

CLXXXVIII.—As-Chlorotetrahydroarsinoline and Some Quaternary Arsonium Compounds.

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As-METHYLTETRAHYDROARSINOLINE (Burrows and Turner, J., 1921, **119**, 426) readily forms a *dichloride*, which, when heated, is smoothly decomposed to give As-chlorotetrahydroarsinoline, the first simple cyclic chloroarsine of this series to be prepared.

Attempts to prepare arsinolines and arsinoles (or the corresponding intermediate compounds) are described in this paper.

The alternation in the physical properties of a series of benzene derivatives having normal side-chains is a subject of considerable interest. The following table shows that there is a marked alternation in the melting points of the first five members of the series of methiodides of the general formula $\text{Ph}\cdot[\text{CH}_2]_x\cdot\text{AsMe}_3\text{I}$.

$\text{Ph}\cdot\text{AsMe}_3\text{I}$	252°	$\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{AsMe}_3\text{I}$	144°
$\text{Ph}\cdot\text{CH}_2\cdot\text{AsMe}_3\text{I}$	194—195	$\text{Ph}\cdot[\text{CH}_2]_4\cdot\text{AsMe}_3\text{I}$	150—151
$\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{AsMe}_3\text{I}$	203—204*		

* Previously given (Turner and Bury, J., 1923, **123**, 2489) as 200°.

There is also a marked difference in the ease with which the five arsines of the type $\text{Ph}\cdot[\text{CH}_2]_x\cdot\text{AsMe}_2$ are prepared by the interaction of the appropriate Grignard reagent and dimethyl-iodoarsine. The respective percentage yields of phenyl-, phenylpropyl-, phenylbutyl-, phenylethyl-, and benzyl-dimethylarsine were 80, 65, 45, 45 (97*), and 20. We regard a low yield as being due to a high tendency, on the part of the arsine, to undergo oxidation, and conversely; we have, however, not conducted quantitative measurements on the subject.

[With F. W. BURY.] In view of the success achieved by Rosenheim and Plato (*Ber.*, 1925, **58**, 2000) and by Mills and Raper (J., 1925, **127**, 2479), experiments on the resolution of arsenic compounds in progress in this laboratory have been discontinued. Two asymmetric types were under examination; it has been found

* Preparation carried out in an inert atmosphere (Turner and Bury, *loc. cit.*).

impossible to resolve cyclohexylphenylbenzylmethylarsonium *d*- α -bromocamphor- π -sulphonate and the phenylbenzylarsinates of strychnine and *l*-menthylamine. One or two compounds prepared incidentally are, however, now described.

EXPERIMENTAL.

γ -Phenylpropyldimethylarsine.—The dimethyliodoarsine required for this preparation (Burrows and Turner, *loc. cit.*) is most conveniently obtained by passing sulphur dioxide into a solution containing 225 g. of cacodylic acid, 450 g. of potassium iodide, 150 g. of concentrated sulphuric acid, and 1850 c.c. of water. *γ -Phenylpropyldimethylethylarsonium iodide* is formed fairly readily from the arsine and methyl iodide, and separates from alcohol-ether in colourless leaflets, m. p. 118° (Found: I, 33.3. $C_{13}H_{22}IA_s$ requires I, 33.4%).

γ -Phenylpropylmethylchloroarsine was heated at 200° in a current of dry carbon dioxide, but although it underwent considerable apparent change, no hydrogen chloride was evolved. This is in interesting contrast to the ease with which *o*-phenoxyphenyl-dichloroarsine passes into 10-chlorophenoarsine (Roberts and Turner, *J.*, 1925, **127**, 2004).

Derivatives of As-Methyltetrahydroarsindole.—The methiodide melts at 239–240°, not at 235°, as previously recorded. The ethiodide is less readily formed than the methiodide, and separates from ether-alcohol in colourless prisms, m. p. 185–186° (Found: I, 34.8. $C_{12}H_{18}IA_s$ requires I, 34.9%). The benzobromide is formed as a glassy mass when the components are warmed together, and is difficult to purify. It crystallises from ether-alcohol in colourless prisms, m. p. 210–211° (Found: Br, 19.9. $C_{17}H_{20}BrAs$ requires Br, 21.1%).

When the arsinoline was treated with 1 mol. of bromine, and the product with alkali, no *As*-oxide could be detected. The main product was γ -phenylpropyl bromide.

