## 263. *Arsonic Acids of Diphenylene Oxide and Diphenyl Ether.*

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The only arsenic derivatives of diphenylene oxide hitherto prepared are 3-nitro-1-arsonodiphenylene oxide and the corresponding amino-compound (Hall and Hamilton, *J. Amer. Chem. Soc.*, **1934**, **56**, 1779). We have now prepared three of the four possible monoarsonic acids directly from diphenylene oxide.

Mercuration of diphenylene oxide yields 1-acetoxymercuridiphenylene oxide, which can be converted into the 1-chloromercuri-compound (Gilman and Young, *J. Amer. Chem. Soc.*, **1934**, **56**, 1415). The latter on treatment with arsenic trichloride is converted into a dichloroarsine which when oxidised gives *diphenylene oxide-1-arsonic acid monohydrate* in rather poor yield.

Nitration of diphenylene oxide gives mainly the 2-nitro-derivative. This on reduction gives the 2-amino-compound, which is converted into *diphenylene oxide-2-arsonic acid monohydrate* by the Bart reaction.

Finally, bromination of diphenylene oxide yields 3-bromodiphenylene oxide which may be converted into the 3-amino-compound. The latter by the Bart reaction gave *diphenylene oxide-3-arsonic acid monohydrate.*

There is no reaction when diphenylene oxide is heated with arsenic chloride, but on addition of a small amount of aluminium chloride there is a slow evolution of hydrogen chloride. In the absence of a solvent there is much carbonisation and formation of coloured substances, but reaction is smoother when a solvent, *o*-dichlorobenzene, is employed. From the product, after oxidation, a small amount of an arsonic acid, identical with the 3-acid synthesised above, was isolated. The group $-AsCl_2$, therefore, enters the 3-position in the direct arsenation of diphenylene oxide.

A fair yield of a dichlorophosphine is obtained when diphenylene oxide is treated with phosphorus trichloride in the presence of aluminium chloride. We have not been able to fix the orientation with certainty, but it is probably the 3-compound.

When a mixture of diphenyl ether and arsenic trichloride is heated in the presence of aluminium chloride a yield of 36—46% of 10-chlorophenoxarsine is obtained (Lewis, Lowry, and Bergeim, *J. Amer. Chem. Soc.*, 1921, **43**, 891; Turner and Shepherd, J., 1925, **127**, 544). Turner and Shepherd have shown that *o*-phenoxyphenyldichloroarsine loses hydrogen chloride when heated, thereby giving the above cyclic compound. Further, diphenyl ether and tellurium tetrachloride in chloroform solution give a phenoxyphenyltelluritrichloride which when heated loses hydrogen chloride, giving 10 : 10-dichlorophenoxtellurine. Drew (J., 1926, 223) considered, without strict proof, that the telluritrichloride was a *p*-compound which when heated isomerised to the *o*-compound, the latter then losing hydrogen chloride to give the cyclic compound. A similar explanation does not hold in the case of arsenic trichloride, since we have synthesised p-*phenoxyphenyldichloroarsine* and shown that it does not yield the cyclic compound when heated at 200°, either alone or in the presence of aluminium chloride. The low yield of 10-chlorophenoxarsine obtained from diphenyl ether and arsenic trichloride is thus explained, only the *o*-dichloroarsine undergoing cyclisation, any simultaneously formed *p*-compound remaining unchanged. It had been observed by Davies and Morris (J., 1932, 2880) that *p*-phenoxyphenyldichlorophosphine, which could be boiled at 12 mm. without change, was obtained in the condensation of diphenyl ether with phosphorus trichloride in the presence of aluminium chloride. No *o*-compound or cyclic compound was obtained.

## Experimental.

*General Method for Arsonic Acids.*—The diazo-solution, prepared in the usual way from the amino-diphenylene oxide or diphenyl ether, was neutralised with sodium bicarbonate, treated with a little copper sulphate, and then added gradually to an arsenious oxide solution containing copper sulphate (prepared by the method of Roberts and Turner, J., 1925, **127**, 2009) at 50—60°. After 2 hours the mixture was filtered; the filtrate was acidified with hydrochloric acid, and the arsonic acid separated. The acids were purified by repeated dissolution in cold sodium hydroxide or carbonate solution, filtering, and reprecipitation with dilute hydrochloric acid; they were recrystallised from aqueous alcohol (diphenylene oxide arsonic acids) or glacial acetic acid (diphenyl ether arsonic acids).

