

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; Cl 31.4). 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.

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Preparation of Lithium Azide

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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

lithium sulfate, which is generally kept on stock in a laboratory, might interact to give lithium azide and sodium sulfate.

The four salts in question are all soluble in water. Lithium azide is soluble and sodium azide is sparingly soluble in ethanol (0.22 g NaN₃ per 100 g at 0 °C), while lithium and sodium sulfate are insoluble. Even in 75–80 % ethanol the solubilities of lithium and sodium sulfate are very small. Based on these facts the following method of preparation has been worked out:

1.30 g of sodium azide and 1.41 g of lithium sulfate, Li₂SO₄ · H₂O, which is 10 % in excess, are dissolved in 7 ml of water by shaking and gentle heating. 35 ml of ordinary 96 % ethyl alcohol are now added in a thin stream, while stirring with a spatula. After 10 min (it has been ascertained that a longer time is of no effect) the mixture is filtered. The precipitate, which consists of sodium and lithium sulfate, is washed with a few ml of ethanol, and the filtrate plus the washing liquid is evaporated on a water bath to near dryness. Finally, it is dried at 80 °C in a drying oven. The theoretical yield of lithium azide is 0.98 g, while actually 1.02–1.04 g is obtained. This raw product contains no sulfate but a few per cent of sodium. It can be purified by 2 min digestion with 10 ml 96 % ethanol at about 35 °C, filtering the undissolved sodium azide, and evaporating and drying as above. The yield is usually ca. 0.6 g lithium azide of a purity not less than 99.5 %. It contains a slight trace of organic material due to the use of ethyl alcohol.

The purified lithium azide has been analyzed by two methods. The content of azide has been determined according to Martin¹ by oxidation with Ce(IV). Analysis of two products of lithium azide gave 99.5 % and 99.5 %. The same two products were analyzed by conversion to lithium sulfate and weighing². The results were 100.2 % and 99.7 % lithium azide, respectively. Thus it seems that the prepared lithium azide is slightly "basic" due to loss of hydrazoic acid when evaporating.

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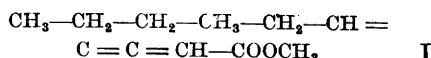
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The Rearrangement of *cis*-2-en-4:6-diyn-oic Acids to $\alpha\beta$ -Unsaturated γ -Lactones

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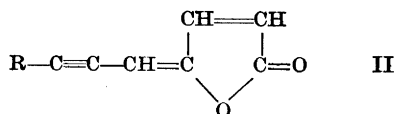
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The so called "Composit-Cumulene I" originally reported by Sørensen and Stavholt¹ was given the structural formula I



based on the UV-absorption and the hydrogenation to a hexahydro derivative with an odour of strawberry like methyl caprate.

A reinvestigation of this compound isolated from scentless mayweed (*Matricaria inodora* L.) showed that the substance contained a disubstituted acetylenic bond (2190 cm⁻¹) and the carbonyl frequency (1793 and 1765 cm⁻¹) indicated a five-ring lactone. Hydrogenation with Pd/BaSO₄ showed a consumption of 5 moles of hydrogen and the product was a saturated five-ring lactone with carbonyl frequency at 1786 cm⁻¹. The formula accordingly had to be revised^{2,3} and the substance was found to be the lactone II (R = *cis* CH₃-CH=CH-)



The formation of this type of lactone from the free 2-*cis*-acid III was first observed when III (R = CH₃C≡C-C≡C-) was treated with dilute sodium hydrogen-carbonate³



On measuring the ultra-violet absorption of an alcoholic solution of *cis:cis* matricaria acid III (R = CH₃CH=CH-C≡C-) in a UV-recorder (Beckman DK) it was noticed that on scanning the spectrum of two solutions with different concentrations, the absorption curve was markedly different the second time. The long wave-