

The success of the present method depends on the following conditions which differ from those in the ordinary crucible method. The substance is weighed in an ampoule, a stronger oxidising acid mixture is used, which is cooled at the start of the reaction, a comparatively thick layer of acid hinders material from escaping, and the large outer crucible diminishes the risk of spoiling the analysis by the frothing of the mixture. As the volume of the acid mixture is kept small by the use of the inner crucible the time required for the expulsion of the acid fumes is shortened too.

1. McHard, J. A., Servais, P. C. and Clark, N. A. *Anal. Chem.* **20** (1948) 325.
2. Smith, B. *Kiselorganiska Studier* (Diss.) Gothenburg 1951.

Received March 19, 1957.

A New Synthesis of Selenanthren-5,10-dioxide

GÖRAN BERGSON

Chemical Institute, University of Uppsala, Sweden

Selenanthren-5,10-dioxide (IV) is of considerable theoretical interest because it might exist in a *cis*- and a *trans*-form if there is a pyramidal configuration at the

selenium atom. Neither optical nor geometrical isomerism has been demonstrated for selenoxides in spite of several attempts¹. Recently Gould and McCullough² suggested that *cis-trans* isomerism was to be expected for 1,4-di-selenane-1,4-dioxide. Owing to the great difficulties in the synthesis of 1,4-diselenane its oxidation products were never prepared. Following a suggestion of professor Arne Fredga the present author started an investigation of the oxides of selenanthren (I). Since then Gould and Burlant³ have reported very promising results of a study of 1,4-diselenane. They have prepared a 1,4-dioxide and will determine its structure by X-ray methods.

The present paper describes a new synthesis of selenanthren-5,10-dioxide. A detailed report of the studies of selenanthren oxides and thianthren oxides will be published elsewhere.

Selenanthren-5,10-dioxide was first prepared by Krafft and Kaschau⁴ by the oxidation of selenanthren with nitric acid. In 1951 Cullinane⁵ reported a modification of the same method, and established the melting point to be 265°. He also characterized a hydrate and a dihydrochloride of IV. The present author has prepared selenanthren-5,10-dioxide in a way represented by the reaction scheme below.

The dioxide obtained by this method is identical with the product of Cullinane, as has been shown by IR-spectra (Fig. 1) and mixed melting points. The peak at 13.05 μ is due to out-of-plane vibration of the hydrogen atoms in the benzene nucleus,

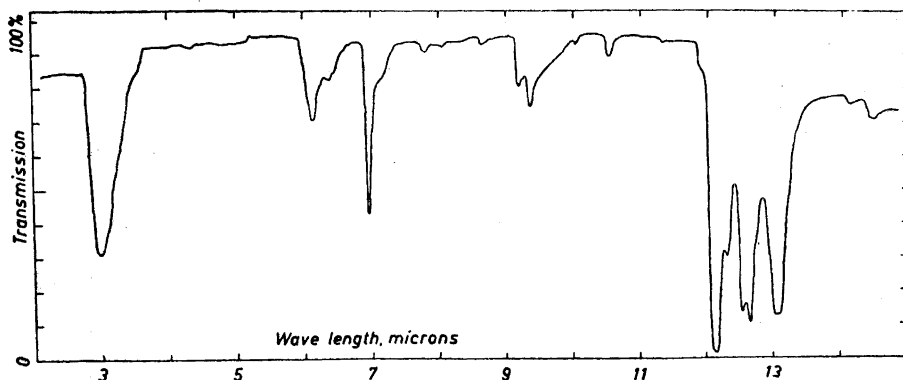
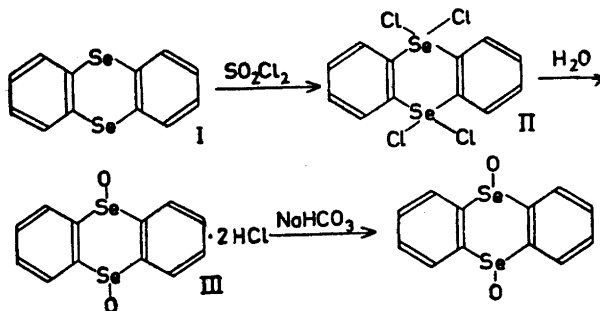