*Diphenylene Oxide-1-arsonic Acid Monohydrate.*—Diphenylene oxide (50 g.) and mercuric acetate (72 g.) were heated at 150° for 4 hours. The cooled melt was powdered, and extracted in a Soxhlet apparatus with a higher alcohol, such as *n*-propyl, *n*-butyl, or *iso*amyl. An ethyl-alcoholic solution of calcium chloride was added to the hot extract, precipitating 1-chloromercuridiphenylene oxide (50 g.) (Gilman and Young, *loc. cit.*), which was purified by precipitation with water from its solution in acetone. The chloromercuri-compound (32 g.) and arsenic trichloride (14 g.) in benzene (50 c.c.) were heated at 100° for 5 hours. The mixture was filtered, the benzene and excess arsenic trichloride removed from the filtrate, the residue dissolved in 20% sodium hydroxide solution, and treated with 20 c.c. of 15% hydrogen peroxide with vigorous shaking. The mixture was filtered, and the filtrate acidified with hydrochloric acid, giving 0·5 g. of *diphenylene oxide-1-arsonic acid monohydrate*, from which a trace of diphenylene oxide was removed only with difficulty by the method of purification already described. The acid was a buff-coloured powder, m. p. 186—188° * (decomp.) (Found : equiv., 158. $C_{12}H_9O_4As,H_2O$ requires *M*, 310). The yield of arsonic acid was even poorer when the benzene was omitted from the heated mixture.

*Diphenylene Oxide-2-arsonic Acid Monohydrate.*—A mixture of 2-nitrodiphenylene oxide (50 g.), prepared by nitration of diphenylene oxide (Ryan and Cullinane, *Sci. Proc. Roy. Dublin Soc.*, 1924, **17**, 321), iron powder (75 g.), water (50 c.c.), and 1 g. of ferric chloride was heated at 100°, cooling being applied whenever the reaction became too vigorous. After 1 hour, the mixture was cooled, shaken with 250 c.c. of ether, and filtered. The ethereal layer was treated with concentrated hydrochloric acid, giving 2-aminodiphenylene oxide hydrochloride (48 g.), which was diazotised and treated with arsenious oxide, yielding *diphenylene oxide-2-arsonic acid monohydrate* (8 g.), m. p. 385° (Found : As, 24·5; $H_2O$, 5·8; equiv., 156. $C_{12}H_9O_4As,H_2O$ requires As, 24·2; $H_2O$, 5·8%; *M*, 310). The water content was determined by heating the

* M. p.'s have not been corrected.

acid for 8 hours at 160°; at 100° there was but little loss. The anhydrous acid was converted into the original hydrated acid (Found : equiv., 153) when its solution in sodium hydroxide was neutralised with hydrochloric acid. Equivalents were determined by dissolving a weighed quantity of the acid in excess of standard sodium hydroxide and titrating the excess with succinic acid, phenolphthalein being the indicator. The 2-arsonic acid was only sparingly soluble in hot water, but was soluble in alcohol and glacial acetic acid.

The *barium* salt, prepared from ammoniacal solution, formed colourless crystals (Found : Ba, 32·1. $C_{12}H_7O_4AsBa$ requires Ba, 32·1%).

*Diphenylene Oxide-3-arsonic Acid Monohydrate.*—A mixture of 3-bromodiphenylene oxide (48 g., recrystallised from alcohol; prepared by the method of Mayer and Krieger, *Ber.*, 1922, **55**, 1661), cuprous chloride (35 g.), and ammonia (500 c.c., *d* 0·88) was heated for 10 hours at 200—210° in a stainless-steel autoclave (Gilman, *J. Amer. Chem. Soc.*, 1934, **56**, 2475). The product was filtered, and the residue (28 g.) diazotised and converted into the *monohydrate* of the 3-arsonic acid, which formed buff-coloured plates, m. p. 213—214° (Found : C, 46·8; H, 3·4; As, 24·1; $H_2O$, 5·8; equiv., 155. $C_{12}H_9O_4As,H_2O$ requires C, 46·5; H, 3·6; As, 24·2; $H_2O$, 5·8%; *M*, 310); yield 3 g. The dehydrated acid, m. p. *ca.* 360°, was converted into the original acid (m. p. and mixed m. p.) by the method described for the 2-arsonic acid. The *barium* salt (Found : Ba, 32·1%) was prepared as above.