As-Chlorotetrahydroarsinoline.—*As*-Methyltetrahydroarsinoline (20 g.) was dissolved in carbon tetrachloride, and a current of dry chlorine allowed to impinge on the surface of the solution. The white solid *dichloride* separated rapidly, and when a slight excess of chlorine was present the mixture was rendered colourless by addition of a drop of arsinoline. The carbon tetrachloride was removed by distillation, and the residue distilled under diminished pressure. Evolution of methyl chloride was regular and rapid, and as soon as it was complete a preliminary fraction distilled at 120–150°/21 mm., and then the whole of the residue at 155°/16 mm. (16 g.). The latter crystallised on cooling, to give large, irregular, hexagonal

rhombs, m. p. 22° , and was pure *As-chlorotetrahydroarsinoline* (Found: Cl, 15.4. $C_9H_{10}ClAs$ requires Cl, 15.5%).

When a solution of the chloroarsine in diethylaniline was boiled for 5 hours, marked decomposition occurred, but no 3:4-dihydroarsinoline was isolated from the product. A small quantity of an arsine was formed, since the distilled product combined or reacted with methyl iodide.

Benzyl dimethylarsine.—Magnesium benzyl chloride reacted smoothly with one equivalent of dimethyliodoarsine. The product was worked up in the usual manner. The final ethereal solution remained clear while being dried over sodium sulphate, but, when filtered, became cloudy. This was due to oxidation and not to the presence of an additive compound with dimethyliodoarsine, since the ethereal solution had, in accordance with usual practice, been washed with alkali. The arsine was finally obtained as a colourless liquid, b. p. $110^{\circ}/8$ mm. The yield (20%) would probably be improved by carrying out all the operations in an inert atmosphere (compare Turner and Bury, *loc. cit.*).

The *methiodide* is formed readily, and separates from alcohol in colourless leaflets, m. p. 195 — 196° (Found: I, 37.4. $C_{10}H_{16}IAs$ requires I, 37.6%). The *ethiodide*, formed moderately readily, crystallises from alcohol-ether in colourless leaflets, m. p. 163 — 165° (Found: I, 36.3. $C_{11}H_{18}IAs$ requires I, 36.1%).

*δ -Phenyl-*n*-butyl dimethylarsine*.—This was prepared from γ -phenylpropyl bromide, *via* the corresponding nitrile (von Braun, *Ber.*, 1910, **43**, 2843; Rupe, *Annalen*, 1912, **395**, 87), δ -phenyl-*n*-butyl alcohol, and δ -phenyl-*n*-butyl bromide (von Braun, *Ber.*, 1911, **44**, 2871).

The bromide readily formed a Grignard reagent; this reacted smoothly with dimethyliodoarsine to give a product which, after the usual treatment, including washing with alkali, afforded the arsine as a colourless liquid, b. p. $150^{\circ}/14$ mm. (yield, 45%).

The *methiodide* is very readily formed, and is sparingly soluble in alcohol, from which it crystallises in colourless leaflets, m. p. 150 — 151° (Found: I, 33.0. $C_{13}H_{22}IAs$ requires I, 33.4%).

The *ethiodide*, formed moderately easily, separates from alcohol in leaflets, m. p. 134 — 135° (Found: I, 32.5. $C_{13}H_{24}IAs$ requires I, 32.2%).

Phenyl- β -phenylethyl methylarsine.—This substance was readily obtained by the interaction of magnesium β -phenylethyl bromide and phenylmethyliodoarsine in ethereal solution. When the ethereal extract of the arsine, obtained by the usual method, was evaporated, a considerable quantity of a gummy solid separated. This was removed before distilling the arsine under diminished

pressure. *Phenyl-β-phenylethylmethylarsine* is a colourless liquid boiling at 187°/12 mm. and 190°/15 mm., and was obtained in 82% yield.

The *methiodide* is formed readily, and crystallises from water in rhombohedra or prisms, m. p. 119° (Found: I, 30·5. C₁₆H₂₀IAs requires I, 30·6%).

Action of β-Phenylethyl Bromide on Arsenites and Arsinites.—

(a) *On sodium arsenite.* A solution of arsenious oxide (0·5 mol.) in aqueous sodium hydroxide (3 mols.) was boiled with the bromide for several days, under reflux. Some bromide was recovered unchanged, and no arsenic acid could be detected in the product.

