CCCXLVII.—*Mercury Compounds of Thiophen and Selenophen.*

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Although it has long been known that thiophen forms compounds with mercuric salts, the composition of these compounds has not been clearly established. Volhard (*Annalen*, 1892, **267**, 172) showed that by shaking thiophen with aqueous mercuric chloride either one or two atoms of hydrogen in the thiophen nucleus could be replaced by HgCl, and that the monochloromercuri-compound, $C_4H_3S{\cdot}HgCl$, was soluble in hot alcohol, from which it could be recrystallised, whereas the dichloromercuri-compound, $C_4H_2S(HgCl)_2$, was an insoluble powder which was only very slightly decomposed by boiling concentrated hydrochloric acid.

By shaking thiophen with saturated mercuric acetate solution, later workers obtained derivatives of varying composition. Dimroth (*Ber.*, 1899, **32**, 758) claimed to have prepared the compound $C_4H_2S(Hg{\cdot}OH)(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)$ as a white insoluble powder, but Schwalbe (*Ber.*, 1905, **38**, 2208) suggested that the substance was a mixture. Paolini (*Gazzetta*, 1907, **37**, i, 58) stated that the substance prepared by this reaction had the composition $C_4H_4S(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)_4$ and on treatment with aqueous sodium chloride gave the chloride, $C_4H_4S(HgCl)_4$, which in turn, on boiling with aqueous alkalis, yielded the corresponding hydroxide, $C_4H_4S(Hg{\cdot}OH)_4$.

It has been found by the present authors that the product obtained by shaking thiophen with a saturated solution of mercuric acetate is *diacetoxymercurithiophen*, $C_4H_2S(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)_2$, a white insoluble compound produced by a reaction similar to that shown by Volhard to occur between thiophen and mercuric chloride. When the diacetoxymercuri-compound was boiled with concentrated aqueous sodium chloride solution, dichloromercurithiophen, $C_4H_2S(HgCl)_2$, was obtained, and quantitative experiments have shown that this reaction proceeds according to the equation $C_4H_2S(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)_2 + 2NaCl = C_4H_2S(HgCl)_2 + 2NaO{\cdot}CO{\cdot}CH_3$. The product of the interaction of thiophen with basic mercuric sulphate was *dihydroxymercurithiophen mercurisulphate*, $C_4H_2S(Hg{\cdot}OH)_2,HgSO_4$, a white insoluble powder identical in composition with the substance obtained by Spielmann and Schotz (*J. Soc. Chem. Ind.*, 1919, **38**, 188T), and this compound and diacetoxymercurithiophen, on boiling with aqueous potash, appeared to yield the same hydroxide, $C_4H_2S(Hg{\cdot}OH)_2$. Similar reactions with selenophen proceed in a strictly similar manner, yielding analogous derivatives.

Because of the small quantities of thiophen and selenophen available for this work, no attempt has been made to isolate the soluble mono-substituted derivatives of these compounds.

The thiophen and selenophen compounds are moderately stable; they are, for example, only partly decomposed on boiling even with concentrated hydrochloric acid. In solution in sulphuric acid they give the indophenin colour reaction. It thus appears very probable that they are not addition compounds, as suggested by Paolini (*loc. cit.*), but are formed by replacement of two atoms of hydrogen in the thiophen or selenophen nucleus by the mercuric salt radical.

Steinkopf and Bauermeister (*Annalen*, 1914, **403**, 50) have already shown that bromine reacts with dichloromercurithiophen to give di- and tetra-bromothiophen; and our attempts to prepare halogen derivatives of these compounds were unsuccessful, yielding always substitution products of thiophen and selenophen with separation of the free mercuric salt.

Dihydroxymercurithiophen mercurisulphate, on treatment with bromine water, yielded tetrabromothiophen, and the corresponding selenophen compound similarly gave tetrabromoselenophen; with iodine, the thiophen compound yielded a small quantity of tetraiodothiophen, m. p. 183—184° after recrystallisation from benzene (Paolini and Silbermann, *Atti R. Accad. Lincei*, 1915, **24**, ii, 206, give m. p. 198°). *Di-iodoselenophen* was obtained on treating *dihydroxymercuriselenophen mercurisulphate* or *diacetoxymercuriselenophen* with iodine. The reaction of chlorine water with these substances appeared to proceed differently, for neither tetrachlorothiophen nor tetrachloroselenophen was obtained, and in the latter case the selenium was directly attacked with formation of selenium tetrachloride, for on boiling with sulphurous acid a precipitate of selenium was produced.

EXPERIMENTAL.

