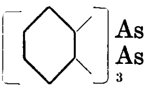
CCLXVI.—*Organic Compounds of Arsenic. Part III. Tri-*o*-phenylenediarsine.*

By Nial Patrick McCleland and James Bell Whitworth.

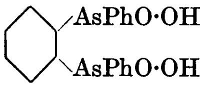
Tri-*o*-phenylenediarsine (I) appears to be the first compound in which it is established that a pair of atoms is linked to each of three benzene rings in the ortho-position in such a way that, a symmetrical grouping being assumed, the planes of the rings are inclined at 120° to one another.

A substance, $C_{18}H_{12}N_2$, described in the literature as triphenylenediamine was obtained by von Dechend and Wichelhaus (*Ber.*, 1875, **8**, 1609) by the action of nitrobenzene on aniline or diphenylamine, but its constitution is unknown.

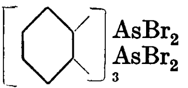
The new substance (I) was obtained as follows: Diazotised *o*-aminodiphenylarsinic acid coupled with phenylarsine oxide to give *phenylene*-1 : 2-*diphenylarsinic acid* (II), which was then reduced with phosphorus trichloride, presumably to phenylene-1 : 2-diphenylchloroarsine; this was not obtained in the pure state and on distillation it gave *tri*-o-*phenylenediarsine* (I), evidently by the loss of two molecules of hydrogen chloride and consequent double ring closure.



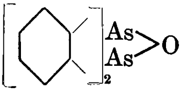
(I.)



(II.)



(III.)



(IV.)

The constitution of the substance (I) is supported by the following observations, which show that triphenylenediarsine bears the same relation to the derivatives of arsanthrene (Kalb, *Annalen*, 1921, **423**, 39) as the triarylarsines do to those of the diarylarsines: (1) as triphenylarsine dichloride decomposes on distillation into diphenylchloroarsine and chlorobenzene (La Coste and Michaelis, *Annalen*, 1880, **201**, 242; Michaelis, *ibid.*, 1902, **321**, 142, 160; Winmill, J., 1912, **101**, 720), so triphenylenediarsine tetrabromide (III) on heating gives (in addition to bromine and triphenylenediarsine) *o*-dibromobenzene and arsanthrene bromide; (2) as di-*p*-tolylarsenious oxide on heating gives tri-*p*-tolylarsine (La Coste, *Annalen*, 1881, **208**, 20), so arsanthrene oxide (IV) on distillation gives triphenylenediarsine and arsenious oxide as indicated by the equation 3 (IV) = 2 (I) + As_2O_3 (compare the decomposition of phenylarsine oxide into triphenylarsine and arsenious oxide on heating; La Coste and Michaelis, *ibid.*, p. 239).

Moreover, the substance behaves as a tertiary arsine, being converted into the oxide by nitric acid and forming a tetrabromide and a mercurichloride.

Triphenylenediarsine is formed in the preparation of arsanthrene chloride by Kalb's method (*loc. cit.*) and probably accounts for the sparingly soluble impurity which he found in arsanthrene oxide.

The stereochemistry of the new system is under investigation, and it is hoped to prepare corresponding compounds with other elements in place of arsenic.

EXPERIMENTAL.

Phenylene-1 : 2-*diphenylarsinic Acid* (II).—Into a well-stirred, diazotised solution of *o*-aminodiphenylarsinic acid (20 g.; concentrated hydrochloric acid, 58 c.c.; water, 700 c.c.; ice, 500 g.) was run a solution of phenyldichloroarsine (18 g.) in 5*N*-caustic soda (64 c.c.) to which sodium acetate (58 g.), dissolved in ice-water (450 c.c.), had been added just previously. The mixture was made alkaline with caustic soda, boiled with charcoal, and filtered. On acidification, the filtrate gave a yellowish-brown, pasty precipitate. This was boiled with alcohol, which removed most of the coloured impurity, the residue was dissolved in a large volume of dilute aqueous ammonia, the solution neutralised with acetic acid and boiled with charcoal, and an excess of dilute acetic acid added to the boiling filtered solution; *phenylene*-1 : 2-*diphenylarsinic acid* (9 g.) then slowly separated in pale yellow, microscopic crystals which did not melt below 310° and were insoluble in water and in the usual organic solvents (Found: C, 49·0; H, 3·5. $C_{18}H_{16}O_4As_2$ requires C, 48·4; H, 3·6%).

Tri-o-*phenylenediarsine* (I).—Phenylene-1 : 2-diphenylarsinic acid (9 g.), suspended in chloroform (100 c.c.), was treated with excess of phosphorus trichloride (25 g.), heat being evolved and most of the acid dissolving. The solution was heated on the water-bath for 3 hours and filtered from a little tar. On distillation of the solvent a dark brown, oily residue was obtained from which no crystalline product could be isolated. It was therefore heated under reduced pressure; vigorous frothing occurred at 120—300°, and at 320—340°, crystals of *triphenylenediarsine* gradually sublimed on the upper part of the distilling flask, but no distillate was obtained. The crystalline product was collected and a further quantity was obtained on extracting the charred residue in the flask with hot benzene. On recrystallisation from benzene (charcoal), triphenylenediarsine (2·5 g.) was obtained in small, almost colourless plates, m. p. 295—296°. It is soluble in benzene, acetone, or light petroleum, readily soluble in chloroform, sparingly soluble in alcohol or ether, and insoluble in water. It can be sublimed without decomposition (Found: C, 57·4; H, 3·2; As, 40·1; *M*, in camphor by Rast's method, 360, 396, 364. $C_{18}H_{12}As_2$ requires C, 57·1; H, 3·2; As, 39·8%; *M*, 378).

