38. *Phenylmethylselenetine Mercuri-iodide.*

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THE finding of Pope and Neville (J., 1902, **81**, 1552) that racemisation occurs during the formation of mercuri-iodides from optically active selenonium bases has been confirmed.

From *dl*-phenylmethylselenetine bromide, by the action of potassium mercuri-iodide, two products are formed. One, m. p. 90°, is the impure mercuritri-iodide, which gradually decomposes. The other, which has the m. p., 140°, recorded by Pope and Neville for the *dl*-mercuritri-iodide, is apparently a *molecular compound* of the selenetine mercuritri-iodide (1 mol.) and the selenetine mercuritetraiodide (3 mols.).

d-Phenylmethylselenetine *d*-bromocamphorsulphonate, prepared by recrystallisation of the *dl*-selenetine *d*-bromocamphorsulphonate, gives a dextrorotatory chloroplatinate, and when treated with aqueous solutions of either potassium mercuritri-iodide or of mercuric iodide (1 mol.) and potassium iodide (5 mols.), yields an optically inactive product, m. p. 135°, having the same composition as the molecular compound mentioned above.

Thus, although the preparation of a mercuri-iodide of the optically active selenetine base, even by methods which yield optically active mercuri-iodides from the sulphonium base (Balfe, Kenyon, and Phillips, J., 1930, 2554), is accompanied by racemisation, the product is not the mercuritri-iodide as stated by Pope and Neville. As in the case of the sulphonium mercuri-iodides, a symmetrical structure need not be postulated for these compounds in order to explain the loss of rotatory power. The formation of an optically inactive product is rather to be ascribed to the instability of the selenetine base, which decomposes even more readily than the sulphonium bases in the presence of a soluble halide. The greater instability of selenonium, as compared with sulphonium, bases has long been recognised and is further shown in the present work by the inability to isolate a pure mercuri-iodide and by the racemisation of the chloroplatinate in solution.

EXPERIMENTAL.

dl-Phenylmethylselenetine chloroplatinate was obtained as a red cryst. solid, m. p. 170°, insol. in all solvents, on adding platinic chloride (1·0 g.; 1 mol.) in conc. HCl (1·7 c.c.; 5 mols.) to *dl*-phenylmethylselenetine bromide (1·0 g.; 1 mol.) in H_2O (10 c.c.). The m. p. is that recorded by Pope and Neville for the chloroplatinates of both the optically active and the *dl*-base.

Preparation of dl-*Phenylmethylselenetine Mercuri-iodides.*—(i) *By means of potassium mercuritri-iodide.* Addition of the mercuritri-iodide (4·1 g.; 1 mol.) in H_2O (5 c.c.) to *dl*-phenylmethylselenetine bromide (2·0 g.; 1 mol.) in H_2O (20 c.c.) produced a yellow oil, which crystallised after 12 hr. (3·9 g., m. p. 80—85°). Recrystn. from acetone separated it into a sol. fraction, m. p. 90° after two further recrystns., which was possibly impure *dl*-phenylmethylselenetine mercuritri-iodide (Found: C, 11·2; H, 1·2. $C_9H_{11}O_2I_3SeHg$ requires C, 13·3; H, 1·3%), and an insol. fraction—the molecular compound (Found: C, 17·0; H, 1·6%).

(ii) *By means of* HgI_2 *and* 5 *mols. of* KI. Solutions of *dl*-phenylmethylselenetine bromide (1·5 g.; 1 mol.) in H_2O (20 c.c.) and of KI (4·1 g.; 5 mols.) and HgI_2 (2·2 g.; 1 mol.) in H_2O (5 c.c.) were mixed. The recryst. product, m. p. 96°, appeared to be the impure *dl*-mercuritri-iodide (Found: C, 11·2; H, 1·2%). The substance, m. p. 140°, was not detected.

