[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Tetraphenylarsonium Halides[1]

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It has been shown that the As=O group in arsenic trioxide[2] and in arylarsine oxides[3] reacts readily with aromatic Grignard reagents. In the event that the As=O nucleus in triarylarsine oxides behaved in a similar manner, tetraarylarsonium compounds should be formed. Although a considerable number of alkyltriarylarsonium derivatives have been described, it seems that the tetraarylarsonium type has not been prepared hitherto.

It was found that triphenylarsine oxide[4] interacts rapidly with phenylmagnesium bromide and upon addition of hydrobromic acid to the reaction mixture tetraphenylarsonium bromide is produced.

$$(C_6H_5)_3As{=}O + C_6H_5MgBr = (C_6H_5)_4As{-}OMgBr$$

$$(C_6H_5)_4As{-}OMgBr + 2HBr = (C_6H_5)_4As{-}Br + MgBr_2 + H_2O$$

Repeated recrystallization of the bromide from hydrochloric acid yields the arsonium chloride[5] in the form of a hydrochloric acid addition product. Upon treatment with alkali the arsonium chloride itself is obtained. Tetraphenylarsonium iodide was prepared by the interaction of triphenylarsine oxide and phenylmagnesium iodide and subsequent addition of hydriodic acid to the reaction mixture and also by the addition of hydriodic acid or sodium iodide to an aqueous solution of the arsonium chloride or bromide.

The arsonium chloride is very soluble in water, the iodide fairly insoluble and the aqueous solutions are neutral to litmus. The arsonium halides react instantly with halogens to form perhalides; the arsonium triiodide is characterized by its beautiful iridescence and its extreme insolubility in water. In very dilute aqueous solution the arsonium chloride yields very insoluble precipitates with a variety of inorganic salts.[6]

The arsonium structure of our compounds seems to be established since we have shown that triphenylarsine oxide reacts with methylmagnesium iodide to yield methyltriphenylarsonium iodide.[7]

It was thought that tetraphenylarsonium halides might also be obtained by reactions A, B and C, illustrated below.

$$\text{A} \quad (C_6H_5)_2AsCl_3 + 2C_6H_5MgBr = (C_6H_5)_4AsCl + 2MgClBr$$

$$\text{A}' \quad (C_6H_5)_2AsCl_3 + 3C_6H_5MgBr = (C_6H_5)_3As + C_6H_5{-}C_6H_5 + 3MgClBr$$

$$\text{B} \quad (C_6H_5)_3AsCl_2 + C_6H_5MgBr = (C_6H_5)_4AsCl + MgClBr$$

$$\text{B}' \quad (C_6H_5)_3AsCl_2 + 2C_6H_5MgBr = (C_6H_5)_3As + C_6H_5{-}C_6H_5 + 2MgClBr$$

$$\text{C} \quad C_6H_5AsO_2 + 3C_6H_5MgBr = (C_6H_5)_4As{-}OMgBr + BrMgOMgBr$$

We found, however, that reaction A took place chiefly as indicated by equation A′; reaction B proceeded in accordance with B′. The arsonium bromide can be obtained, in rather poor yield, from the anhydride of phenylarsonic acid and phenylmagnesium bromide (C).

It was hoped that the tetraphenylarsonium radical might be obtained by electrolysis of tetraphenylarsonium chloride. Accordingly, a current of 0.2 ampere was passed through 2 g. of the chloride, dissolved in 120 cc. of water, for eighteen hours. Platinum electrodes were used and the anode was placed in a porous cup. At the cathode there precipitated 0.25 g. of triphenylarsine. A very small amount of material, presumably tetraphenylarsonium trichloride, $(C_6H_5)_4AsCl_3$,[8] formed by the action of liberated chlorine on unchanged tetraphenylarsonium chloride, separated at the

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[1] This paper represents the first part of a dissertation to be submitted to the Graduate School by Mr. Monroe in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Sachs and Kantorowicz, *Ber.*, **41**, 2767 (1908); Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 307 (1925); Blicke and Smith, THIS JOURNAL, **51**, 1558 (1929).