The authors are indebted to Professor Hutchinson for the determination of the crystallographic constants:

System: Monoclinic (holohedral). $a : b : c = 1{\cdot}589 : 1 : -$; $\beta = 113°\ 15'$. Forms present: *a*(100), *c*(001), *m*(110). Angles observed: *am* 55° 35′, *ac* 66° 45′.

The crystals are elongated parallel to the axis of the zone [*am*] and are either tabular parallel to *a* with *m* and *c* small or bounded by *m* and *c* planes with *a* small or absent. The face *c* is invariably somewhat rounded. The optic axial plane is perpendicular to the plane of symmetry and lies in the obtuse axial angle. A negative acute bisectrix emerges obliquely from *a*. On viewing the crystal in monochromatic convergent light perpendicular to a pair of *m* faces, the emergence of an optic axis near the edge of the field can be seen. In white light, the dark brush passing through the centre of the ring system is replaced by brilliant red and blue fringes, indicating strong dispersion, and no extinction can be obtained on the *m* face in parallel light. The material available did not lend itself to an accurate determination of the optical constants, but β for sodium light was found to be 1·790 approximately.

The *mercurichloride* was obtained in short, colourless needles from the diarsine and mercuric chloride in cold acetone; after recrystallisation from alcohol, in which it was sparingly soluble, it melted at 285—286°. It was readily decomposed by warm dilute caustic soda solution.

The *oxide* was obtained on boiling the diarsine with concentrated nitric acid and pouring the resulting solution into water. It was readily soluble in alcohol and separated from dilute aqueous alcohol in short, thin, colourless needles, which did not melt below 360° (Found: C, 52·6; H, 3·0. $C_{18}H_{12}O_2As_2$ requires C, 52·7; H, 2·9%).

The *tetrabromide* (III) was precipitated as an orange-red, crystalline substance, m. p. 255—256°, when the diarsine was treated with a small excess of bromine in dry chloroform (Found: Br, 45·7.

$C_{18}H_{12}Br_4As_2$ requires Br, 45·9%). It is readily soluble in acetone or alcohol and in hot glacial acetic acid (with decomp.), sparingly soluble in chloroform, and insoluble in ether, benzene, or light petroleum. It is readily decomposed by dilute caustic soda solution or even by water, giving the colourless oxide (Found : As, 36·4. Calc. for $C_{18}H_{12}O_2As_2$: As, 36·7%).

When the tetrabromide was heated under reduced pressure (15 mm.), decomposition took place at about 260°, much bromine was evolved, and a small quantity of a yellow liquid distilled; the residue set to a crystalline mass on cooling. The liquid product was dissolved in ether, treated with caustic soda to remove free bromine, and distilled in a vacuum, being thus obtained as a colourless oil, b. p. 104—105°/15 mm., 224°/ordinary pressure (Found : Br, 68·2. Calc. for $C_6H_4Br_2$: Br, 67·8%). On intensive cooling, the liquid set to a colourless solid, m. p. 4°. It was concluded that the liquid was *o*-dibromobenzene, which has b. p. 224° and m. p. 5·6°. (The *m*-isomeride has b. p. 220° and m. p. − 7°, and the *p*-isomeride, m. p. 87°.)

As it would probably have been difficult to separate the small amount of arsanthrene bromide from the triphenylenediarsine by recrystallisation, the crystalline residue was treated with alcoholic ammonia to convert the arsanthrene bromide into the oxide. After dilution with water, the product was collected and extracted with hot alcohol, the portion remaining undissolved consisting of triphenylenediarsine, which after recrystallisation from benzene gave m. p. and " mixed m. p." 295—296°. The cooled alcoholic extract was filtered from a small amount of the diarsine which had separated and was then concentrated. Arsanthrene oxide, which separated on cooling, crystallised from alcohol in small, lustrous plates which, alone or mixed with pure arsanthrene oxide, melted at 194—195°.

The presence of bromide in the ammoniacal liquor was verified.

Treatment of triphenylenediarsine with chlorine yielded a light yellow compound, which has not been investigated. Methyl iodide gave no addition compound on prolonged heating with the diarsine in a sealed tube at 50—60°.

Formation of Triphenylenediarsine from Arsanthrene Oxide.— Pure arsanthrene oxide distilled under 15 mm. pressure, without appreciable decomposition, as a yellow liquid, which rapidly solidified. When, however, the pure oxide was distilled in a current of carbon dioxide under only slightly reduced pressure, considerable decomposition took place. Arsenious oxide sublimed into the receiver, and a crystalline substance on the upper part of the distilling flask. The crystalline product was extracted with hot alcohol to remove any unchanged oxide and then recrystallised from benzene, from which it separated in small, colourless plates, m. p. 295—296°, and at the same temperature after mixture with pure triphenylenediarsine. The dark brown residue in the distilling flask gave a further small quantity of the diarsine on extraction with benzene.

Triphenylenediarsine appears to be formed during the distillation of arsanthrene chloride, for, when arsanthrene chloride prepared by Kalb's method (*loc. cit.*) was converted into the oxide by alcoholic ammonia, and the oxide crystallised from alcohol, a small quantity of triphenylenediarsine remained undissolved. It separated from benzene in small, colourless plates, m. p. and " mixed m. p. " with the pure diarsine 295—296° (Found : C, 57·3 ; H, 3·1%), and on oxidation with nitric acid it gave triphenylenediarsine oxide as fine needles (Found : C, 52·7 ; H, 2·8%).

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