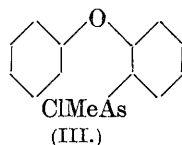
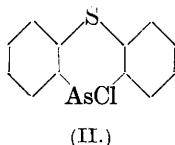
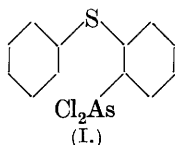


CLV.—10-Chlorophenthiarsine, and its Rate of Formation from *o*-Phenylthiolphenyldichloroarsine.

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IN continuation of previous work (Roberts and Turner, J., 1925, 127, 2004), *o*-phenylthiolphenyldichloroarsine (I) has been prepared, and its rate of conversion into 10-chlorophenthiarsine (II) determined. Whereas *o*-phenoxyphenyldichloroarsine undergoes nearly 60% conversion into the ring compound, the sulphur analogue undergoes only about 20% conversion under the same conditions, *i.e.*, when heated at 200° in a current of carbon dioxide.



A further comparison has been made between *o*-phenoxyphenyldichloroarsine and *o*-phenoxyphenylmethylchloroarsine (III) from the same point of view. The chloroarsine is even more stable towards heat than the above phenylthiol compound, undergoing in 6 hours at 200° only about 10% of the possible loss of hydrogen chloride. Moreover, side reactions appear to occur, and it has not been found possible to detect the presence of the expected 10-methylphenoxarsine in the product of decomposition. The latter, when treated with methyl iodide, afforded a little 10-iodophenoxarsine, but no 10 : 10-dimethylphenoxarsonium iodide. This substance has been prepared, for purposes of comparison, by treating with methyl iodide the product of interaction of magnesium methyl iodide and 10-chlorophenoxarsine.

It has been pointed out (Turner and Sheppard, J., 1925, 127, 544) that arsenic trichloride and diphenyl ether do not interact in absence of aluminium chloride. It seemed possible that this might be due to the low boiling point of the mixture, which is well below the temperature at which phenoxyphenyldichloroarsine undergoes conversion into the chlorophenoxarsine. It has, however, been

found that a mixture of phenyldichloroarsine and diphenyl ether boils unchanged at 250—260°, so that the ring closures in question are evidently determined more by collision effects than by those of activation due to increase of temperature.

EXPERIMENTAL.

o-Nitrodiphenyl Sulphide.—This substance, previously obtained by Mauthner (Ber., 1906, **39**, 3593), is more conveniently prepared by the following method: Potassium hydroxide (61 g.; 1 mol.) was dissolved in 5 c.c. of water, 120 g. (1 mol.) of thiophenol, and then 173 g. (1 mol.) of *o*-chloronitrobenzene and 8 g. of copper bronze were added. The mixture was heated at 170—185° for 2 hours after the initial vigorous reaction had subsided. The cooled product was extracted with carbon tetrachloride, the extract washed successively with alkali and water, and dried over calcium chloride. The solvent was removed, and the residue distilled under diminished pressure. In this manner, 138 g. of *o*-nitrodiphenyl sulphide were obtained, b. p. 210°/15 mm. Crystallisation from light petroleum removed traces of a disulphide, the pure nitro-compound having m. p. 79° (Mauthner gives 77°).

o-Aminodiphenyl Sulphide.—The foregoing nitro-compound was reduced with iron, water and ferric chloride (Roberts and Turner, *loc. cit.*). A little thiophenol is formed during the reduction, which proceeds less vigorously than in the case of *o*-nitrodiphenyl ether, but affords not less than an 85% yield of the amine hydrochloride.

o-Phenylthiolphenylarsinic Acid.—The pure acid was obtained in 12% yield by the method used for the preparation of phenoxyphenylarsinic acids, and crystallised from alcohol in irregular plates, m. p. 192—194° (Found: As, 24.0. $C_{12}H_{11}O_3SA$ s requires As, 24.2%). The acid is sparingly soluble in water, and was not converted into the corresponding phenthiarsinic acid when heated with concentrated sulphuric acid, no doubt owing to sulphonation.

