

A SYNTHESIS OF FLUORENE-2,7-DICARBOXYLIC ACID

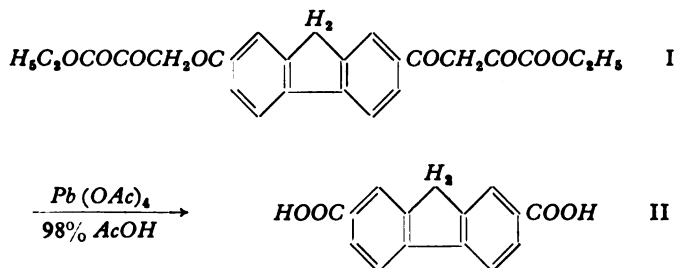
by

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The formation of aryl carboxylic acids by oxidative cleavage of ethyl esters of aroylpyruvic acid with lead tetraacetate was first reported by Jančulev and Podolešov⁽¹⁾. They also established that oxidative cleavage of ethyl 2-fluorenylpyruvate gives fluorene-2-carboxylic acid. Since very little is known about fluorene-2,7-dicarboxylic acid, the purpose of this communication is to report the synthesis of this compound.

Sheldrick *et al.*⁽³⁾ have shown that fluorene-2,7-dicarboxylic acid can be obtained by hydrolyzing (with strong acid or alkali reagents) the corresponding *N*-alkyl-*N*-phenylamides, which are prepared by treating fluorene with alkylphenyl-carbamyl halides in the presence of anhydrous aluminum chloride. The same diacid has also been prepared⁽³⁾ by the Wolff-Kishner-Huang-Minlong reduction of 9-fluorenone-2,7-dicarboxylic acid. We used the oxidative cleavage of γ,γ -fluorene-2, 7-di(α,γ -diketobutyric acid) diethyl ester with lead tetraacetate.

First γ,γ -fluorene-2,7-di(α,γ -diketobutyric acid) diethyl ester (I), yellow crystals m.p. 195—196°, was obtained by acylation of 2,7-diacetylfluorene with diethyl oxalate (1 : 2 molar ratio) in the presence of sodium ethoxide:



By oxidative cleavage of γ,γ -fluorene-2,7-di (α,γ -diketobutyric acid) diethyl ester (I) by means of lead tetraacetate, a product was obtained in the form of a light yellow powder (II), which had no definite melting point, but which upon heating to above 300°C partly

carbonized and partly sublimed. No suitable solvent was found for recrystallization. The properties of product (II) were in agreement with those described by Ishikava *et al.*⁽³⁾.

For characterization of the oxidation product, i.e. fluorene-2,7-dicarboxylic acid, its dimethyl and diethyl esters were prepared. The dimethyl ester consists of light yellow needles which melt at 190—192°C, and the diethyl ester crystallizes in the form of light yellow platelets which melt at 165—167°C.

The fact that fluorene-2,7-dicarboxylic acid (II) is obtained by lead tetraacetate oxidation of the acylation product of 1,7-diacetylfluorene confirms that this compound is γ , γ -fluorene-2,7-di(α , γ -diketobutyric acid) diethyl ester (I), i.e. that acylation of 2,7-diacetylfluorene with diethyl oxalate takes place on the acetyl groups in positions 2 and 7 rather than on the methylene group of fluorene in position 9.

EXPERIMENTAL

1. γ , γ -Fluorene-2,7-di (α , γ -diketobutyric acid) diethyl ester [or γ , γ -2,7-fluorenylenedi (α , γ -diketobutyric acid) diethyl ester] — Anhydrous sodium ethoxide was prepared in the usual manner, in a 500 ml round-bottom flask fitted with a reflux condenser and drying tube. 0.92 g (0.04 mole) of sodium and 1.84 g (0.04 mole) of anhydrous ethanol in 100 ml of anhydrous benzene were used. A hot solution of 5.006 g (0.02 mole) 2,7-diacetylfluorene and 5.85 g (0.04 mole) freshly distilled diethyl oxalate in 300 ml anhydrous benzene was added to sodium ethoxide with shaking. The reaction mixture was heated on a water bath for an hour and then allowed to stand for 24 hours: a dark orange precipitate was obtained. In order to remove unreacted 2,7-diacetylfluorene, the reaction mixture was filtered hot and the product washed with 100 ml hot benzene.

The sodium derivative was treated by rubbing with hydrochloric acid (1 : 1), then filtered and washed with water. The yield was 8.5 g (94.4%) of crude, yellow-orange product. Recrystallization from acetic acid and benzene gave yellow crystals melting at 195—196°C.

Anal. Calc. for $C_{25}H_{22}O_8$: C 66.66 H 4.92%

Found : C 66.85 H 4.68%

2. Fluorene-2,7-dicarboxylic acid — Oxidative cleavage of γ , γ -Fluorene-2,7-di(α , γ -diketobutyric acid) diethyl ester.

1.126 g (0.0025 mole) of γ , γ -fluorene-2,7-di(α , γ -diketobutyric acid) diethyl ester was dissolved in 250 ml of 98% acetic acid and 11.06 g (0.025 mole) of powdered lead tetraacetate was added to the solution. The reaction mixture was gradually heated with stirring and a yellow precipitate began to appear at about 62°C.

The reaction mixture was heated and stirred for another 6 hours at 61—65°C. The light yellow precipitate was filtered off and washed with acetic acid. The yellow powder (210 mg, 33%) had no definite melting point; when heated above 300°C it gradually carbonized and sublimed. The product was practically insoluble in all common

organic solvents. Its properties corresponded to those of fluorene-2,7-dicarboxylic acid⁽³⁾. For characterization its dimethyl and diethyl esters were prepared.

3. *2,7-Fluorene-dicarboxylic acid dimethyl ester* — 0.4 g of the oxidation product (II) was heated under reflux with 15 ml thionyl chloride for 5 hours. The thionyl chloride was then evaporated *in vacuo* and the yellow residue was heated under reflux on a water bath with 50 ml methanol for 3 hours.

The methanol was evaporated and the residue was recrystallized from acetic acid. 0.3 g of light yellow needles, melting at 190—192°C, was obtained. The melting point was in good agreement with that given in the literature.⁽³⁾

Anal. Calc. for $C_{17}H_{14}O_4$: C 72.33 H 5.00%
 Found : C 72.52 H 5.10%

4. *2,7-Fluorene-dicarboxylic acid diethyl ester* — 200 mg of the oxidation product (II) was heated under reflux with 150 ml anhydrous ethanol and 4 ml concentrated sulfuric acid for 10 hours, and 100 ml of water was then added to the reaction mixture. Extraction with ether, washing with water, drying and removal of the solvent by distillation left a solid which, upon four recrystallizations from acetic acid gave light yellow platelets, melting at 165—167°C. (Lit. ⁽³⁾ 166—167°C).

Anal. Calc. for $C_{19}H_{18}O_4$: C 73.53 H 5.85%
 Found : C 73.25 H 6.05%

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Received December 10, 1965.

REFERENCES

1. Jančulev, J. and B. Podolešov. "Oxydativer Abbau von Aroyl-brenztraubensäurenäthylester mit Bleitetraacetat" — *Croatica Chemica Acta* 33 : 59—64, 1961.
2. Sheldrick, G., and M. Wyler. "Fluorene Derivatives" — *Chemical Abstracts* 33 : 645, 1939.
3. Ishikawa, N. and T. Ozawa. "Fluorene Derivatives. XIII. Fluorene-2- and 2,7-Dicarboxylic Acid" — *Yûki Môsei Kagaku Kyokai Shi* 17 : 553—556, 1959.