## 123. *Mercury Derivatives of Camphor. Part II.*

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The successful application of Peters' reaction (*Ber.*, 1905, **38**, 2567), *viz.*,

$$R{\cdot}SO_2H + HgCl_2 \longrightarrow R{\cdot}HgCl + SO_2 + HCl$$

to the preparation of camphor-10-mercurichloride (Part I, J., 1933, 823) has led to investigation of other camphorsulphinic acids as sources of the related mercury derivatives. The results now obtained reveal marked differences in the reactivities of these acids towards mercuration. Thus, 3-chloro- and 3-bromo-camphor-10-sulphinic acids reacted with mercuric chloride to give yields of the corresponding mercury derivatives which were distinctly lower than that obtained from the unhalogenated acid under the same conditions. Considerable improvement has been effected by the use of pyridine as reaction medium or by employing the aqueous alkali sulphinates instead of the free acid (cf. "Organic Syntheses," III, p. 99)—both modifications being designed to protect the mercurated products from the attack of mineral acids formed in the reaction, and the former yielding slightly better results. On the other hand, 3-chloro- and 3-bromo-camphor-$\pi$-sulphinic acids, although much less stable than their "10" sulphinic analogues from the point of view of preservation, were so resistant to mercuration that evolution of sulphur dioxide was not perceptible and, at best, mere traces of mercurated products resulted. The investigation of these $\pi$-derivatives has consequently been abandoned.

The halogenated camphor-10-mercurichlorides were more stable than the parent substance to reduction by alkaline stannite solution, but their conversion into symmetrical mercury derivatives was readily accomplished by the action of copper gauze in pyridine (cf. Hein, Wagler, and Retter, *Ber.*, 1925, **58**, 1499).

## EXPERIMENTAL.

3-*Chlorocamphor*-10-*sulphinic Acid.*—3-Chlorocamphor-10-sulphonyl chloride (10 g.) was shaken for 3 hours with a concentrated solution of sodium sulphite (30 g. of the hydrate) and ice (20 g.). After precipitation by concentrated sulphuric acid the product separated from alcohol–chloroform in small compact crystals, m. p. 157° (decomp.) markedly affected by the rate of heating (Found: Cl, 14·3. $C_{10}H_{15}O_3ClS$ requires Cl, 14·2%).

3-*Bromocamphor*-10-*sulphinic acid* was prepared and purified in a similar way: m. p. 165° (decomp.) (Found: Br, 27·2. $C_{10}H_{15}O_3BrS$ requires Br, 27·1%).

3-*Chlorocamphor*-π-*sulphinic acid* was most conveniently prepared by adding the sulphonyl chloride in small quantities to a hot aqueous solution of sodium sulphite. After acidification of the cooled solution the product was obtained as a fine white powder, which melted with decomposition and could not be satisfactorily crystallised (Found: Cl, 14·0. $C_{10}H_{15}O_3ClS$ requires Cl, 14·2%).

3-*Bromocamphor*-π-*sulphinic acid*, prepared in the same way, had similar properties; m. p. 149° (decomp.) (Found: Br, 26·9. $C_{10}H_{15}O_3BrS$ requires Br, 27·1%).

3-*Chlorocamphor*-10-*mercurichloride.*—3-Chlorocamphor-10-sulphinic acid (9 g.) was refluxed with mercuric chloride (18 g.) in pyridine (30 c.c.) for 3 hours. The cooled solution, freed from metallic mercury, was cautiously added to an excess of dilute hydrochloric acid and the precipitate was collected, washed (finally with alcohol), dried, and extracted (Soxhlet) with chloroform, from which, on cooling, the pure compound separated in long needles, m. p. 218—219°. Yield, 40—50% of the theoretical $[\alpha]_{5461}^{16^\circ} \pm 0{\cdot}0^\circ$ ($c = 1{\cdot}24$ in pyridine), $+ 5{\cdot}0^\circ$ ($c = 1{\cdot}00$ in chloroform) (Found: Hg, 47·3. $C_{10}H_{14}OCl_2Hg$ requires Hg, 47·5%).

