CCCCXI.—*Co-ordinated Mercaptides.*

By ALAN MACLEAN DRUMMOND and DAVID TEMPLETON GIBSON.

MANY investigations have been undertaken to determine which of the formulæ $R{\cdot}SO_2{\cdot}SR$ (I) and $R{\cdot}SO{\cdot}SO{\cdot}R$ (II) better represents the reactions of disulphoxides. Hilditch (J., 1910, **97**, 1091), who examined the rotations of camphor disulphoxide and related substances, supported (II), whereas the recent work of Smiles (J., 1924, **125**, 176; 1925, **127**, 224) is decidedly in favour of (I).

Our original aim was to prepare *d*-camphoryl *l*-camphoryl disulphoxide, for according as this substance is (I) or (II) it should be

$$(d)C_{10}H_{15}O{\cdot}SAg + Cl{\cdot}SO_2{\cdot}C_{10}H_{15}O(l) = AgCl + \\ (d)C_{10}H_{15}O{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_{15}O(l) \text{ or } (d)C_{10}H_{15}O{\cdot}SO{\cdot}SO{\cdot}C_{10}H_{15}O(l)$$

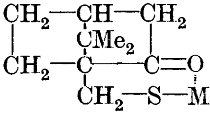
optically active or internally compensated; but all our attempts were unsuccessful. We eventually traced the failure to the fact that the silver derivative of thiolcamphor is not a normal mercaptide, but has the composition $C_{10}H_{15}O\cdot SAg,AgNO_3,H_2O$ (A); and only one-half of the silver is ionised in aqueous alcohol. It is readily soluble in benzene containing thiolcamphor and from the resulting orange-red solution a yellow solid was obtained in which one-third of the silver is ionisable.

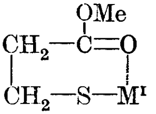
$$3C_{10}H_{15}O\cdot SAg,AgNO_3,H_2O + C_{10}H_{15}O\cdot SH = 2(C_{10}H_{15}O\cdot SAg)_2,AgNO_3,H_2O + HNO_3 + H_2O.$$

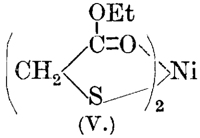
The substance depressed the freezing point of benzene so slightly that it was thought desirable to test the solution for colloidality; but neither Tyndall cone nor Brownian movement was observed and a solution in benzene diffused rapidly through parchment. The nickel derivative (B), $(C_{10}H_{15}O\cdot S)_2Ni,C_{10}H_{15}O\cdot SH$, is a mahogany coloured powder, very soluble in benzene.

These remarkable properties—non-ionisable character, solubility in anhydrous organic solvents, anomalous colour, and, in certain cases, stability on heating—support the view that the metallic atom is combined, not only with the sulphur atom of the thiolcamphor complex (III) by a principal valency, but also with the carbonyl group by residual affinity (compare the acetylacetone derivatives; Morgan and Moss, J., 1914, **105**, 189).

Recent work on the constitution of Reychler's acid (Wedekind, Schenk, and Stüsser, Ber., 1923, **56**, 633; Burgess and Lowry, J., 1925, **127**, 271) indicates that thiolcamphor is probably a β-thiol ketone. The co-ordinated ring structure of thiolcamphor derivatives, therefore, is six-membered, as with the β-diketones, nitroso-β-naphthol, etc., discussed by Sidgwick and Callow (J., 1924, **125**, 533). The new compounds differ from these in not having conjugated double bonds.


(III.)


(IV.)


(V.)

We have also examined methyl β-thiolpropionate, as it is the simplest compound containing the group we consider responsible for the abnormal behaviour of thiolcamphor derivatives. Its metallic derivatives (see IV) show similar abnormalities. The silver compound (C), $AgS\cdot C_4H_7O_2,AgNO_3,H_2O$, is, however, only sparingly soluble in a solution of the parent ester. The nickel derivatives of methyl β-thiolpropionate and of ethyl thiolacetate (V) are brown and crystalline and are very soluble in benzene, but, unlike (B), they do not contain an extra molecule of the mercaptan. The five-membered ring compound seems to be more stable than the six-membered ones, for, whereas the other nickel compounds soften gradually on heating, (V) melts sharply without decomposition like Sidgwick and Plant's co-ordination compounds of the alkali metals (J., 1925, **127**, 209).

The metallic derivatives of hydroxymethylenecamphor prepared by Lifschitz (*Rec. trav. chim.*, 1922, **41**, 627) are probably similar in constitution to the preceding. On the other hand, nickel β-thiolpropionate is similar to the previous compounds only in colour, and nickel thiolacetate is dirty green.

These experiments were rendered possible by the discovery that Lowry and Donington's original method (J., 1903, **83**, 480) for preparing thiolcamphor from the sulphonyl chloride is very materially improved by first reducing the chloride to the sulphinic acid and then reducing this to the mercaptan.

EXPERIMENTAL.

Thiolcamphor.—Camphorsulphonyl chloride was reduced to the sulphinic acid in the way described by Hilditch (J., 1910, **97**, 1096) except that no acetone was used as solvent. The oily sulphinic acid (12 g.) was added cautiously to a vigorously boiling mixture of granulated tin (20 g.) and concentrated hydrochloric acid (500 c.c.), and the whole immediately steam-distilled. The mercaptan, which solidified in the condenser (yield, 5 g.), was contaminated with a small quantity of a volatile tin compound, which was removed by two crystallisations from spirit. The mercaptan was obtained as cubic crystals and as needles, each form melting at 66°. Much poorer yields were obtained with zinc, aluminium, magnesium, or nickel in place of tin.

