

223. Tetra-aryl Phosphonium, Arsonium, and Stibonium Salts. Part I. A New Method of Preparation.

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It is shown that tetraphenylarsonium salts can be obtained by the interaction of aluminium chloride with (i) arsenic trichloride and benzene, (ii) phenyldichloroarsine, (iii) diphenylchloroarsine, (iv) triphenylarsine, (v) triphenylarsine and bromobenzene, the highest yield being obtained in (v). Tetraphenyl-phosphonium and -stibonium salts can also be obtained by methods analogous in particular to (v). The mechanism of the reactions is still under investigation.

DODONOV and MEDOX (*Ber.*, 1928, **61**, 907) obtained tetraphenylphosphonium bromide by the interaction of triphenylphosphine and phenylmagnesium bromide in ethereal solution: the yield was 13–14% in presence of air, 72% in presence of oxygen, and only 5% in a hydrogen atmosphere. If oxidation is an essential stage in the reaction, it does not apparently proceed through triphenylphosphine oxide, since no yield of the bromide was obtained when this oxide was used in place of the phosphine itself.

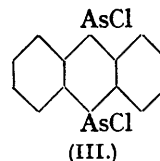
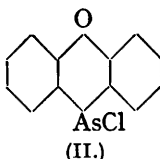
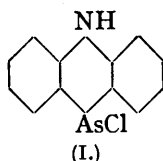
Blicke and his co-workers (*J. Amer. Chem. Soc.*, 1933, **55**, 3056; 1935, **57**, 720; 1939, **61**, 88) obtained tetraphenylarsonium bromide by the interaction of triphenylarsine oxide and phenylmagnesium bromide; the arsonium bromide was also obtained, although in smaller yield, by the action of the Grignard reagent on diphenylarsenic trichloride (AsPh_2Cl_3) and on phenylarsonic acid anhydride (AsPhO_2), but not by the action of the Grignard reagent on triphenylarsine dichloride (AsPh_3Cl_2). The arsonium salt resembled the phosphonium compound in forming a strong electrolyte in aqueous solution.

We have discovered a method by which these phosphonium and arsonium salts can be prepared without the use of a Grignard reagent, and which has also furnished the hitherto unknown tetra-arylstibonium salts. The arsenic compounds will be considered first, since they have been investigated in the greatest detail.

It is known that diphenylamine condenses readily with arsenic trichloride to give 10-chloro-5 : 10-dihydrophenarsazine (I) (F. Bayer & Co., D.R.P. 281049; Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1), and that diphenyl ether similarly condenses with arsenic trichloride in the presence of aluminium chloride to give 10-chlorophenoxarsine (II) (Lewis, Lowry, and Bergheim, *J. Amer. Chem. Soc.*, 1921, **43**, 892).^{*} It appeared

^{*} The preparation of the compounds (I) and (II) was, of course, investigated in detail during 1917 and 1918 by British chemists, who were the first to synthesise (II). The above references are, however, the earliest available in the literature.

probable that diphenylchloroarsine would condense with arsenic trichloride under the influence of aluminium chloride to give "arsanthrene chloride" (or 5 : 10-dichlorodihydro-



arsanthren) (III), a synthesis which would have been much shorter than that of Kalb (*Annalen*, 1921, 423, 74). It was found, however, that a mixture of these three compounds when heated ultimately to 280° afforded a deposit of elementary arsenic, and that when a hot aqueous extract of the final product was treated with potassium iodide, the slightly soluble tetraphenylarsonium iodide was precipitated. No evidence of the compound (III) could be obtained.

