156. *Organic Derivatives of Sulphur, Selenium, and Tellurium. Part I.*

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The action of hydrogen sulphide, selenide and telluride on the benzoyl chloride–pyridine additive complex and on chloral hydrate has been studied.

New methods are described for the preparation of thiobenzoic and selenobenzoic acids. Certain related derivatives have been isolated, and their properties recorded.

The nature of the additive compound of pyridine and benzoyl chloride was investigated by Dehn and Ball (*J. Amer. Chem. Soc.*, 1912, **34**, 1399; 1914, **36**, 2091). Deninger (*J. pr. Chem.*, 1894, **50**, 479) showed that, in the presence of anhydrous sodium carbonate, it yields benzoic anhydride (cf. Minunni and Caberti, *Gazzetta*, 1891, **20**, 655). Claisen (*Ber.*, 1898, **31**, 1024), investigating the action of hydrogen cyanide on an ethereal solution of benzoyl chloride containing pyridine, isolated benzoyl cyanide and bis-benzoyl cyanide. The present work deals with the mechanism of the reaction between the additive compound and the hydrides of sulphur, selenium and tellurium.

It was thought probable that the reaction might afford a simple means of preparing dibenzoyl sulphide or dibenzoyl disulphide. Fromm and Schmoldt (*Ber.*, 1907, **40**, 2682) obtained the monosulphide by means of the reaction $2C_6H_5{\cdot}COCl + Na_2S = (C_6H_5{\cdot}CO)_2S + 2NaCl$ and it might be surmised that hydrogen sulphide would react similarly. In pyridine, however, the reaction takes a more complex course, though some of the preceding compounds have been isolated as by-products.

Staudinger and Freudenberger (*Ber.*, 1928. **61**, 1576) and Fromm (*Ber.*, 1895, **28**, 898) have shown that the oxygen atom of a ketone may be replaced by sulphur, with the formation of a thioketone, by mere saturation of an alcoholic solution of the ketone with dry hydrogen sulphide (cf. Linnell and Sharma, *J. Pharm. Pharmacol.*, 1939, **12**, 263), and the present work shows that a similar substitution occurs when the pyridine–acid chloride complex is subjected to the action of this gas. No apparent reaction occurs when benzoic anhydride is substituted for benzoyl chloride.

Derivatives of Chloral.—Bis-(βββ-trichloro-α-hydroxyethyl) sulphide, $[CCl_3{\cdot}CH(OH)]_2S$, was obtained by Hageman (*Ber.*, 1872, **5**, 154) by the action of hydrogen sulphide on an ethereal solution of chloral. Although it is decomposed by water, it is fairly stable in hydrochloric acid solution (Wyss, *Ber.*, 1874, **7**, 211), and use has been made of this fact in the preparation of the *selenium* analogue. The tellurium analogue could not be prepared.

Experimental.

Dithiobenzoyl Oxide $(C_6H_5{\cdot}CS)_2O$.—Freshly distilled benzoyl chloride (20 c.c.) was added slowly to " AnalaR " pyridine (30 c.c.); after 5 minutes the additive compound began to separate. Hydrogen sulphide (dried over phosphoric oxide) was led over the mixture, stirred under a reflux condenser, at such a rate that the heat of reaction maintained a moderate temperature; after 1 hour, the initial pink colour disappeared and a viscous yellow paste formed. This was stirred with 400 c.c. of dilute hydrochloric acid (1 : 1) to remove the pyridine; oily globules of thiobenzoic acid were set free. The solid was filtered off and dissolved in hot alcohol; at 0°, *dithiobenzoyl oxide* separated in colourless crystals, m. p. 112° (after three recrystallisations from hot alcohol), readily soluble in benzene, carbon disulphide, and acetic acid, slightly soluble in ether, and insoluble in water and hot aqueous alkali (Found : C, 65·0; H, 4·1; S, 24·0; *M*, cryoscopic in benzene, 263. $C_{14}H_{10}OS_2$ requires C, 65·1; H, 3·9; S, 24·8%; *M*, 258·3). Warming with alcoholic potassium hydroxide caused immediate decomposition; after removal of the alcohol, acidification of the residue with hydrochloric acid gave hydrogen sulphide and benzoic and thiobenzoic acids. Dithiobenzoyl oxide dissolved in concentrated sulphuric acid to give a yellow solution, and was oxidised by concentrated nitric acid to benzoic acid. Gentle heating with 50% nitric acid gave a small quantity of *dibenzoyldisulphone*, which formed white needles from alcohol, m. p. 141° (Found : S, 18·95. $C_{14}H_{10}S_2O_6$ requires S, 18·95%). Dithiobenzoyl oxide was boiled under reflux with an excess of aniline, and the cooled mixture poured into hydrochloric acid; benzanilide (m. p. 163°) was precipitated, but no thiobenzanilide was isolated.

The original alcoholic filtrate was evaporated to dryness after addition of concentrated aqueous ammonia. Some ammonium thiobenzoate was formed, but the white crystals obtained on recrystallisation from hot water consisted mainly of benzamide, m. p. 127°; no thiobenzamide was isolated.

α-Selenobenzoic Acid, $C_6H_5{\cdot}CO{\cdot}SeH$.—An attempt was made to prepare diselenobenzoyl oxide in a similar manner. Reaction with the benzoyl chloride–pyridine complex occurred, and a black mass resulted when the product was poured into hydrochloric acid (1 : 1). A hot alcoholic extract of the mass was filtered and cooled; it gave α-selenobenzoic acid, m. p. 132—133° after two recrystallisations from hot alcohol and one from carbon disulphide [Found : C, 45·0; H, 2·95; Se, 42·6. Found (micro-analysis by Drs. Weiler and Strauss of Oxford): C, 45·4; H, 2·95. Calc.: C, 45·4; H, 3·2; Se, 42·7%]. Mingoia (*Gazzetta*, 1926, **56**, 835) gives m. p. 133°. The present method affords a rapid and simple means of preparing the acid in good yield.

The acid has a tendency to decompose, depositing red selenium, if its alcoholic solution is too strongly heated, and it is immediately decomposed by concentrated nitric acid and slowly by warming with aqueous alkali, though rapidly in alcoholic solution.

α-Tellurobenzoic acid could not be prepared in a similar way.

Bis-(ββββ*-trichloro-α-hydroxyethyl*) *Sulphide.*—Pure chloral was obtained from chloral hydrate and distilled over phosphoric oxide (b. p. 98·3°). An ethereal solution was saturated with hydrogen sulphide for 6 hours, the ether removed, and the residue shaken with dilute hydrochloric acid and recrystallised from ether; m. p. 126—127° (Hageman, *loc. cit.*, gives 127—128°). A much purer product can be obtained by saturating a concentrated acidified aqueous solution of chloral hydrate with hydrogen sulphide. After some hours a mass of white crystals is thrown down; after washing with hydrochloric acid and recrystallisation from ether, the m. p. is 128°. The product has a strong mercaptan odour, and reduces alcoholic mercuric chloride, mercurous chloride being precipitated; the solution then smells of black currants, but no definite compound can be isolated. Treatment with sodium in alcohol gives a similar odour.

Bis-(βββ*-trichloro-α-hydroxyethyl*) *Selenide.*—This particularly unstable *compound* was prepared by passing hydrogen selenide into a saturated solution of chloral hydrate containing an excess of hydrogen chloride. It was precipitated after some hours in reddish needles and was purified in the same way as the corresponding sulphur compound; m. p. 94—98° (decomp. into chloral and hydrogen selenide) (Found : Se, 21·2. $C_4H_4O_2Cl_6Se$ requires Se, 21·0%).

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