

949. *The Preparation of Some Tertiary Di-o-halogenophenylarsines*

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TERTIARY arsines having two *o*-halogenophenyl groups are not easily prepared, and few such compounds have been described. We now record the preparation of some compounds of this type, and certain of their properties.

Di-*o*-bromophenylarsinic acid could not be prepared by a Bart reaction from *o*-bromobenzenediazonium chloride and *o*-bromophenylarsenoxide, in solutions containing sodium hydroxide and sodium acetate having pH between 9 and 14, and by the use of tetrammine-cupric catalyst. Oxidation-reduction with formation of *o*-bromophenylarsonic acid and bromobenzene occurred, the acid being isolated in 78% yield in some experiments. Similar results are recorded by Goldsworthy *et al.*,¹ who found that although phenyl- and the three tolyl-arsenoxides in alkaline solutions underwent the Bart reaction with a variety of diazotised amines to give arsinic acids, *o*- and *p*-chlorophenylarsenoxides failed to give arylarsinic acids with diazotised aniline or *o*-chloroaniline, the only products noted being the *o*- and *p*-chlorophenylarsonic acids. This failure of the Bart reaction when applied to the synthesis of these di-*o*-halogenophenylarsinic acids is curious, since Burton and Gibson² prepared *o*-bromophenyl-*o*-nitrophenylarsinic acid, under the usual conditions of the reaction, by using *o*-bromophenylarsenoxide and diazotised *o*-nitroaniline. The reaction of diazonium tetrafluoroborates with arsenic trichloride also gives only low yields of di-*o*-halogenophenylarsinic acids.³

However, we find that di-*o*-bromophenylchloroarsine can be prepared in good yield by

¹ L. J. Goldsworthy, W. H. Hook, J. A. John, S. G. P. Plant, J. Rushton, and L. M. Smith, *J.*, 1948, 2208.

² H. Burton and C. S. Gibson, *J.*, 1926, 450.

³ G. O. Doak and L. D. Freedman, *J. Amer. Chem. Soc.*, 1951, **73**, 5656; 1955, **77**, 6374.

heating *o*-bromophenyldichloroarsine with *o*-bromophenylarsenoxide (the Pope–Turner reaction, $\text{ArAsCl}_2 + 3\text{ArAsO} \longrightarrow 2\text{Ar}_2\text{AsCl} + \text{As}_2\text{O}_3$), and from this chloroarsine the appropriate Grignard reagents yield di-*o*-bromophenylphenylarsine and di-(*o*-bromophenyl)ethylarsine.

The latter was also prepared, in low yield, by the reaction of *o*-bromophenylmagnesium iodide with ethylarsinous dichloride.

Di-(*o*-bromophenyl)ethylarsine undergoes lithiation on treatment with *n*-butyl-lithium, the product giving di-(*o*-carboxyphenyl)ethylarsine in good yield on carboxylation. However, this dilithio-compound gives only an intractible, and probably polymeric, product with ethylphosphonous dichloride. It may be noted that di-(*o*-bromophenyl)ethylamine⁴ and di-*o*-bromophenylamine⁵ similarly undergo lithiation, but the latter compound also gives polymeric material with phenylphosphonous dichloride. However, di-(*o*-lithiophenyl)ethylphosphine reacts with ethylphosphonous dichloride in tetrahydrofuran to give 5,10-diethyl-5,10-dihydrophosphanthren.⁶

Experimental.—All reactions in which tertiary arsines were formed or used were performed under nitrogen. M. p.s were determined on a Kofler hot-stage apparatus. Compounds are colourless unless otherwise described.

Di-o-bromophenyldichloroarsine. *o*-Bromophenyldichloroarsine⁷ (22 g.) was heated with *o*-bromophenylarsenoxide⁸ (54 g., 3 moles) under nitrogen at 260–270° for 1½ hr. After being cooled, the product was extracted with hot benzene; the insoluble material was dissolved in aqueous sodium hydroxide and carbon dioxide passed through the solution, when unchanged *o*-bromophenylarsenoxide (5 g.) was precipitated. The benzene extract was distilled under nitrogen, giving (a) *o*-bromophenyldichloroarsine, b. p. 125–130°/0.1 mm. (8.5 g.), m. p. 63–64° after crystallisation from light petroleum (b. p. 60–80°); (b) the *arsine*, b. p. 160–166°/0.1 mm. (43.5 g., 71%); a sample further purified by fractionation (b. p. 166°/0.2 mm.) and crystallisation from the light petroleum had m. p. 108–109° (Found: C, 34.2; H, 1.9. $\text{C}_{12}\text{H}_8\text{AsBr}_2\text{Cl}$ requires C, 34.1; H, 1.9%). A sample in acetone was mixed with sodium iodide in acetone; the precipitated sodium chloride was filtered off, the solvent removed, and the residue washed with ice–water and quickly crystallised from ethanol, giving yellow *di-o-bromophenyliodoarsine*, m. p. 103–104° (Found: C, 28.0; H, 1.8. $\text{C}_{12}\text{H}_8\text{AsBr}_2\text{I}$ requires C, 28.0; H, 1.6%).