o-Phenylthiolphenyldichloroarsine.—The preceding arsenic acid, when reduced by the usual process, afforded the crude dichloroarsine as a dark oil, which was purified by conversion into the corresponding oxide (see below), the latter then being reconverted into the dichloroarsine. The latter was thus obtained as a pale yellowish-brown, viscous oil (Found: Cl, 21.3. $C_{12}H_9Cl_2SA$ s requires Cl, 21.5%). (Traces of the carbon tetrachloride used for the extraction of the pure dichloroarsine were removed by gently heating the substance under diminished pressure for a few minutes.)

o-Phenylthiolphenylarsenious oxide separates from benzene in small, white, irregular rhombs, m. p. 187—189° (Found: As, 26.5. $C_{12}H_9OSA$ s requires As, 27.2%).

Conversion of o-Phenylthiolphenyldichloroarsine into 10-Chlorophenylthiarsine.—When heated at 200° under the conditions previously described in connexion with the conversion of the phenoxyphenyldichloroarsines into the corresponding chlorophenoxarsines, *o*-phenylthiolphenyldichloroarsine underwent the following course of decomposition :

Time (hours)	1	2	3	4	5	6
% decomposition	2.2	4.5	7.2	10.2	13.6	17.2

The heating was actually allowed to continue for 24 hours ; the product, almost solid when cold, then readily crystallised from light petroleum (b. p. 80—100°) in sulphur-yellow, rhombohedral masses, apparently consisting of rectangular plates, m. p. 129—130° (Found : Cl, 12.1. $C_{12}H_8Cl_2SA$ requires Cl, 12.1%).

o-Phenoxyphenylmethylchloroarsine.—*o*-Phenoxyphenyldichloroarsine (19 g.) was dissolved in alcohol containing a little acetone, and a solution of 12 g. of sodium hydroxide in 90 c.c. of water added. The mixture was cooled to 40°, and 8 c.c. of methyl iodide were added slowly. The initial reaction over, the whole was left over-night, when a pale yellow oil separated. The alcohol and acetone were distilled off and the residue was acidified with concentrated hydrochloric acid (25 c.c.); a gummy solid then separated. Potassium iodide (19 g.) was added, and the warmed mixture saturated with sulphur dioxide. The dark red, oily iodoarsine so obtained was converted into the corresponding oxide, and then, by the usual process, into the chloroarsine, which was obtained as a brownish-yellow, viscous oil ; it contained a little dichloroarsine (Found : Cl, 13.8. $C_{13}H_{12}OCl_2A$ requires Cl, 12.1%).

When this substance was heated at 200° in a current of dry carbon dioxide under the same conditions as before, the course of decomposition was as follows :

Time (hours)	1	2	3	4	5	6
% decomposition	2.5	3.9	5.0	6.4	7.8	9.9

Some methyl chloride was also evolved, and when the decomposition had proceeded for 24 hours, methyl iodide was added to the cooled residue. From the product so obtained, a very small quantity of 10-iodophenoxarsine, m. p. 144°, was isolated (Found : I, 33.8. Calc. : I, 34.3%).

10 : 10-Dimethylphenoxarsonium Iodide.—Finely-powdered 10-chlorophenoxarsine (4 g.) was added gradually to an ethereal solution of magnesium methyl iodide (twice the theoretical amount). It dissolved immediately with evolution of heat, and formation, locally, of a yellow coloration. As soon as it had all been added, the mixture was decomposed by addition of water and then dilute

hydrochloric acid, the ethereal layer separated, washed once with water, dried over sodium sulphate, filtered, and then treated with methyl iodide. After most of the ether had been evaporated, solid separated, which, after crystallisation from alcohol, formed colourless prisms, m. p. 207° (with effervescence) (Found: I, 31.1. $C_{14}H_{14}OIA$ s requires I, 31.7%). The tedious method adopted by Lewis, Lowry, and Bergeim (*J. Amer. Chem. Soc.*, 1921, **43**, 890) and by Aeschlimann (*J.*, 1925, **127**, 811) does not appear to be necessary in the interaction between Grignard reagents and chlorophenoxarsine.

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