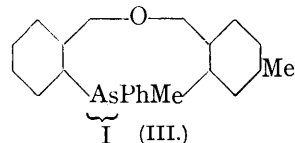
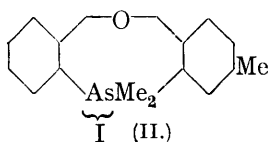
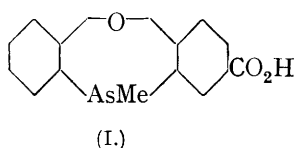


## 242. The Configuration of Heterocyclic Compounds. Part II. Some Phenoxarsonium Salts.

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It was shown (J., 1934, 1170) that the addition of either methyl or ethyl iodide to optically active 10-methylphenoxarsine-2-carboxylic acid (I) was accompanied by racemisation. Although this result suggests that the racemisation was due to the conversion of ter- into "quinque-" valent arsenic, with consequent change in the effective valency angle of the arsenic atom, it might have been caused by the carrying out of a reaction at the seat of dissymmetry, on the conceivable view that the acid (I) contained an "asymmetric



tervalent arsenic atom." It was therefore necessary to attempt the resolution of two types of phenoxarsonium salts, containing the structures  $\cdot\text{AsR}_2\text{X}$  and  $\cdot\text{AsRR}'\text{X}$ . We have prepared 2:10-dimethyl- and 10-phenyl-2-methyl-phenoxarsine and their methiodides (II and III). The *d-camphor-10-sulphonate* and *d- $\alpha$ -bromocamphor- $\pi$ -sulphonate* corresponding to (II) and the *d-camphor-10-sulphonate* corresponding to (III) were submitted to exhaustive fractional crystallisation, but were found to be entirely homogeneous. Although no final conclusions can follow from this negative result, we regard the present data as further support for the theory advanced in Part I, as to the cause of the dissymmetry of the acid (I).

At first sight it appeared as if the experiments of Aeschlimann (J., 1925, 127, 811) provided the information we required, but examination of his memoir shows that the compounds he attempted to resolve contained a plane of symmetry on any view of the configuration of phenoxarsonium salts. Our failure to obtain any indication of resolution in the case of the phenyldimethyl derivative (III) is interesting, since Kamai (*Ber.*, 1933, 66, 1779; *J. Gen. Chem. Russ.*, 1934, 4, 184) appears to have confirmed the resolution partially effected by Burrows and Turner (J., 1921, 119, 426) of simple arsonium compounds of the type  $\text{As}abc\bar{d}\text{X}$ .

### EXPERIMENTAL.

*10-Chloro-2-methylphenoxarsine*.—2-Methylphenoxarsinic acid (47 g.), prepared as described in Part I, was suspended in a mixture of concentrated hydrochloric acid and chloroform, and reduced at about 50° with sulphur dioxide, in presence of a little iodine. The chloroform layer was evaporated, and the residue dried in a vacuum. The 50 g. of crude chloroarsine obtained were crystallised from alcohol, containing some concentrated hydrochloric acid, or

from light petroleum (b. p. 60—80°), pale yellow needles being obtained, m. p. 100—101° (Found: Cl, 12.1.  $C_{13}H_{10}OAsCl$  requires Cl, 12.1%).

**2:10-Dimethylphenoxarsine.**—To the decanted Grignard reagent prepared from 50 g. of methyl iodide (4 mols.) and 15 g. of magnesium, 29 g. (1 mol.) of the chloroarsine were added in benzene solution during 10 mins. The mixture was heated for 1 hr., and then left over-night. It was decomposed with water and hydrochloric acid, separated, and the ethereal extract dried over potassium carbonate, evaporated, and the residue distilled under reduced pressure. A colourless oil (22 g.; 85% yield), b. p. 195°/17 mm., was obtained (Found: As, 27.5.  $C_{14}H_{13}OAs$  requires As, 27.5%).

**2:10:10-Trimethylphenoxarsonium Iodide.**—The last-named arsine (21 g.) was heated in ethyl-alcoholic solution with methyl iodide under reflux for 3 hrs. Addition of dry ether to the cooled solution gave 29 g. of crude methiodide. This crystallised from absolute alcohol in colourless leaflets (24.5 g.), m. p. 205° (decomp.) (Found: I, 30.2.  $C_{15}H_{16}OIA$  requires I, 30.7%).