Di(o-bromophenyl)phenylarsine. The above chloroarsine (15 g.) in benzene (60 ml.) was added dropwise with cooling and stirring to a solution of phenylmagnesium bromide prepared from bromobenzene (6.6 g.) and magnesium (1 g.) in ether (50 ml.). The mixture was boiled under reflux for one hour, cooled, and hydrolysed with saturated aqueous ammonium chloride; the organic layer was separated, dried (Na_2SO_4), and the solvents removed. The residue, crystallised from ethanol, gave the *arsine*, m. p. 112–113° (15.7 g., 95%) (Found: C, 46.8; H, 3.1. $\text{C}_{18}\text{H}_{13}\text{AsBr}_2$ requires C, 46.6; H, 2.8%). The *arsine* was unchanged when boiled under reflux with excess of methyl iodide for ½ hr., or when heated with excess of methyl bromide at 100° for 10 hr.

Di(o-bromophenyl)ethylarsine. This was prepared similarly to the above *arsine*, by using the chloroarsine (31.7 g.) in benzene (120 ml.) and a solution of ethylmagnesium bromide prepared from ethyl bromide (32.7 g.) and magnesium (7.3 g.) in ether (200 ml.). The *arsine*, recrystallised from ethanol, had m. p. 97–98° (27 g., 86%) (Found: C, 40.6; H, 3.6. $\text{C}_{14}\text{H}_{13}\text{AsBr}_2$ requires C, 40.4; H, 3.15%). The *arsine* was also prepared as follows. A Grignard solution⁹ was prepared by adding *o*-bromo-iodobenzene (56.2 g., 2 moles) in ether (250 ml.) to a stirred suspension of magnesium (4.86 g., 1 atomic equivalent) in ether (50 ml.) during 2 hr., followed by stirring at room temperature for 1 hr. It was then cooled in ice while ethylarsinous dichloride (20 g.) in benzene (100 ml.) was added, and the complete mixture was stirred at room temperature for 1 hr. and boiled under reflux for 1 hr., then cooled and hydrolysed. The separated organic layer was dried and distilled, giving the *arsine* as a fraction b. p. 158–162°/0.1 mm., m. p. 95–96° (from ethanol), undepressed by admixture with a sample prepared as

⁴ H. Gilman and E. A. Zuech, *Chem. and Ind.*, 1958, 1227.

⁵ Emrys R. H. Jones and F. G. Mann, *J.*, 1956, 786.

⁶ M. Davis and F. G. Mann, *J.*, 1964, 3770.

⁷ Emrys R. H. Jones and F. G. Mann, *J.*, 1955, 4472.

⁸ C. S. Gibson and J. D. A. Johnson, *J.*, 1930, 1124.

⁹ H. Heaney, F. G. Mann, and I. T. Millar, *J.*, 1957, 3930.

above (2.1 g., 6%). When boiled under reflux with methyl iodide for $\frac{1}{2}$ hr. the arsine was unchanged but when heated with excess of methyl bromide and a trace of methanol at 100° for 6 hr., it gave *di-(o-bromophenyl)ethylmethylarsonium bromide*, m. p. 203—204° (decomp.) (from methanolic acetone) (Found: C, 34.95; H, 3.3. $C_{15}H_{16}AsBr_3$ requires C, 34.25; H, 3.15%).

Lithiation. Di-(*o*-bromophenyl)ethylarsine (6.24 g.) dissolved in ether (50 ml.) and light petroleum (b. p. 40—50°, 17 ml.), was added rapidly to a well stirred solution of *n*-butyl-lithium in the light petroleum (33 ml. *n*-solution; 2 equivalents). The mixture at once became yellow. Portions of 25 ml. were removed at intervals of 5, 10, 30, and 60 min. after mixing, and carboxylated. The product from each carboxylation was hydrolysed with dilute aqueous hydrochloric acid, made alkaline, and extracted with aqueous sodium hydroxide. Re-acidification and extraction with ether, followed by removal of the ether and crystallisation of the residue from aqueous ethanol, gave *di-(o-carboxyphenyl)ethylarsine*, m. p. 226—228° (Found: C, 56.0; H, 4.4. $C_{16}H_{15}AsO_4$ requires C, 55.5; H, 4.5%) in yields of 44, 54.5, 61, and 37%, respectively. The combined neutral fractions, after extraction with ether, drying of the extract, removal of solvent and recrystallisation from ethanol, gave di-(*o*-bromophenyl)ethylarsine, m. p. and mixed m. p. 95—96° (1.2 g.). The arsine in benzene was also lithiated with *n*-butyl-lithium (2 equivalents) in the light petroleum; the product was boiled under reflux for 12 hr., and then carboxylated to give the above acid, m. p. and mixed m. p. 226—229° (58%).

Reaction of di-(o-lithiophenyl)ethylarsine with ethylphosphonous dichloride. The dilithio-compound, prepared and used in benzene and the light petroleum, or in ether and the light petroleum, was boiled under reflux with ethylphosphonous dichloride (one equivalent) in benzene for 3 hr. After hydrolysis with cold air-free water, separation of the organic layer and removal of the solvents gave a resinous residue, which failed to crystallise, and from which crystalline derivatives could not be obtained. When heated to a high temperature under low pressure in nitrogen, the material partly distilled, but crystalline derivatives could not be obtained from the distillate. A similar product was obtained from the reaction carried out in ether and the light petroleum under conditions of high dilution.

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