*Direct Arsonation of Diphenylene Oxide.*—A mixture of diphenylene oxide (17 g.), arsenic trichloride (20 g.), *o*-dichlorobenzene (50 g.), and commercial aluminium chloride (1 g.) was refluxed for 4 hours. There was a slow evolution of hydrogen chloride. Excess arsenic trichloride and solvent were removed by distillation at reduced pressure, and the residue was extracted with light petroleum; the solvent was evaporated, and the residue extracted with warm dilute sodium hydroxide. The alkaline extract was then treated with hydrogen peroxide, and after 1 hour the mixture was acidified with hydrochloric acid. The precipitate obtained, after purification, was shown to be diphenylene oxide-3-arsonic acid monohydrate (m. p. and mixed m. p. with synthetic acid).

*Diphenylene Oxide and Phosphorus Trichloride.*—A mixture of diphenylene oxide (168 g.), phosphorus trichloride (87 c.c.), and aluminium chloride (20 g.) was refluxed for 36 hours, and fractionally distilled at reduced pressure. Diphenylene oxide passed over, followed by 20 g. of a dichlorophosphine of diphenylene oxide, b. p. 245—250°/25 mm., solidifying at ordinary temperatures, and converted into a crystalline phosphinous acid, m. p. 125°, by boiling with water.

Diphenyl ether was nitrated by Suter's method (*J. Amer. Chem. Soc.*, 1929, **51**, 2581). The pure *p*-nitro-compound and the crude *o*-compound were reduced separately by means of iron, water, and a little ferric chloride. The mixtures were filtered, and the filtrates made acid with sulphuric acid. *p*-Aminodiphenyl ether sulphate was precipitated at once, but *o*-aminodiphenyl ether was obtained as an oil (which slowly solidified) when the filtered acid solution was basified with sodium hydroxide.

p-*Phenoxyphenylarsonic acid* was prepared from the *p*-amino-sulphate by the Bart reaction; yield of crude acid, 26%. It was best recrystallised from glacial acetic acid, forming colourless plates, m. p. 365° (Found : As, 25·1, 25·3; equiv., 148. $C_{12}H_{11}O_4As$ requires As, 25·4%; *M*, 294). The acid is soluble in cold alcohol, but only sparingly soluble even in boiling water.

The arsonic acid was suspended in warm concentrated hydrochloric acid, a trace of iodine added, and the mixture saturated with sulphur dioxide. The precipitated oil was extracted with carbon tetrachloride, and the solvent removed from the dried extract (sodium sulphate), leaving an oil which solidified to a pale yellow crystalline mass of p-*phenoxyphenyldichloroarsine*, m. p. 66° (Found : As, 23·3. $C_{12}H_9OCl_2As$ requires As, 23·8%), which was pressed out on a porous plate. Similarly, *o*-phenoxyphenyldichloroarsine (Turner and Shepherd, *loc. cit.*) was obtained as an orange-red oil.

*Attempted Ring Closure.*—Portions of the *o*- and *p*-dichloroarsines were heated for 6 hours at 200° at 10 mm. When cold, the former was solid, but the latter liquid. Both were treated with a little warm chloroform, the extract filtered, and warm light petroleum added. Crystals of 10-chlorophenoxarsine (m. p. 124°) quickly separated from the first, but none from the second. This method was shown to be satisfactory for detecting small quantities of the cyclic compound. Further, no cyclic compound was obtained from the *p*-dichloroarsine when it was heated as before, but with the addition of a little aluminium chloride.

p-*Bromo*-p'-*arsonodiphenyl ether*, prepared from *p*-bromo-*p'*-aminodiphenyl ether by the Bart reaction, formed colourless needles, m. p. 354—355° (Found : As, 20·0; equiv., 185. $C_{12}H_{10}O_4BrAs$ requires As, 20·1%; *M*, 373).