This remarkable reaction clearly involves ultimately the migration of two phenyl groups from one arsine molecule to another; it is, however, an even more complicated reaction, since free benzene was evolved during the reaction. We have therefore investigated the interaction of aluminium chloride and various phenylarsines: the results are summarised in the accompanying table. In each of these experiments 10 g. of aluminium chloride

Reactants.	Yield of crude Ph ₄ AsI, g.	Yield, %, calc. on Ph groups present.	As converted to Ph ₄ As ion, %.
(1) AlCl ₃ + AsCl ₃ + 3C ₆ H ₆	2.0	22	16
(2) AlCl ₃ + AsPhCl ₂	2.9	53	13
(3) AlCl ₃ + AsPh ₂ Cl	7.0	73	36
(4) AlCl ₃ + AsPh ₃	5.0	41	30
(5) AlCl ₃ + AsPh ₃ + C ₆ H ₅ Br	9.0	54	54

were used. Expt. 1 differs from the others in that a phenylarsine was not initially used, but 10 g. of a mixture of arsenic trichloride (1 mol.) and benzene (3 mols.) were boiled with the aluminium chloride under reflux for 6 hours, and the temperature then increased to 280° for 1 hour, any unchanged benzene being allowed to escape through the reflux air condenser. In Expts. 2—5, 10 g. of the requisite phenylarsine were employed, and in Expt. 5, 1 mol. of bromobenzene was added to the 10 g. of arsine. In all these four experiments, the mixture was heated under reflux for 1 hour at 200°, and the temperature then gradually increased to 280° for 1 hour more. The yield of tetraphenylarsonium iodide, obtained by adding potassium iodide to the filtered aqueous extract of the final product, is given in Col. 2. These yields form the only reliable guide to the progress of the reaction; in view of the complicated reaction which must occur, no strictly comparable percentage yields can be calculated. For general interest, however, the percentage yield, based on the assumption that all the phenyl groups available entered the tetraphenylarsonium ion, are given in Col. 3: it must be borne in mind, however, that this assumption is not justifiable, since free benzene was certainly eliminated in Expt. 3, and possibly in all the others. In Col. 4 is recorded the percentage of the total arsenic converted into the arsonium ion; it is only in Expt. 5, however, where 1 mol. of bromobenzene was present, that there were sufficient phenyl groups available to convert all the arsenic into the ion. It is noteworthy that, when Expt. 5 was repeated with an excess of bromobenzene to act as a general solvent, the yield of the arsonium iodide fell to 6.5 g.

Considerable further investigation is required before the mechanism of the formation of the arsonium ion in all these experiments is elucidated. It is already clear, however, that free phenyl radicals must be formed in all cases and must migrate to certain arsenic atoms or residues. This is confirmed by Expt. 5, where the bromobenzene, presumably under the influence of the aluminium chloride, furnished the phenyl radical for direct addition to the triphenylarsine, with the resulting high yield of the arsonium ion.

This is further confirmed by the results with the phosphorus derivatives. When aluminium chloride and triphenylphosphine were heated first to 230° and finally to 280°, and

the product treated as before, no tetraphenylphosphonium iodide was obtained. When, however, 1 mol. of bromobenzene was added to the reaction mixture and the experiment repeated, a comparatively high yield of the phosphonium *iodide* was obtained, and the function of the bromobenzene in providing the necessary phenyl radical was again demonstrated. A large excess of bromobenzene, on the other hand, reduced the yield of the phosphonium salt to a negligible amount, possibly by affecting adversely the temperature of the reaction mixture. No experiments were made on the effect of aluminium chloride on phenyldichloro- and diphenylchloro-phosphine; such experiments would probably have failed in view of the negative result obtained with triphenylphosphine; moreover, a boiling mixture of aluminium chloride, phosphorus trichloride, and benzene is known to interact to give solely phenyldichlorophosphine, although the arrest at this stage may again be due to the comparatively low temperature employed.

Similar results were obtained with antimony derivatives. A mixture of aluminium chloride, triphenylstibine, and 1 mol. of bromobenzene, heated to 230° and then treated as before with potassium bromide or iodide, gave *tetraphenylstibonium bromide* or *iodide* in even higher yield than that of the phosphonium salt under similar conditions; when, however, the bromobenzene was omitted, the yield of the stibonium salt was considerably reduced. The presence of a considerable excess of bromobenzene in the reaction mixture almost completely inhibited the reaction, as in the case of the phosphonium derivatives. Furthermore, a mixture of aluminium chloride, triphenylstibine dibromide, and benzene, when heated under reflux for 4 hours, also gave no stibonium ion.