*Attempted Resolution of 2:10:10-Trimethylphenoxarsonium d-Camphorsulphonate and d- $\alpha$ -Bromocamphor- $\pi$ -sulphonate.*—A solution of 22.8 g. of the methiodide in alcohol was treated with 18.6 g. of silver *d*-camphorsulphonate, dissolved in 80% alcohol, and the solution heated for 15 mins., then cooled and filtered; 27.7 g. of crystalline salt were obtained on removal of the solvent. Systematic crystallisation of this *d*-camphorsulphonate from absolute alcohol gave crops of the same rotation,  $[\alpha]_{5791}^{20} + 22.0^\circ$ , and  $[\alpha]_{5461}^{20} + 26.2^\circ$ , in ethyl alcohol ( $c = 1.89$ ;  $l = 2$ ;  $\alpha_{5791}^{20} + 0.83^\circ$ ,  $\alpha_{5461}^{20} + 0.99^\circ$ ). It had m. p. 275—276° (decomp.) with slight previous softening. Similarly, fractional crystallisation from water gave crops of rotation identical with the above (Found: C, 56.1; H, 6.3.  $C_{25}H_{31}O_5SAs, H_2O$  requires C, 55.9; H, 6.2%). Decomposition gave inactive methiodides.

The *bromocamphorsulphonate* (22.8 g.) was prepared in a similar manner. Fractional crystallisation from water gave rectangular needles, and the salt showed no indication of resolution. The crops obtained had  $[\alpha]_{5791}^{20} + 56.5^\circ$  and  $[\alpha]_{5461}^{20} + 67.1^\circ$ , in ethyl alcohol ( $c = 2.087$ ;  $l = 2$ ;  $\alpha_{5791}^{20} + 2.36^\circ$ ;  $\alpha_{5461}^{20} + 2.80^\circ$ ), and  $[\alpha]_{5791}^{20} + 53.6^\circ$  and  $[\alpha]_{5461}^{20} + 64.2^\circ$ , in chloroform ( $c = 1.893$ ;  $l = 2$ ;  $\alpha_{5791}^{20} + 2.03^\circ$ ;  $\alpha_{5461}^{20} + 2.43^\circ$ ). The variations in specific rotation were less than 0.5°. All the crops melted at 263—264° (decomp.), and gave rise to inactive methiodides (Found: C, 48.9; H, 5.3.  $C_{25}H_{30}O_5SAsBr, H_2O$  requires C, 8.8; H, 5.2%).

**10-Phenyl-2-methylphenoxarsine.**—To the decanted Grignard reagent prepared from 75 g. of bromobenzene (6 mols.) were added 26 g. of 10-chloro-2-methylphenoxarsine (1 mol.) in benzene solution. The mixture was heated in boiling water for 6 hrs., the ether being allowed to distil off gradually. The product was decomposed with ice and hydrochloric acid. The benzene solution was dried, and the solvent removed. The residue was distilled in a vacuum, and 24.5 g. (82% yield) of *arsine* were obtained, b. p. 250°/10 mm. It remained as a thick oil for 14 days in spite of repeated strong chilling and scratching, then suddenly crystallised. After recrystallisation from absolute alcohol, it formed rhombic prisms, m. p. 61—62° (Found: As, 22.4.  $C_{19}H_{15}OAs$  requires As, 22.4%).

The *methiodide* (21 g.) was obtained by heating 24 g. of the *arsine* in a sealed tube with excess of methyl iodide for 2 days at 100°. Treatment with dry ether, followed by crystallisation from absolute alcohol, gave opaque needles, m. p. 179—180° (decomp.) (Found: I, 26.8.  $C_{20}H_{18}OAsI$  requires I, 26.7%).

*Attempted Resolution of 10-Phenyl-2:10-dimethylphenoxarsonium d-Camphorsulphonate and of the d- $\alpha$ -Bromocamphor- $\pi$ -sulphonate.*—The *camphorsulphonate*, prepared by interaction, in boiling alcoholic solution, of 14.25 g. of the methiodide with 10.2 g. of silver *d*-camphorsulphonate, crystallised in rectangular plates from acetone—light petroleum (b. p. 60—80°). The various fractions obtained had  $[\alpha]_{5791}^{20} + 21.4^\circ$  and  $[\alpha]_{5461}^{20} + 25.5^\circ$ , in ethyl alcohol ( $c = 2.055$ ;  $l = 2$ ;  $\alpha_{5791}^{20} + 0.88^\circ$ ;  $\alpha_{5461}^{20} + 1.05^\circ$ ). Recrystallisation gave no appreciable variation in specific rotation, and inactive methiodides were always produced (Found: C, 61.9; H, 5.8.  $C_{30}H_{33}O_5SAs$  requires C, 62.0; H, 5.7%).

The *d*-bromocamphorsulphonate, obtained in the usual manner, remained in a glass which could not be induced to crystallise.

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