*Bis*-3-*chlorocamphor*-10-*mercury.*—Copper gauze (5 g.) was kept in a solution of 3-chlorocamphor-10-mercurichloride (5 g.) in pyridine (30 c.c.) in a stoppered flask for 24 hours. After removal of the pyridine under reduced pressure, the semi-solid residue was shaken with concentrated aqueous ammonia and finally washed with water. The straw-coloured product was purified from alcohol–chloroform and then had m. p. 175°; $[\alpha]_{5461}^{16^\circ} - 22{\cdot}8^\circ$ ($c = 1{\cdot}14$ in pyridine) (Found: Hg, 35·2. $C_{20}H_{28}O_2Cl_2Hg$ requires Hg, 35·1%).

Treatment of acetone solutions of the compound with mercuric halides gave the corresponding mercurihalides, which were purified from alcohol–chloroform.

3-*Chlorocamphor*-10-*mercuribromide*, needles, m. p. 176° (Found: Hg, 43·1. $C_{10}H_{14}OClBrHg$ requires Hg, 43·1%), and 3-*chlorocamphor*-10-*mercuri-iodide*, needles, m. p. 184° (Found: Hg, 39·1. $C_{10}H_{14}OClIHg$ requires Hg, 39·1%), were also prepared by shaking the mercurichloride at the ordinary temperature with bromine (iodine) in aqueous potassium bromide (iodide) solution.

Similar methods were employed for the corresponding 3-bromocamphor-10-mercury derivatives. 3-*Bromocamphor*-10-*mercurichloride* was obtained from the sulphinic acid (pyridine) in 30—35% yields: m. p. 232°, $[\alpha]_{5461}^{16^\circ} + 44{\cdot}8^\circ$ ($c = 1{\cdot}07$ in pyridine) (Found: Hg, 43·3. $C_{10}H_{14}OBrClHg$ requires Hg, 43·1%). *Bis*-3-*bromocamphor*-10-*mercury* melted at 188—189° after crystallisation from acetone; $[\alpha]_{5461}^{16^\circ} + 29{\cdot}13^\circ$ ($c = 1{\cdot}03$ in pyridine) (Found: Hg, 30·4. $C_{20}H_{28}O_2Br_2Hg$ requires Hg, 30·4%). 3-*Bromocamphor*-10-*mercuribromide* had m. p. 195° (Found: Hg, 39·5. $C_{10}H_{14}OBr_2Hg$ requires Hg, 39·3%), and 3-*bromocamphor*-10-*mercuri-iodide* m. p. 173° (Found: Hg, 36·4. $C_{10}H_{14}OBrIHg$ requires Hg, 36·0%).

*Replacement of Mercury by Halogens.*—A suspension of 3-chlorocamphor-10-mercurichloride in an aqueous solution of bromine and potassium bromide was warmed until the solid was converted into a heavy oil. The latter was extracted with chloroform; after being freed from bromine, the concentrated extract yielded 3-chloro-10-bromocamphor, m. p. 98° (Armstrong and Lowry, J., 1902, **81**, 1452, give m. p. 98°).

3 : 10-Dibromocamphor (αβ-dibromocamphor), m. p. 114° (lit. 114°), was prepared in a similar way.

3-*Chloro*-10-*iodocamphor.*—The mercurichloride (1 g.) was refluxed for ½ hour with iodine (1 g.) in benzene (30 c.c.). After removal of the excess of iodine by washing with sulphite and carbonate solutions the crystalline deposit from the concentrate separated from alcohol in colourless needles, m. p. 89° (Found: C, 38·3; H, 4·6. $C_{10}H_{14}OClI$ requires C, 38·4; H, 4·5%).

3-*Bromo*-10-*iodocamphor*, similarly prepared, melted at 88—89° (Found: C, 33·7; H, 4·1. $C_{10}H_{14}OBrI$ requires C, 33·6; H, 3·9%).

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