201. *Mercury Derivatives of Camphor. Part I. The Constitution of Reychler's Acid.*

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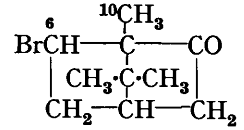
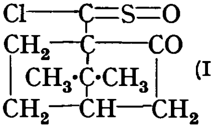
THE sulpho-group of Reychler's camphorsulphonic acid has been assigned position 6 or 10 in the camphor nucleus. The evidence for the former rests upon the properties of " β "-bromocamphor obtained by thermal decomposition of the sulphonyl bromide and given the constitution (I) (Armstrong and Lowry, J., 1902, **81**, 1449; Forster, *ibid.*, p. 264; compare Burgess and Lowry, J., 1925, **127**, 271), whilst in support of the latter, Wedekind, Schenk, and Stüsser (*Ber.*, 1923, **56**, **633**) have shown that the chlorosulphoxide resulting from the action of pyridine on the sulphonyl chloride must have the structure (II).

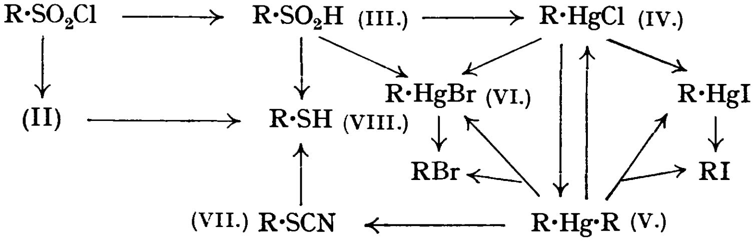
(I.)





(II.)

In adopting these two compounds as criteria for the constitution of Reychler's acid, it has never been conclusively demonstrated that their formation from the parent acid is free from intramolecular change, for Wedekind, Schenk, and Stüsser (*loc. cit.*) were unable to characterise the reduction product of (II), and although Lipp and Lausberg (*Annalen*, 1924, **436**, 274) concluded that the bromine in (I) occupies the 10-position, their evidence depends on the validity of formulating the " dibromide " from camphene as 2 : 10-dibromocamphane.



R = camphor-10-radical.

It has now been found that mercury derivatives of camphor may be prepared from the sulphinic acids by the method devised by Peters in the aromatic series (*Ber.*, **1906**, **39**, 3626), and the opportunity has been taken here to re-examine the constitutional relationships of the compounds mentioned above. Thus, as the diagram shows, the sulphinic acid (III) derived from Reychler's acid was converted into the mercurated camphors (IV) and (V), each of which on bromination yielded " β "-bromocamphor with intermediate formation of (VI). Iodination followed a similar course. Proof that the halogen occupies the same position as the original sulphur was obtained from the action of thiocyanogen on (V). Söderbäck (*Annalen*, 1919, **419**, 266) has shown that with diphenylmercury the products are phenyl mercurithiocyanate and phenyl thiocyanate; in the present case, without any attempt to isolate (VII), the product was reduced directly to the thiol (VIII) identical with that obtained from (III) (Drummond and Gibson, J., 1926, 3073). The same thiol resulted from the reduction of (II), thus establishing the constitutional similarity of the various compounds and, in conjunction with the oxidation of (II) to ketopinic acid (Wedekind, Schenk, and Stüsser, *loc. cit.*), also fixing position 10 in the camphor nucleus as the seat of substitution.

The misleading properties of " β "-bromocamphor must, therefore, be attributed to the peculiar position of the bromine atom in the molecule.

EXPERIMENTAL.

Camphor-10-sulphinic acid was prepared either by the method of Hilditch (J., 1910, **97**, 1096) or by the more general procedure described by Krishna and Singh (*J. Amer. Chem. Soc.*, 1928, **50**, 792). In each case the product was an oil difficult to crystallise but directly applicable without disadvantage to the preparation of the mercury derivatives.

Camphor-10-*mercurichloride*.—Camphor-10-sulphinic acid (1 mol.) was heated for 4—5 hours with an alcoholic solution of mercuric chloride (2 mols.). The product was poured into water and after 12 hours the precipitate was collected, washed with alcohol, and extracted with hot chloroform. Concentration of the extract yielded *camphor*-10-*mercurichloride* contaminated with mercury salts, and a residue consisting of a variable quantity of oil containing some unchanged sulphinic acid and some disulphoxide. The mercurichloride was crystallised twice from alcohol to which a little chloroform had been added; m. p. 166°, $[\alpha]_{5461}^{18^\circ}$ — 62·4° (c = 10·32 in pyridine) (Found : Hg, 52·0; Cl, 9·0. $C_{10}H_{15}OClHg$ requires Hg, 51·8; Cl, 9·2%). The compound is slightly soluble in cold sodium hydroxide solution, is stable towards inorganic sulphides and cold dilute acids, but is decomposed by concentrated sulphuric acid.