In view of these results, attempts were made to utilise this method for the preparation of tetraphenylammonium salts, although it was recognised that the chance of success was small: a mixture of aluminium chloride, triphenylamine, and either bromo- or iodo-benzene, when heated under various conditions, gave no indication of the formation of the required ammonium ion. Similarly, a mixture of aluminium chloride, pyridine, and bromobenzene gave no evidence of the formation of phenylpyridonium ion. Finally, when the pyridine was replaced by triphenylbismuthine, no tetraphenylbismuthonium salt could be isolated, a result which was not unexpected in view of the known reluctance of bismuth to become 4-covalent.

The foregoing preparative method has a rather similar counterpart in the selenium series. Hilditch and Smiles (J., 1908, **93**, 1384) showed that aluminium chloride, selenium dioxide, and phenetole react at 100° to give the triphenetylselenonium ion, and Leicester and Bergstrom (J. Amer. Chem. Soc., 1929, **51**, 3587) showed that aluminium chloride, diphenylselenium dichloride, and benzene react in the cold to give triphenylselenonium chloride.

We hope to elucidate the mechanism of the reaction which gives (in particular) the tetra-arylarsonium salts by the use of mixed radicals as indicator groups, and also to utilise the reaction for the preparation of aryls*piro*arsonium derivatives.

EXPERIMENTAL.

Tetraphenylarsonium Salts.—*Expt. 1.* A mixture of powdered dry aluminium chloride (10 g.), arsenic trichloride (4.4 g., 1 mol.), and benzene (5.6 g., 3 mols.) was boiled under reflux for 6 hours, and then heated at 280° for 1 hour in a metal-bath. During this heating, reddish-brown arsenic rapidly separated. The product was mixed with cold water (200 c.c.) and the mixture boiled (charcoal), filtered, and when cold treated with potassium iodide (10 g.) dissolved in a few c.c. of water. The crude, yellow tetraphenylarsonium iodide (2 g.) which separated was purified by recrystallisation from hot water containing a small quantity of potassium iodide and sodium sulphite (1–2 g.) to reduce any arsonium tri-iodide. (If too much potassium iodide is added, the arsonium iodide becomes almost insoluble. The sodium sulphite was used in excess because of the stable nature of the tri-iodide.) The filtrate on cooling deposited the iodide as white needles, m. p. 314–319° (decomp.) (Found: C, 56.0; H, 4.05; I, 24.7. Calc. for $C_{24}H_{20}IAs$: C, 56.5; H, 3.9; I, 24.9%). Concentration of the original filtrate, followed by treatment with potassium bromide solution, caused the separation of beautiful, white, hydrated needles of the arsonium bromide, which, after recrystallisation from water, required heating at 200° for $\frac{1}{2}$ hour for complete dehydration, and then had m. p. 277–281° (Found:

Br, 17.2. Calc. for $C_{24}H_{20}BrAs$: Br, 17.3%). Blicke and Monroe (*loc. cit.*) give 312—313° and 273—275° for the m. p.'s of the iodide and bromide respectively.

Expts. 2—5. In these experiments, aluminium chloride (10 g.) and the phenylarsine compound (10 g.) were used throughout, and in Expt. 5 bromobenzene (5.2 g., 1 mol.) was also added. In these four experiments, the mixture was heated directly at 200° under a reflux air condenser for 1 hour, vigorous boiling usually occurring at first and later subsiding; finally the temperature was raised to 280° during $\frac{1}{2}$ hour, and then maintained at this value for a further $\frac{1}{2}$ hour. The product was then poured into 400 c.c. of water, and the mixture treated as in Expt. 1, a rather larger quantity of sodium sulphite (3—4 g.) being added, however. In Expt. 3, vapours issuing from the reflux condenser were passed through a water condenser, and almost pure benzene (*ca.* 1.5 g.) was collected. In the other experiments, no attempts were made to collect volatile by-products. The yields of the arsonium iodide, recorded in the table, show clearly that Expt. 5 provides the best conditions.

Expt. 5 was repeated, but 52 g. (10 mols.) of bromobenzene were used; the mixture was heated under reflux for 3 hours and the aqueous extract finally boiled to remove excess of bromobenzene; the yield of crude arsonium iodide was now only 6.5 g.