Diacetoxymercurithiophen, $C_4H_2S(Hg\cdot O\cdot CO\cdot CH_3)_2$.—Thiophen was shaken with a concentrated solution of mercuric acetate, prepared by addition of mercuric oxide (20 g.) to hot glacial acetic acid (200 c.c.), and the white solid formed was washed with water and dried at 100° (Found: C, 16·0; H, 1·4; S, 5·8. $C_8H_8O_4SHg_2$ requires C, 16·0; H, 1·3; S, 5·4%).

Diacetoxymercurithiophen decomposed on heating. It was kept with excess of bromine water; the supernatant solution then gave the reactions for mercury and the yellow residue, when recrystallised from benzene, gave tetrabromothiophen as a white solid, m. p. 112° (Found: C, 12·1; Br, 80·0. Calc. for C_4Br_4S: C, 12·0; Br, 80·0%).

Dichloromercurithiophen, $C_4H_2S(HgCl)_2$, obtained as a white insoluble powder by warming a concentrated aqueous sodium chloride solution with diacetoxymercurithiophen, was well washed with water and dried at 100°. It darkened on exposure to bright sunlight and decomposed on heating with formation of a white sublimate (Found: C, 9·3; H, 0·5. Calc. for $C_4H_2Cl_2SHg_2$: C, 8·7; H, 0·4%).

Dihydroxymercurithiophen mercurisulphate,

$$C_4H_2S(Hg\cdot OH)_2,HgSO_4,$$

was prepared as a white insoluble powder by shaking thiophen with aqueous mercuric sulphate (Denigès's solution). It easily decomposed on heating. The nature of this substance renders purification impossible and the analysis given is the mean of results obtained for several specimens (Found : C, 5·8; H, 0·5; S, 8·3. $C_4H_4O_6S_2Hg_3$ requires C, 5·9; H, 0·5; S, 7·9%). On treatment with excess of iodine in potassium iodide solution at 80° for several hours, it gave tetraiodothiophen as a pale yellow solid of characteristic pleasant smell; this darkened rapidly on exposure to bright sunlight (Found : C, 8·4; I, 84·6; S, 5·6. Calc. for C_4I_4S : C, 8·2; I, 86·4; S, 5·4%). That this reaction is complex and that small quantities of other iodo-derivatives of thiophen are also formed was shown by allowing a known weight of dihydroxymercurithiophen mercurisulphate to stand in contact with a known volume of standard iodine solution and titrating the excess of iodine with sodium thiosulphate solution. It was thus found that one molecule of the mercurisulphate reacts with 5 atoms of iodine.

Diacetoxymercuriselenophen, $C_4H_2Se(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)_2$, a cream-coloured, insoluble powder, was prepared by shaking selenophen with mercuric acetate solution prepared in the manner described above (Found : C, 15·2; H, 1·4. $C_8H_8O_4SeHg_2$ requires C, 14·8; H, 1·2%). On long standing with bromine water, it gave tetrabromoselenophen, but in so small a yield that it could not be completely purified by recrystallisation from benzene and had m. p. 94° (Found : C, 10·9; Br, 71·7. Calc. for C_4Br_4Se : C, 10·7; Br, 71·6%). With iodine in potassium iodide solution, the diacetoxymercuri-compound yielded a small amount of *di-iodoselenophen*, a pale yellow solid of characteristic pleasant smell, m. p. 45° after recrystallisation from benzene (Found : C, 12·4; H, 0·9; I, 68·5. $C_4H_2I_2Se$ requires C, 12·6; H, 0·5; I, 66·3%).

Dichloromercuriselenophen, $C_4H_2Se(HgCl)_2$, was obtained as a white powder by boiling the acetate with concentrated sodium chloride solution (Found : C, 8·7; H, 0·7. $C_4H_2Cl_2SeHg_2$ requires C, 8·0; H, 0·3%).

Dihydroxymercuriselenophen, $C_4H_2Se(Hg{\cdot}OH)_2$, a dark grey, insoluble powder which, like the corresponding thiophen compound, decomposed explosively on heating, was obtained on boiling the acetate or mercurisulphate with aqueous potassium hydroxide (Found : C, 8·4; H, 0·65. $C_4H_4O_2SeHg_2$ requires C, 8·5; H, 0·7%).

Dihydroxymercuriselenophen mercurisulphate,

$$C_4H_2Se(Hg{\cdot}OH)_2,HgSO_4,$$

was prepared as a white or cream-coloured powder by shaking selenophen with concentrated mercuric sulphate solution (Found : C, 6·6; H, 0·2. $C_4H_4O_6SSeHg_3$ requires C, 5·6; H, 0·2%). It reacts generally in a very similar manner to diacetoxymercuriselenophen: on treatment with aqueous sodium chloride solution, it gives the corresponding chloride; with bromine water, it gives tetrabromoselenophen; and with iodine in aqueous potassium iodide, a mixture of iodo-substitution products of selenophen is produced.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research which enabled one of us (J. B. P.) to take part in this work.

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[*Received, December 8th*, 1928.]