*Action of Bromine on* p-*Phenoxyphenylarsonic Acid.*—The acid was suspended in carbon tetrachloride and warmed with the calculated quantity of bromine. The solvent was expelled, and the residue recrystallised from glacial acetic acid, giving *p*-bromo-*p'*-arsonodiphenyl ether, m. p. 353—355°, mixed m. p. 354—356°. It must be inferred that the directive power of the group $O{\cdot}C_6H_4{\cdot}AsO(OH)_2$ is similar to that of the phenoxy-group itself. A similar result was obtained by Davies and Morris (*loc. cit.*) in the bromination of *p*-phenoxyphenylphosphonic acid.

p-*Chloro*-p'-*arsonodiphenyl ether*, prepared from *p*-chloro-*p'*-aminodiphenyl ether, formed colourless needles, m. p. 375° (Found : As, 22·8; equiv., 166. $C_{12}H_{10}O_4ClAs$ requires As, 22·8%; *M*, 328). *Barium* salt (Found : Ba, 29·6. $C_{12}H_8O_4ClAsBa$ requires Ba, 29·6%).

p-*Phenoxyphenyldimethylarsine.*—A solution of dimethyliodoarsine (38 g.) in ether (75 c.c.) was gradually stirred into a cooled Grignard solution, prepared from *p*-bromodiphenyl ether (83 g.), magnesium (8 g.), and ether (300 c.c.). The mixture was boiled for 2 hours, again cooled, and treated with aqueous ammonium chloride. The ethereal solution was dried (sodium sulphate), the ether removed, and the residue fractionally distilled under reduced pressure. Finally, the arsine fraction was redistilled. p-*Phenoxyphenyldimethylarsine* (21 g.) is a colourless liquid, with an odour resembling pineapple, and has b. p. 189—190°/10 mm.; $d_4^{17°}$ 1·2690; $n_D^{17°}$ 1·6122; $[R_L]_D$ 75·09 (Found : C, 61·3; H, 5·5. $C_{14}H_{15}OAs$ requires C, 61·3; H, 5·5%). A convenient method for testing the purity of this and similar tertiary bases is to make a standard solution of the base in aqueous acetone and treat an aliquot portion with an excess of methyl iodide in a stoppered flask. After 24 hours, light petroleum is added, and the mixture extracted with water. The aqueous extract is titrated with standard silver nitrate solution with potassium chromate as indicator. In the present case, 5 c.c. of an *M*/20-solution of the arsine required 10·05 c.c. of *N*/40-silver nitrate.

The value of the atomic refractivity, $[R_L]_D$, of arsenic is 12·70, calculated by deducting the refractivities of two methyl groups and a phenoxyphenyl group (Eisenlöhr, *Z. physikal. Chem.*, 1910, **75**, 585); there is thus an optical exaltation due to the attachment of the phenoxyphenyl group to arsenic, since the mean value for arsenic in non-exaltative systems is 11·96 (Jones, J., 1932, 2292).

p-*Phenoxyphenyltrimethylarsonium Iodide.*—A 3% solution of the arsine in acetone was treated with an excess of methyl iodide. The crystalline precipitate which gradually separated was recrystallised from water, forming glistening leaflets, m. p. 240° (Found : I, 30·4. $C_{15}H_{18}OIAs$ requires I, 30·5%). The *ethiodide* was similarly obtained as leaflets, m. p. 237° (Found : I, 29·4. $C_{16}H_{20}OIAs$ requires I, 29·5%).

p-*Phenoxyphenyldimethylarsine di-iodide*, m. p. 134° (Found : I, 48·6. $C_{14}H_{15}OI_2As$ requires I, 48·1%), was obtained as a yellow precipitate when a solution of iodine in light petroleum was slowly added to a solution of the arsine in the same solvent. The solution of the di-iodide in water contains all the iodine in a form precipitatable as silver iodide.

*o*-Phenoxyphenyldimethylarsine was obtained from the product of the reaction of *o*-phenoxyphenyldichloroarsine and methylmagnesium iodide in ethereal solution. It had b. p. 205—207°/30 mm., but insufficient was available for a complete study. It was characterised by conversion into the *methiodide*, which formed glistening plates (from water), m. p. 229—230° (Found : I, 30·7%).

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