In all these experiments, the arsonium iodide was precipitated because its very low solubility in cold water enabled its yield to be accurately determined. It is, however, liable to be discoloured by traces of the tri-iodide, and for general purposes precipitation of the white, crystalline and rather more soluble bromide is to be preferred.

Tetraphenylphosphonium Salts.—(1) A mixture of aluminium chloride (10 g.), triphenylphosphine (10 g.), and bromobenzene (6 g., 1 mol.) was heated under an air reflux at 230° for 2 hours, and then at 280° for 1 hour more. The reaction mixture was poured into water (400 c.c.) and then worked up precisely as for the arsonium iodide. The crude *tetraphenylphosphonium iodide* (8.2 g.) separated as a yellow solid, m. p. 326—339° (some decomp.). Recrystallisation from water containing a small quantity of sodium sulphite ultimately gave the phosphonium iodide as colourless needles, m. p. 333—343°, which became pale yellow on standing for a few days (Found: C, 61.3; H, 4.4; I, 27.5. $C_{24}H_{20}IP$ requires C, 61.8; H, 4.3; I, 27.2%. Low carbon values were always obtained). Dodonov and Medox (*loc. cit.*) give m. p. 333° for this compound, but do not give analyses.

(2) This experiment was repeated, but with 40 c.c. of bromobenzene, the mixture being boiled under reflux for 2 hours and the excess of bromobenzene being finally removed by boiling the aqueous extract. Yield of crude phosphonium iodide, 0.5 g.

(3) A further repetition, in which the bromobenzene was omitted but the conditions were otherwise identical with those in (1), gave no phosphonium iodide.

Tetraphenylstibonium Salts.—(1) A mixture of aluminium chloride (10 g.), triphenylstibine (10 g.), and bromobenzene (4.5 g., 1 mol.) was heated at 230° for $1\frac{1}{2}$ hours, and then poured into water (600 c.c.). The mixture was boiled until only a small black deposit remained, and the solution, after addition of charcoal, was filtered hot. Potassium bromide (20 g.) in hot concentrated aqueous solution was then added, and on cooling the *tetraphenylstibonium bromide* (8.2 g., m. p. 200—213°) separated. Recrystallisation from water occurred readily but was not satisfactory, as the bromide then often contained some slight impurity. Crystallisation from alcohol (charcoal) gave the stibonium bromide as colourless crystals (3.8 g.), m. p. 210—218°, the range depending mainly on the speed of heating (Found: C, 56.5; H, 4.4; Br, 15.5. $C_{24}H_{20}BrSb$ requires C, 56.5; H, 4.0; Br, 15.7%). Addition of ether to the alcoholic mother-liquor precipitated a second crop of pure bromide.

(2) When the bromobenzene in the above reaction mixture was increased to 40 c.c., only a minute quantity of the stibonium bromide was obtained.

(3) When the bromobenzene was omitted, and the experiment otherwise performed precisely as in (1), the initial crop of crude stibonium bromide weighed only 2.2 g.

(4) Bromine (1.4 g., 1 mol.) was added with shaking to a solution of triphenylstibine (3 g.) in benzene (10 c.c.), a precipitate of the stibine dibromide being formed. Aluminium chloride (3 g.) was then added, and the mixture boiled under reflux for 4 hours. No hydrogen chloride or bromide was evolved, and no stibonium salt could be isolated.

(5) A mixture of aluminium chloride (10 g.), antimony chloride (5 g.), and benzene (5 g.) was boiled under reflux for 6 hours and then heated to 210° for 1 hour. After the usual extraction, only a trace of stibonium bromide could be isolated.

Tetraphenylstibonium iodide. Addition of potassium iodide to the aqueous extract obtained in (1) (above) always gave an impure sample of this compound. The *iodide* is best prepared as follows. A hot solution of potassium iodide (2 g.) in water (50 c.c.) was added to one of the

stibonium bromide (2 g.) also in hot water (200 c.c.), and the iodide separated as colourless needles, which were recrystallised from water, and had m. p. *ca.* 200°, dependent on the rate of heating (Found : I, 22·45. $C_{24}H_{20}ISb$ requires I, 22·8%).

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