Silver Thiolcamphor Argentinitrate (A).—Thiolcamphor (5 g.) in alcohol (50 c.c.) was added to silver nitrate (11 g.) in 90% alcohol (100 c.c.) with stirring. A yellow precipitate momentarily formed and dissolved again. Kept in subdued light, the solution slowly deposited white crystals (14 g.) [Found : C, 25·2; H, 3·6; S, 7·1; N, 3·2; Ag (total), 45·1; Ag (ionised), 22·6. $C_{10}H_{17}O_5NSAg_2$ requires C, 25·1; H, 3·6; S, 6·7; N, 2·9; Ag (total), 45·1; Ag (ionised), 22·6%]. The compound chars at 200—210°, and in chloroform solution has $[\alpha]_{5461}^{19^\circ} + 21^\circ$. It is soluble in ethylene dibromide and in hot alcohol, but insoluble in benzene and ligroin. This and the following compound gave the brown-ring test for nitrate.

The orange-red solution obtained by warming 2 g. of (A) for a few minutes with a solution of thiolcamphor (0·8 g.) in dry benzene (12 c.c.) was separated from the water formed, concentrated in a vacuum, and poured into ligroin (50 c.c.). The precipitated yellow solid (80% yield) decomposed above 230° without melting. It is extremely readily soluble in benzene, less soluble in alcohol, and has $[\alpha]_{5461}^{15^\circ}$ + 64° in chloroform solution [Found : C, 31·8; H, 4·1; S, 8·2; N, 1·6; Ag (total), 41·8; Ag (ionised), 13·5. $C_{20}H_{32}O_6NS_2Ag_3$ requires C, 31·2; H, 4·2; S, 8·3; N, 1·8; Ag (total), 42·1; Ag (ionised), 14·0%].

Thiolcamphor Cadmibromide.—Crystalline cadmium bromide (0·8 g.) dissolved in alcohol was added to a similar solution of thiolcamphor (0·4 g.). The *cadmibromide* separated immediately in fine, white crystals insoluble in all the usual solvents (Found : Cd, 29·3; Br, 21·8. $C_{10}H_{15}OBrSCd$ requires Cd, 30·0; Br, 21·4%).

Thiolcamphor Stannochloride.—A filtered solution of stannous chloride (0·4 g.) in dry ether was added to thiolcamphor (0·3 g.) in the same solvent. The *stannochloride* separated over-night as glistening crystals, soluble in benzene and other organic solvents; m. p. 187° without decomp. [Found : Sn, 25·8; Cl, 15·8 (by Robertson's method, J., 1915, **107**, 902); S, 10·3; H, 4·9. $(C_{10}H_{16}OS)_3,Sn_2Cl_4$ requires Sn, 25·7; Cl, 15·4; S, 10·4; H, 4·9%].

Nickel Thiolcamphor (B).—Thiolcamphor (0·4 g.) in alcohol was added to a solution of nickel chloride (0·8 g.) and sodium acetate (0·4 g.) in aqueous alcohol. The deep red solution was evaporated in a vacuum and extracted with benzene. Evaporation of this solution gave a mahogany-coloured solid soluble in all the usual organic solvents, but insoluble in water (Found : Ni, 9·4; S, 15·5. $C_{30}H_{46}O_3S_3Ni$ requires Ni, 9·7; S, 15·8%).

Cupric chloride, like ferric chloride, oxidises thiolcamphor to the disulphide, m. p. 222°.

Methyl β-*thiolpropionate*, prepared by esterifying β-thiolpropionic acid with methyl alcohol and a few drops of concentrated sulphuric acid, is a colourless, mobile, pungent liquid, b. p. 54—55°/14 mm.; n^{19° 1·4628 (Found : S, 26·3. $C_4H_8O_2S$ requires S, 26·6%).

Methyl silver β-*thiolpropionate argentinitrate* was prepared as (A) above, and is similar to it in properties (Found : Ag, 52·4; S, 8·0. $AgC_4H_7O_2S,AgNO_3,H_2O$ requires Ag, 52·0; S, 7·7%). The compound gives a positive brown-ring test.

Methyl nickel β-*thiolpropionate*, prepared as (B), was obtained in brown, rhombic plates after crystallisation from ether [Found : Ni, 19·7; S, 21·3. $(C_4H_7O_2S)_2Ni$ requires Ni, 19·9; S, 21·5%].

Ethyl nickel thiolacetate was obtained in good yield in dark brown, lustrous needles after crystallising from benzene–ligroin. These crystals smelt faintly of the ester. This smell was easily removed by heating for a short time in a high vacuum at 70°. The compound then melted sharply at 101°, without decomposition, to a clear brown liquid [Found: Ni, 20·0; S, 21·0. $(C_4H_7O_2S)_2Ni$ requires Ni, 19·9; S, 21·5%].

Nickel thiolpropionate is a brown powder soluble in dilute alkali, reprecipitated by acid, and insoluble in organic solvents [Found: Ni, 22·3. $(C_3H_5O_2S)_2Ni$ requires Ni, 21·9%].

Under the same conditions nickel chloride and thiolacetic acid gave a dirty green solid of variable composition (Found: Ni, 28·4, 29·1; S, 11·2%).

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