Phenylmethylselenetine d-*Bromocamphorsulphonate.*—The filtered solution obtained from *dl*-phenylmethylselenetine bromide (52 g.) in H_2O (200 c.c.) and silver *d*-bromocamphorsulphonate (69 g.; 1 mol.) in H_2O (750 c.c.) was, after addition of *d*-bromocamphorsulphonic acid (4 g.), concentrated at 40 mm. to 200 c.c. The crystals which separated (30 g., m. p. 169°) were recrystallised once from warm EtOH, then twice by solution in cold MeOH and removal of part of the solvent at room temp., giving *d*-phenylmethylselenetine *d*-bromocamphorsulphonate (7 g.), m. p. 174°, $[\alpha]_{5893}$ + 61·2°, $[\alpha]_{5780}$ + 63·4°, $[\alpha]_{5461}$ + 73·8° (c = 1·60, l = 2) (Found: C, 42·1; H, 4·6. Calc. for $C_{19}H_{25}O_3BrSe$: C, 41·8; H, 4·6%). Pope and Neville (*loc. cit.*) give m. p. 168° and $[\alpha]_{5893}$ + 61·5°. The salt was sparingly sol. in cold EtOH and no satisfactory change in m. p. or rotation was obtained when the resolution was attempted by recrystn. from warm EtOH; after six such crystns. the product decomposed without melting at 275° (Found: C, 58·7; H, 4·8%), and from it no derivatives could be prepared.

The *d*-bromocamphorsulphonate of the lævo-base could not be isolated from the mother-liquors of the successful resolution.

d-*Phenylmethylselenetine Chloroplatinate.*—To a solution of the *d*-selenetine *d*-bromocamphorsulphonate (1·8 g.; 1 mol.) in EtOH (10 c.c.), platinic chloride (1·0 g.; 1 mol.) in conc. HCl (1·7 c.c.; 5 mols.) was added. The red cryst. product had m. p. 90°, $[\alpha]_{5893}$ + 8·3°, $[\alpha]_{5780}$ + 8·3°, $[\alpha]_{5461}$ + 10·4° (c = 1·44, l = 2). After recrystn. from hot aq. acetone it had m. p. 95°, $[\alpha]_{5893}$ + 11·8°, $[\alpha]_{5780}$ + 10·8°, $[\alpha]_{5461}$ + 15·8° (c = 1·30, l = 2). Pope and Neville give m. p. 171° and $[\alpha]_{5893}$ +6·3°. After 7 days this solution was optically inactive (Found: C, 26·6; H, 3·3; Pt, 21·2. Calc. for $C_{18}H_{22}O_4Cl_6Se_2Pt,C_2H_6O$: C, 26·2; H, 3·1; Pt, 21·3%). The EtOH of crystn. accounts for the low m. p.

The Mercuri-iodide obtained from d-*Phenylmethylselenetine* d-*Bromocamphorsulphonate.*—(i) *By means of potassium mercuritri-iodide.* A solution of potassium mercuritri-iodide (1·2 g.; 1 mol.) in H_2O (3 c.c.) was added to *d*-phenylmethylselenetine *d*-bromocamphorsulphonate (1·0 g.; 1 mol.) in H_2O (7 c.c.). The pptd. white solid (1·1 g., m. p. 125°) was sparingly sol. in acetone and EtOH, and was optically inactive in both solvents. After recrystn. from EtOH–Et_2O it had m. p. 135° (Found: C, 17·1; H, 1·7; I, 42·5. $3C_{18}H_{22}O_4I_4Se_2Hg,C_9H_{11}O_2I_3SeHg$ requires C, 17·5; H, 1·8; I, 44·2%). No change in composition or m. p. was brought about by further recrystn. (Found: C, 17·1; H, 1·7%).

(ii) *By means of* HgI_2 *with* 5 *mols. of* KI. A solution of HgI_2 (0·9 g.; 1 mol.) and KI (1·6 g.; 5 mols.) in H_2O (5 c.c.) was added to *d*-phenylmethylselenetine *d*-bromocamphorsulphonate (1·0 g.; 1 mol.) in H_2O (5 c.c.). An optically inactive white solid (1·0 g.), m. p. 125°, was obtained as in the previous expt. After recrystn. from EtOH and Et_2O it had m. p. 135° (Found: C, 17·1; H, 1·8%).

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