(b) *On sodium arsenite in presence of copper bronze.* The bromide was stirred and heated at 140—180° for 7 hours in presence of dry sodium arsenite (Kahlbaum) and copper bronze. No change was observed.

(c) *On potassium methylarsinite.* An aqueous-alcoholic solution containing methylarsenious oxide (1 mol.), potassium hydroxide (2 mols.), and the bromide (1 mol.) was boiled under reflux for 2 days. Styrene, but no arsenic acid, was formed.

[With F. W. BURY.] *Dicyclohexylphenylarsine.*—This was prepared by adding phenyldichloroarsine to a solution of magnesium cyclohexyl bromide, the reaction product being worked up in the usual manner. The arsine is a colourless liquid, b. p. 220°/14 mm. The *methiodide* and *ethiodide* are formed readily and crystallise from alcohol-ether in prisms, m. p. 187° (Found: I, 27·5. C₁₉H₃₀IAs requires I, 27·6%), and plates, m. p. 188—189° (Found: I, 26·6. C₂₀H₃₂IAs requires I, 26·8%), respectively.

Tricyclohexylarsine.—When arsenious iodide was added to an ethereal solution of magnesium cyclohexyl chloride or bromide, only half of the calculated quantity reacted. The arsine was, however, obtained mixed with a little dicyclohexyl as a colourless oil, b. p. 235°/12 mm. The *methiodide* was formed readily and crystallised from water in prisms, m. p. 153—154°. The *benzobromide* melts at 197° with slight decomposition (Found: Br, 16·2. C₂₅H₄₀BrAs requires Br, 16·2%).

cycloHexylphenylmethylarsine.—A Grignard reagent prepared from 24 g. of cyclohexyl chloride was treated with phenylmethyl-iodoarsine until the yellow colour of the latter persisted, *i. e.*, when about 75% of the iodo-compound had been added. The reaction product was worked up as usual, and gave 30 g. of *cyclohexylphenylmethylarsine* as a highly refractive oil, b. p. 152—153°/12 mm., having no marked tendency to oxidise.

When the arsine was heated at 100° with one equivalent of benzyl bromide and a little alcohol, large, colourless crystals began to form, but subsequently disappeared. On cooling, only a little white

powder separated, and crystallisation was induced by addition of excess of ether. *cycloHexylphenylbenzylmethylarsonium bromide* was thus obtained; recrystallised from alcohol-ether, it formed rectangular plates, m. p. 193° (Found: Br, 19.0. $C_{20}H_{26}BrAs$ requires Br, 19.0%).

The corresponding *d- α -bromocamphor- π -sulphonate* was prepared. The crude material melted at 109–113°, and crystallisation experiments gave unpromising results, mixtures of crystalline, amorphous, and gel-like material being obtained.

Phenylbenzylarsinic Acid.—Excellent yields of this acid are obtained by the following method, which is more expeditious than that described by Berthelm (*Ber.*, 1915, **48**, 350): Crude phenylarsenious oxide (75 g.) as obtained from phenyldichloroarsine and sodium hydroxide was dissolved in 150 c.c. of methylated spirit. Sodium hydroxide (36 g.) in 52 c.c. of water was added. To the hot solution, 60 g. of benzyl chloride were added gradually, keeping the initial vigorous reaction in progress. Sodium chloride separated at once. The mixture was left until cold, freed from alcohol by distillation, acidified, and the resulting precipitate of acid washed with water and ether.

Strychnine Phenylbenzylarsinate.—This salt was prepared by mixing hot alcoholic solutions of the base and the acid, and formed colourless needles (Found: N, 4.5; As, 11.4, 11.4.

$C_{21}H_{22}O_2N_2, C_{13}H_{13}O_2As, 3H_2O$
requires N, 4.2; As, 11.3%). It had $[\alpha]_D^{20} = -31.2^\circ$ in 50% aqueous acetone, and when crystallised from this solvent gave a mixture of free acid and strychnine salt. When hot alcoholic solutions of strychnine (1 mol.) and the acid (2 mols.) were mixed, the free acid separated first.

1-Menthylamine Phenylbenzylarsinate.—Equivalent quantities of the base and acid were together dissolved in alcohol, and the solution was allowed to evaporate in a vacuum over sulphuric acid. The whole set to a mass of hairy needles. These were collected, dissolved in benzene, and the solution treated with light petroleum; a crystalline precipitate was obtained, which consisted of a mixture of base and acid.

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