[3] Blicke and Smith, *ibid.*, **51**, 3479 (1929).

[4] We found that triphenylarsine sulfide reacts readily with phenylmagnesium bromide but treatment of the reaction mixture with hydrobromic acid yielded mainly triphenylarsine and thiophenol; only a small amount of the arsonium bromide was obtained.

[5] When excess chlorobenzene is heated almost to its boiling point with magnesium for a number of hours, phenylmagnesium chloride is produced and this reacts with benzophenone to form triphenylcarbinol in good yield. So far, however, we have not been able to prepare tetraphenylarsonium chloride satisfactorily by interaction of phenylmagnesium chloride and triphenylarsine oxide.

[6] It has been shown by Dr. H. H. Willard that the arsonium salts possess unique and valuable properties as analytical reagents. This work will be published by him at a later date.

[7] As far as we have been able to determine no compound of the arsonium type has been prepared previously by the aid of a Grignard reagent.

[8] When chlorine is passed into an aqueous solution of tetraphenylarsonium chloride, a precipitate forms rapidly. This compound, which may be tetraphenylarsonium trichloride, does not melt sharply and is decomposed by electrolysis; thus, when 0.5 g. of the product was electrolyzed for eighteen hours 0.4 was converted into water soluble products.

anode. Apparently the tetraphenylarsonium radical decomposes spontaneously into triphenylarsine and the phenyl radical; the latter then polymerizes to diphenyl or is reduced to benzene.

Through the courtesy of Dr. Oliver Kamm the following data were obtained from the Parke, Davis and Company laboratories. Administered intravenously to rats the maximum tolerated dose of tetraphenylarsonium chloride was found to be 25 mg. per kilogram; the minimum lethal dose is 30 mg. per kilogram. The trypanocidal action against *T. equiperdum* was very slight. The chloride exhibited no germicidal effect when tested in 1% solution against *Strep. Hemolyticus* but it was found to be germicidal against *Staph. aureus* in a dilution of 1 part in 600 parts of water.

The following physical chemical data were obtained under the supervision of Dr. A. L. Ferguson, to whom we wish to acknowledge our indebtedness.

The properties of tetraphenylarsonium chloride as an electrolyte were determined through measurements of conductivity, hydrogen-ion concentration and chloride-ion concentration over an equivalent concentration range from 0.0405 to 0.000156. The equivalent conductance (plotted on the accompanying curve) and dissociation values are given in Table I. These results are typical of those obtained for a strong electrolyte. The *p*H values for the same solutions showed no consistent variation; in fact, all the values were between 6.5 and 7.7. This also indicates that tetraphenylarsonium chloride is a strong electrolyte.

The equivalent conductance of the chloride ion at infinite dilution is 77 at 25°. Thus the equivalent conductance of the tetraphenylarsonium ion is only 13, which is about the order of magnitude to be expected for such a complex ion, though it does appear rather small.

The chloride-ion concentration measurements furnished less conclusive results. Silver chloride electrodes were used, and in pure hydrochloric acid solutions of various concentrations gave highly satisfactory values; when placed in the tetraphenylarsonium chloride, however, their behavior, for some undeterminable reason, was not satisfactory. Nevertheless, the data did support, qualitatively, the conclusions drawn from conductivity measurements.

Dissociation values for several solutions were obtained from freezing point data, which agreed fairly well with those given by conductivity.

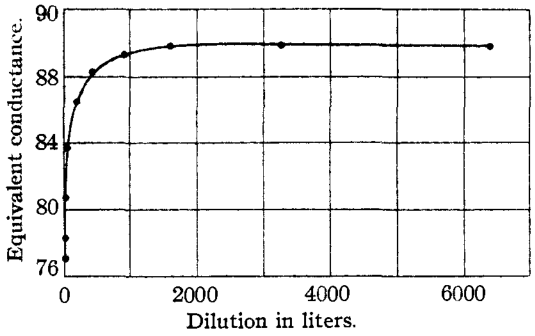

Fig. 1.