Biscamphor-10-*mercury*.—The mercurichloride (12 g.), dissolved in hot acetone, was added to water (150 c.c.), and the suspension treated with alkaline stannous chloride (from 10 g. of sodium hydroxide, 8 g. of stannous chloride, and 200 c.c. of water). The mixture was stirred for 2 hours, and the solid was then collected and extracted with boiling acetone. On careful dilution with water and subsequent cooling, the product separated in crystalline form, m. p. 255—256°; $[\alpha]_{5461}^{18°}$ − 80·87° (c = 10·14 in pyridine) (Found : Hg, 40·0. $C_{20}H_{30}O_2Hg$ requires Hg, 39·9%). When it was heated in alcoholic solution with mercuric halides (mol. proportions), the corresponding camphor mercurihalides resulted.

Camphor-10-*mercuribromide*, also prepared by the direct action of mercuric bromide on the sulphinic acid (compare above), had m. p. 156° (Found : Br, 18·5. $C_{10}H_{15}OBrHg$ requires Br, 18·5%). *Camphor*-10-*mercuri-iodide* had m. p. 146° (Found : I, 26·4. $C_{10}H_{15}OIHg$ requires I, 26·5%). The same compounds were formed together with the corresponding halogenated camphors (compare below) during bromination and iodination of biscamphor-10-mercury.

10-*Bromocamphor* (β-*Bromocamphor*).—Camphor-10-mercurichloride, suspended in an aqueous solution of bromine in potassium bromide, was shaken at 60° for 10 minutes. The resulting mixture was extracted with chloroform, and the extract washed with aqueous solutions of potassium sulphite and potassium carbonate, dried over calcium chloride, and concentrated. The crystalline product was recrystallised from alcohol; m. p. 77°; *oxime*, m. p. 156°, in accordance with the literature values. When the same reaction was conducted at the ordinary temperature, only camphor-10-mercuribromide resulted.

10-*Iodocamphor* was prepared by heating the mercurichloride (1 mol.) with iodine (1½ mols.) in benzene for 1 hour. The liquid was washed with potassium sulphite and carbonate solutions and, after drying, removal of the solvent yielded a crystalline product which was recrystallised from alcohol; m. p. 75° (Found : I, 45·6. $C_{10}H_{15}OI$ requires I, 45·7%). When the reaction was carried out in potassium iodide solution, the results were analogous to those in bromination, but the iodocamphor was less readily purified.

10-*Iodocamphoroxime* was prepared by the usual procedure and crystallised from alcohol; m. p. 158° (Found : I, 43·1. $C_{10}H_{16}ONI$ requires I, 43·3%).

Camphor-10-*thiol*.—(1) Biscamphor-10-mercury (5 g.) was kept for a week at room temperature with 40 c.c. of *N*-thiocyanogen in chloroform. After removal of the yellow precipitate, the filtrate was evaporated and the residual oil was dissolved in alcohol and reduced with zinc and hydrochloric acid for 1 hour. Thereafter the mixture was steam-distilled, the solid which collected in the receiver was shaken with sodium hydroxide, and after filtering from camphor (formed by reduction of camphor mercurithiocyanate) the thiol was precipitated with sulphuric acid. Crystallised from aqueous alcohol, the product had m. p. 66° (unaffected by admixture with an authentic specimen), gave the characteristic coloration (extracted by benzene) on treatment with aqueous-alcoholic nickel acetate (Drummond and Gibson, *loc. cit.*), and on titration with iodine yielded the disulphide, m. p. and mixed m. p. 225° (Lowry and Donnington, J., **1903**, **83**, 479, give m. p. 224°). (2) 10-Chlorocamphor sulphoxide, prepared and purified as described by Wedekind, Schenk, and Stüsser (*loc. cit.*), was similarly reduced. Steam distillation yielded the same thiol, m. p. 65—66° after crystallisation; disulphide, m. p. 224°; nickel acetate test was positive.

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