

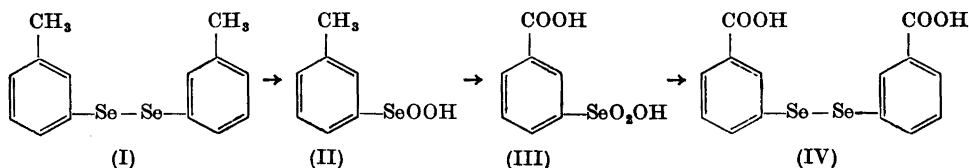
Diphenyldiselenide-3,3'-dicarboxylic Acid

ARNE FRÉDGA and
CHRISTINA EVERTSDOTTER

Chemical Institute, University of Uppsala,
Uppsala, Sweden

The diphenyldiselenide-2,2'-dicarboxylic acid is easily obtained from diazotised anthranilic acid and alkali diselenide¹. The 4,4'-isomer has been prepared in the same way² and also *via* the 4-selenocyanobenzoic acid³, but all attempts to obtain the 3,3'-compound (IV) from diazotised 3-aminobenzoic acid have failed^{3,4}. It is known that the corresponding sulphur compounds behave in the same manner, but here the 3,3'-isomer is easily obtained from 3-chlorosulphonyl-benzoic acid⁵.

As the isomeric diphenyldiselenide-dicarboxylic acids and their methyl esters were needed for spectrochemical studies, we have tried to prepare the 3,3'-isomer by the following route:



The difficulty is to oxidise the methyl group without loss of selenium and destruction of the molecule. It was found that careful oxidation with permanganate on a small scale and subsequent reduction with tin and hydrochloric acid gave the desired acid (IV) in very good yield. It was not necessary to isolate the intermediate III.

The methyl ester was easily obtained from the acid and diazomethane.

Experimental: The 3,3'-ditolyl diselenide (I) was prepared from 3-tolylmagnesium bromide and elementary selenium. The procedure of Foster⁶ was followed with some minor modifications. The compound was obtained as an orange-coloured oil, which did not crystallise even after standing at -15°C for 8 months.

3-Tolylseleninic acid (II) was obtained by oxidation of the diselenide with perhydrol in ethereal solution according to Mc Cullough and Gould⁷.

Diphenyldiselenide-3,3'-dicarboxylic acid (IV). In a 250 ml three-necked flask, fitted

with a stirrer, a reflux condenser and a dropping funnel, was placed a solution of 2.03 g 3-tolylseleninic acid and 0.85 g sodium hydrogen carbonate in 30 ml of water. A solution of 2.99 g potassium permanganate in 45 ml of water was added dropwise with stirring, after which the solution was heated gently for 15 min. 5.08 g of solid potassium permanganate were then added, and the stirring and gentle heating continued for 1 h. The excess permanganate was then destroyed by adding 20 ml of ethanol. The manganese oxides were filtered off and washed with water. The combined filtrates were then concentrated to 100 ml and heated with 10 g tin and 100 ml concentrated hydrochloric acid. A current of air was passed through the solution to oxidise any selenol groups which might have been formed. The acid separated as a yellow microcrystalline powder which was filtered off, dissolved in sodium hydrogen carbonate solution, and reprecipitated with hydrochloric acid. The yield was nearly quantitative. M. p. 238° (decomp.). (Found: Se 39.4. Calc. for C₁₄H₁₀O₄Se₂: Se 39.47.)

Dimethyl diphenyldiselenide-3,3'-dicarboxylate. 1.0 g acid was dissolved in 50 ml of ether,

and an ethereal solution of diazomethane was added drop by drop until nitrogen was no longer evolved. The ether was evaporated and the residue recrystallised from methanol. The ester was obtained as small yellow needles. M. p. 74–75°. (Found: Se 36.8. Calc. for C₁₆H₁₄O₄Se₂: 36.88.)

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1. Schoeller, A. *Ber.* **52** (1919) 1517.
2. Lesser, R. and Weiss, R. *Ber.* **46** (1913) 2651.
3. Gaythwaite, W. R., Kenyon, J. and Phillips, H. *J. Chem. Soc.* **1928** 2286.
4. Bergson, G. *Private communication.*
5. Smiles, S. and Stewart, J. *J. Chem. Soc.* **119** (1921) 1792.
6. Foster, G. *Org. Syntheses* **24** (1944) 89.
7. Mc Cullough, J. D. and Gould, E. S. *J. Am. Chem. Soc.* **71** (1949) 674.

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