TABLE I

DEGREE OF DISSOCIATION OF TETRAPHENYLARSONIUM CHLORIDE DETERMINED BY CONDUCTIVITY MEASUREMENTS AT 25°

Equivalent concentration	Equivalent conductance	Degree of dissociation, %
0.0405	77.03	85.6
.0337	78.30	86.8
.0228	80.73	89.6
.0127	83.73	93.0
.0050	86.44	96.2
.0025	88.29	98.2
.00125	89.36	99.3
.000625	89.83	99.8
.000312	89.86	99.9
.000156	89.82	99.8

Experimental Part

Tetraphenylarsonium Chloride, Bromide and Iodide

Bromide.—Phenylmagnesium bromide was prepared from 2.4 g. of magnesium, 10.5 cc. of bromobenzene and 60 cc. of ether in a three-necked flask fitted with a reflux condenser and a stirrer which passed through a mercury seal. The solution was stirred vigorously and 12 g. of triphenylarsine oxide, dissolved in 225 cc. of hot, dry benzene, added rapidly. The mixture was stirred for one-half hour, the benzene-ether layer decanted and the solid material triturated with 40 cc. of water; after the addition of 75 cc. of constant boiling hydrobromic acid, the mixture was poured immediately into a beaker, whereupon the crystalline arsonium bromide began to separate. After some time the latter was filtered, washed thoroughly with benzene and recrystallized from water to which charcoal had been added. The bromide was obtained in the form of long, colorless, glistening needles; m. p. 273–275°; yield of pure product 12 g.

Anal. Calcd. for $C_{24}H_{20}AsBr$: As, 16.18; Br, 17.25. Found: As, 16.06; Br, 17.02.

Dissolved in acetic acid the bromide reacts instantly with bromine; the precipitated, yellow tetraphenylarsonium tribromide melts at 215–216°.

Anal. Calcd. for $C_{24}H_{20}AsBr_3$: As, 12.02; Br, 38.52. Found: As, 12.32; Br, 38.51.

When treated with hot, dilute sodium hydroxide solution, the tribromide dissolves due to its conversion into the bromide; the latter precipitates when the solution is cooled.

When an alcoholic solution of mercuric chloride is added to the arsonium bromide, dissolved in the same solvent, a crystalline addition product is obtained; m. p. 167–168°.

Chloride.—Five grams of the arsonium bromide was recrystallized three times from a hot mixture of 15 cc. of concd. hydrochloric acid and 5 cc. of water. The chloride–hydrochloric acid addition product, which separated in the form of long, glistening needles, was filtered on a Jena filter. A titration indicated that this product has the composition $(C_6H_5)_4AsCl{\cdot}HCl$: 0.3275 g. of the material required 8.5 cc. of 0.07788 *N* sodium hydroxide solution for neutralization; calcd., 9.2 cc. The addition product, dissolved in hot water, was boiled with charcoal, the mixture filtered and the aqueous acidic filtrate neutralized with sodium carbonate. The solution was evaporated to dryness, the residue extracted with absolute alcohol, the alcohol removed from the extract and the residue rubbed under absolute ether. The product was dissolved in the least possible amount of absolute alcohol or ethyl acetate and precipitated by the addition of absolute ether; m. p. 256–257°.

Anal. Calcd. for $C_{24}H_{20}AsCl$: As, 17.90; Cl, 8.47. Found: As, 17.64; Cl, 8.41.

Iodide.—The iodide, obtained by interaction of phenylmagnesium iodide and triphenylarsine oxide and subsequent addition of hydriodic acid to the reaction mixture, is contaminated by a small amount of the arsonium triiodide, hence the material should be recrystallized from water which contains sodium hydroxide.

The colorless iodide melts at 312–313°, the reddish-brown iridescent triiodide at 228–230° with decomposition; the latter can be recrystallized, in small amounts, from alcohol.

Anal. Calcd. for $C_{24}H_{20}AsI$: As, 14.69; I, 24.88. Found: As, 14.75; I, 24.83. Calcd. for $C_{24}H_{20}AsI_3$: As, 9.81; I, 49.84. Found: As, 9.81; I, 49.26.