Fig. 1. Infrared absorption spectrum of selenanthren-5,10-dioxide in pressed KBr. Perkin Elmer model 21 spectrometer with NaCl prism.



and the peaks at 12.15, 12.32, 12.55 and 12.65 μ must be due to the presence of the Se-O groups. (IR-spectra of selenoxides have not been described in the literature.) A comparison of this peak system with the characteristic absorption peaks for S-O in the *trans*- and *cis*-form of thianthren-5,10-dioxide suggests that the selenoxide is not a pure *trans*-form but rather a *cis*-form or a mixture of both or perhaps a dioxide with planar configuration ⁶.

Experimental: *Selenanthren-5,5-10,10-tetrachloride (II)*. To a solution of 1.55 g of selenanthrene in 100 ml of dry benzene, 5.0 g (excess) of SO_2Cl_2 in 50 ml of benzene was added. The mixture was boiled under reflux for 30 min. The tetrachloride separated as a yellow fine crystalline solid. About 70 ml of benzene was then removed by distillation, and from the cooled reaction mixture the tetrachloride was obtained by filtration. It was washed with dry benzene and then dried in vacuum, m. p. 208–209.5° (decomp.). Yield 2.10 g (89 %). (Found: Se 34.3; 34.7; Cl 31.3. Calc. for $\text{C}_{12}\text{H}_8\text{Se}_2\text{Cl}_4$: Se 34.9; Cl 31.4).

Selenanthren-5,10-dioxide dihydrochloride (III). 2.00 g of selenanthren tetrachloride was hydrolysed with 100 ml of boiling water. After filtration and evaporation the dihydrochloride was obtained as a white solid in quantitative yield, m. p. 228–229° (decomp.). (Found: Se 38.1; Cl 17.1. Calc. for $\text{C}_{12}\text{H}_8\text{O}_2\text{Se}_4 \cdot 2\text{HCl}$: Se 38.4; Cl 17.1).

Selenanthren-5,10-dioxide (IV). 1.25 g of selenanthren-5,10-dioxide dihydrochloride was dissolved in 100 ml of water. 0.56 g of NaHCO_3 was added and the solution evaporated on a water bath. The residue was extracted with 100 ml of boiling chloroform and after evaporation the crude dioxide (m. p. 256–258°) was obtained in quantitative yield. This product was washed with 50 ml of ether and 15 ml of water and then recrystallized from water. The dioxide separated on cooling as a hydrate which

was dried to constant weight at 120°. In this way selenanthren-5,10-dioxide with m. p. 264–265° (decomp.) was obtained. Yield 0.68 g (66 %). (Found: Se 46.3. Calc. for $\text{C}_{12}\text{H}_8\text{O}_2\text{Se}_4$: Se 46.2). The selenium analyses have been carried out according to Fredga ⁷.

Thanks are due to Mr. Stig Bergwall for technical assistance with the IR-spectra. A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

- Campbell, T. W., Walker, H. G. and Copping, G. M. *Chem. Revs.* **50** (1952) 335.
- Gould, E. S. and McCullough, J. D. *J. Am. Chem. Soc.* **73** (1951) 1105.
- Gould, E. S. and Burlant, Wm. *J. Am. Chem. Soc.* **78** (1956) 5825.
- Krafft, F. and Kaschau, A. *Ber.* **29** (1896) 443.
- Cullinane, N. M. *J. Chem. Soc.* **1951** 237.
- Bergson, G. *To be published*.
- Fredga, A. *Diss. Uppsala Universitets Årsskrift* 1935:5, p. 16.

Received March 20, 1957.

Preparation of Lithium Azide

NIELS HOFMAN-BANG

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

The most common methods for the preparation of lithium azide, LiN_3 , are interaction of lithium sulfate and barium azide, and, especially, neutralization of aqueous hydrazoic acid with lithium hydroxide. Considering that preparation and handling of hydrazoic acid require care, it occurred to me that sodium azide and