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Received December 1, 1950.

## Reactions of Diselenium Dichloride with Sodium Sulphinates

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This note is a preliminary report on the synthesis of two new types of selenium sulphur compounds, viz., diselenium and triselenium disulphinates.

The diselenium disulphinates, Se<sub>2</sub>(SO<sub>2</sub>R)<sub>2</sub>, are formed when diselenium dichloride reacts, under cooling in ice, with an excess of finely powdered, anhydrous sodium benzene- or p-toluenesulphinate, suspended in benzene:

$$Se_2Cl_2 + 2 RSO_2Na = Se_2(SO_2R)_2 + 2 NaCl$$

The following proportions of reagents have been used: 10 g of sodium benzenesulphinate in 20 ml of benzene, or 12 g of sodium p-toluenesulphinate in 40 ml of benzene; 2 ml of diselenium dichloride. The contents of the flask are stirred with a glass rod for a few minutes, until the diselenium dichloride colour disappears. The mixture is subsequently heated rapidly, the sodium chloride and the excess of so-

dium sulphinate are filtered off, and ligroin is added to the filtrate.

The benzene compound melts at 79-80°C, the p-toluene compound at 104-106°C (dec.).

0.1801 g substance: 33.34 ml of 0.09754 N iodine (Norris & Fay).

Se<sub>2</sub>(SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (440.3) Calc. Se 35.86 Found Se 35.63 0.1408 g substance: 23.61 ml of 0.1022 N iodine.

 $Se_2(SO_2C_7H_7-p)_2$  (468.3) Calc. Se 33.72 Found Se 33.83

The triselenium disulphinates,  $Se_3(SO_2R)_2$ , result if, for the above process, the sodium sulphinates are suspended in dry ether instead of in benzene. Probably a rearrangement of primarily formed diselenium disulphinate takes place:

$$2 \operatorname{Se}_{2}(SO_{2}R)_{2} = \operatorname{Se}(SO_{2}R)_{2} + \operatorname{Se}_{3}(SO_{2}R)_{2}$$

The last change is in accordance with the behaviour of the corresponding sulphur compounds,  $S_2(SO_2R)_2$ , which undergo rearrangement to give trithionic and pentathionic compounds 1, 2.

Triselenium di(benzenesulphinate) melts and decomposes rapidly at  $101-102^{\circ}$  C, while the triselenium di(p-toluenesulphinate) crystals liberate selenium at  $130-140^{\circ}$  C (preheated bath).

0.1069 g substance: 25.33 ml of 0.09754 N iodine.

 $Se_3(SO_2C_7H_7-p)_2$  (547.3) Calc. Se 43.28 Found Se 43.44

The diselenium and triselenium disulphinates form greenish yellow crystals, which appear to be relatively stable at room temperature; thus, some samples have so far been kept unchanged for several weeks.

Apart from the alkali triselenides, the only compounds known hitherto, with three selenium atoms, mutually bonded, in the molecule, appear to be the selenium selenocyanate, Se(SeCN)<sub>2</sub>, of Verneuil <sup>3</sup>, and the diethyl triselenide, Se<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, of Baroni <sup>4</sup>.

Further work on reactions of diselenium dichloride with sodium sulphinates, and also with sodium or potassium thiosulphonates, is in progress.

The author is indebted to Norges Almenvitenskapelige Forskningsråd for a grant.

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Received December 14, 1950.