Diphenylarsine Trichloride and Phenylmagnesium Bromide (A, A′).—Phenylmagnesium bromide was prepared from 4.9 g. of bromobenzene, 0.77 g. of magnesium and 30 cc. of ether, most of the ether removed and 4.8 g. of diphenylarsine trichloride,[9] dissolved in 75 cc. of hot, dry benzene, added. The mixture was stirred, heated for one hour, decomposed with 20 cc. of water, 50 cc. of hydrobromic acid (48%) added and the benzene layer decanted. The crystalline tetraphenylarsonium bromide, suspended in the aqueous layer, weighed 1 g.; m. p. 273–275°. The solvent was removed from the decanted benzene layer and the triphenylarsine residue dissolved in absolute ether. Upon the addition of mercuric chloride, dissolved in ether, 5.6 g. of the compound $(C_6H_5)_3As{\cdot}HgCl_2$ precipitated; m. p. 247–248°.

Triphenylarsine Dichloride and Phenylmagnesium Bromide (B, B′).—The ether was removed from a solution of phenylmagnesium bromide, prepared from 12.6 g. of bromobenzene, 1.9 g. of magnesium and 40 cc. of ether and 5 g. of triphenylarsine dichloride,[10] dissolved in 40 cc. of hot benzene added. The mixture was heated and stirred for several hours and 20 cc. of water added. Upon the addition of 50 cc. of hydrobromic acid no arsonium bromide was obtained. The benzene layer was separated, washed with water and the solvent removed. From the residue there was obtained 3.7 g. of triphenylarsine, isolated as the mercuric chloride addition product.

Anhydride of Phenylarsonic Acid and Phenylmagnesium Bromide (C).—In the manner described above 4.6 g. of the anhydride,[11] suspended in hot benzene, was allowed to react with phenylmagnesium bromide, prepared from 19.6 g. of bromobenzene, 3.0 g. of magnesium and 50 cc. of ether. After the addition of 50 cc. of hydrobromic acid a brown oil was obtained. The latter was boiled with dilute sodium hydroxide solution, filtered, the hot filtrate treated with charcoal and the mixture filtered again; when the solution was cooled 2.0 g. of tetraphenylarsonium bromide was obtained; m. p. 272–274°.

Triphenylarsine Oxide and Methylmagnesium Iodide.—Methylmagnesium iodide was prepared from 14.2 g. of methyl iodide, 2.4 g. of magnesium and 30 cc. of ether. Most of the ether was removed and 12 g. of the arsine oxide, dissolved in 225 cc. of benzene, added. The mixture was heated, stirred for one hour, decomposed with 60 cc. of water and 50 cc. of hydriodic acid (sp. gr. 1.50) added. The water and benzene layers were decanted and the viscous red oil dissolved in 35 cc. of alcohol. The solution was treated with 14 g. of iodine, dissolved in alcohol. The crystalline, highly iridescent, permanganate colored precipitate obtained weighed 15.4 g.; m. p. 108–109° after three recrystallizations from alcohol. This compound, methyltriphenylarsonium triiodide, was shown to be identical with the iodide obtained by the addition of iodine to methyltriphenylarsonium iodide. Moreover, when the arsonium triiodide was dissolved in hot alcohol, treated with sodium hydroxide solution, the alcohol allowed to evaporate and the residue recrystallized from alcohol, methyltriphenylarsonium iodide was obtained; m. p. 173–174°.[12]

Summary

The preparation of tetraphenylarsonium chloride, bromide and iodide has been described. The chloride has been tested physiologically and electrochemical experiments prove that it is a strong electrolyte.

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[9] La Coste and Michaelis, *Ann.*, **201**, 184 (1880); Steinkopf and Schmidt, *Ber.*, **61**, 676 (1928).

[10] Michaelis, *Ann.*, **321**, 162 (1902).

[11] Michaelis, *Ber.*, **10**, 626 (1877).

[12] Michaelis [*Ann.*, **321**, 166 (1902)] reported the melting point to be 176°.