C^- + Cl^-$. Since sodium triphenylmethyl is an electrolyte in ammonia, the ionic equation above properly describes the reaction.

Solutions of triphenylmethyl chloride in liquid ammonia conduct the electric current, as do also solutions of sodium triphenylmethyl.[11] The triphenylmethyl group is an example of a numerous class of substances the members of which exhibit amphoteric properties with respect to the positive and negative charges, that is, which are capable of existing either as anions or as cations, depending upon conditions. As has elsewhere been pointed out by one of the present authors, this is a property common to practically all the free groups.[12] In this respect the free groups closely resemble the elements with which they are allied, namely elements which are weakly electropositive and electronegative. All such elements exhibit amphoteric properties, acting either as anions or cations, depending upon conditions, and the same is true of the free groups. The chief distinction between the groups and the elements lies in the fact that, with the exception of hydrogen, all the intermediate elements in the potential series are multivalent, while the free groups are, as a rule, univalent.

The closest analog to the free groups among the elements is hydrogen, which exhibits marked amphoteric properties, being electropositive when combined with more strongly electronegative elements as, for example, the halogens, and being electronegative when combined with the more electropositive elements as, for example, the alkali metals.

Summary

The strongly electropositive metals react with triphenylmethyl chloride in liquid ammonia to form the chloride of the metal and a compound of the metal with the triphenylmethyl group. The sodium and potassium compounds are readily soluble in liquid ammonia and are fairly soluble in benzene and toluene. The solutions exhibit a strong red color and the sodium compound has been obtained in the form of red needles. The potassium compound is stable up to 100°, the sodium compound is unstable at room temperatures, while the calcium compound is unstable even at the temperature of boiling ammonia.

The free triphenylmethyl group may be synthesized by the action of triphenylmethyl chloride on sodium triphenylmethyl in the presence of toluene. A corresponding synthesis could not be carried out with potassium triphenylmethyl. The free triphenylmethyl group in liquid ammonia reacts readily with sodium to form the sodium salt.

Tetraphenylmethane is formed by the action of phenyl bromide on sodium triphenylmethyl in liquid ammonia.

[11] R. Rosen, *Dissertation*, Clark University, 1923.

[12] Kraus, *Rec. trav. chim.*, **42**, 588 (1923).

The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF MERCURIC SALTS TO ALPHA-BETA-UNSATURATED KETONES

BY EDMUND B. MIDDLETON[1]

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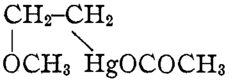
It is well known that mercuric salts react more or less readily with various unsaturated compounds to give products whose compositions are represented by unsaturated compound plus —HgX and —OH, if the reaction is carried out in aqueous solution, or unsaturated compound plus —HgX and —OR if the reaction is carried out in alcohol. There has been some question as to their structure, whether they are saturated compounds formed by addition to the double linkage or complex compounds of the double salt or molecular type.[2] For example, when ethylene is passed into a methyl alcoholic solution of mercuric acetate, it forms a compound whose composition is represented by $C_2H_4.HgOCOCH_3.OCH_3$ and which according to these two views, is either a molecular compound, or the saturated compound,[3]  $\underset{OCH_3}{CH_2}-\underset{HgOCOCH_3}{CH_2}$ The principal reason why substances of this type have been regarded as molecular compounds is the ease with which the unsaturated compounds are regenerated by acids. $C_2H_4.HgX.OCH_3 + HX \longrightarrow C_2H_4 + CH_3OH + HgX_2$. The most recent work of Adams, Roman and Sperry[4] shows conclusively that in some cases these are saturated compounds formed by addition to the double bond. The following investigation of the reaction between mercuric acetate and α,β-unsaturated ketones was undertaken with the purpose of getting further evidence on this point and on the mode of addition. The results show that α,β-unsaturated ketones with one double linkage, such as benzalacetophenone, will react with but one mol. of mercuric acetate while with dibenzalacetone, which has two double linkages, two mols. of mercuric acetate reacted. It appears from this that addition to the double linkages has taken place. Furthermore, all the compounds were white. Cinnamalacetophenone, a ketone which has two double

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[1] National Research Fellow in Chemistry.

[2] For an account of the arguments in favor of and against 'molecular' structures, see Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., 1921, Chap. 5.

[3] Schoeller and Schrauth, *Ber.*, **46**, 2867 (1913). Manchot, *Ber.*, **53**, 986 (1920).

[4] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922). Mills and Adams, *ibid.*, **45**, 1842 (1923).