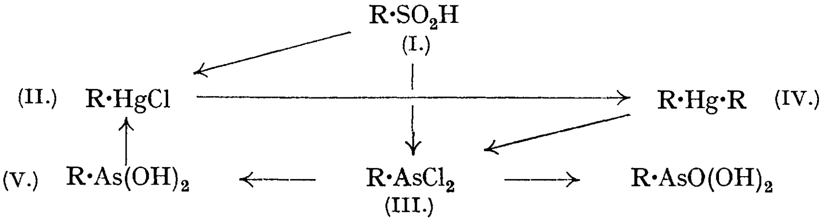
81. *The Preparation of Camphor*-10-*dichloroarsine from Camphor*-10-*sulphinic Acid.*

By James D. Loudon.

The formation of organo-mercury compounds from sulphinic acids by the method discovered by Peters (*Ber.*, 1905, **38**, 2567) suggests the possibility of utilising these acids as a source of organic derivatives of other metals or metalloids which form with carbon a link of sufficient stability to survive the reaction conditions. It has previously been shown (Loudon, J., 1933, 823) that, with mercuric chloride, camphor-10-sulphinic acid (I) furnishes camphor-10-mercurichloride (II) and it has been found that the corresponding *dichloroarsine* (III) is readily produced by a similar process employing arsenic trichloride. The nature of the product is established by an alternative preparation from arsenic trichloride and biscamphor-10-mercury (IV), and by the interesting observation that it is hydrolysed to a stable *arsinic acid* (V), from which, by treatment in aqueous solution with mercuric chloride, camphor-10-mercurichloride is quantitatively produced.



R = camphor-10-radical

Although no other instance of this type of arsenuration has, to the author's knowledge, been published, Kharasch (*J. Amer. Chem. Soc.*, **1921**, **43**, 610, footnote) also claims to have observed the same reaction in cases which are not specified. The reaction does not, however, appear to be of general application, since with *p*-toluenesulphinic acid and naphthalene-2-sulphinic acid reduction products chiefly resulted.

EXPERIMENTAL.

Camphor-10-*dichloroarsine.*—(A) A mixture of camphor-10-sulphinic acid (10 g. of oil) and arsenic trichloride (9 g.) was heated for 3—4 hours at 100°. The formation of sulphur dioxide was quickly perceptible. The excess of arsenic trichloride together with some water (which always appeared and was probably introduced with the sulphinic acid) were distilled off under reduced pressure and the residue, which solidified on cooling, was extracted with ether (charcoal). Concentration of the extract yielded a crystalline mass which, after repeated crystallisation from light petroleum, was obtained in long colourless needles, m.p. 89—90°.

(B) Biscamphor-10-mercury (5 g.) and arsenic trichloride (20 g.) were refluxed on an oil-bath (190—200°) for 3—4 hours and the product was worked up as in (A). To separate the *dichloroarsine* from camphor-10-mercurichloride, the ethereal extract after evaporation was again extracted with small quantities of hot petroleum, from which the dichloroarsine separated on cooling; m. p. and mixed m. p. 89—90° (Found: C, 40·2; H, 5·05; Cl, 23·6. $C_{10}H_{15}OCl_2As$ requires C, 40·4; H, 5·05; Cl, 23·9%).

Camphor-10-*arsinic Acid.*—Camphor-10-dichloroarsine was shaken with warm concentrated sodium hydroxide solution until complete dissolution was effected. The precipitate obtained by acidification (after cooling) was recrystallised from hot water and formed long needles, m. p. 100° (decomp.) (Found : C, 43·4; H, 6·8. $C_{10}H_{17}O_3As,H_2O$ requires C, 43·2; H, 6·8%). When a suspension of the *compound* in benzene or light petroleum was gently warmed, it appeared first partly to dissolve and then suddenly to lose water. A white insoluble powder, melting indefinitely at 190°, was produced, but could not be purified and had a somewhat variable composition (Found : C, 33·9, 34·2; H, 4·9, 5·7%).

Camphor-10-mercurichloride was formed in excellent yield when an aqueous solution of the arsinic acid (0·5 g.) and mercuric chloride (0·5 g.) was heated for 1 hour. The solid formed was extracted with chloroform, and the extract recrystallised from alcohol; m. p. and mixed m. p. with an authentic specimen, 166—167°.

Camphor-10-*arsonic acid* was obtained by concentrating the solutions produced (1) by passing chlorine into an aqueous suspension of the dichloroarsine and (2) by oxidising the same compound with hydrogen peroxide in acetic acid. The product crystallised from alcohol in massive prisms or in fine needles, melting in each case at 210° (Found : C, 43·2; H, 6·3. $C_{10}H_{17}O_4As$ requires C, 43·5; H, 6·2%). The barium salt was more soluble in cold than in hot water.

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THE UNIVERSITY, GLASGOW.

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