

THE OXIDATIVE SPLITTING OF SOME FLUORENONE DERIVATIVES BY MEANS OF LEAD TETRAACETATE

by

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As a continuation of our work on the condensation and properties of polyoxo compounds ^(1,2) we have carried out the condensation of 2-acetylfluorene with diethyl oxalate in the presence of sodium ethylate. From earlier investigations made by Wislicenus⁽³⁾ and Jančulev and Podolešov⁽¹⁾, and on the basis of the experimental conditions employed in this condensation, we expected it to take place at the active methylene group in the 9-position and at the acetyl group in the 2-position of the fluorene nuclei.

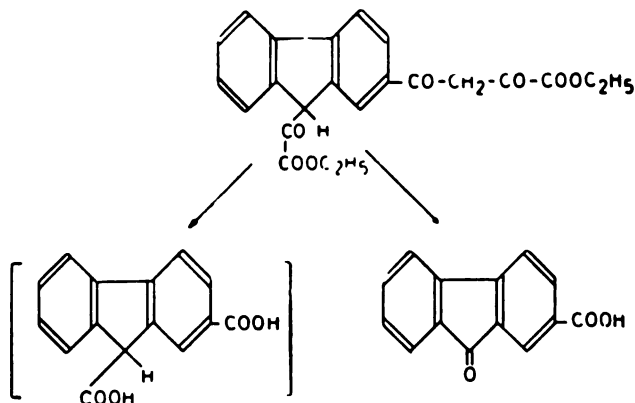
In this condensation two compounds were isolated. The main product melted at 114—117°C and its elementary analysis corresponded to 9-oxalo-fluorenyl-2-pyruvate. The other product, which was isolated in a smaller amount, melted at 173°C and its elementary analysis corresponded to the formula $C_{40}H_{30}O_6$. The structure of this compound will be reported in a forthcoming paper.

According to the works of E. Bear⁽⁴⁾ the oxidative splitting of arylcarboxylic acids by means of lead tetraacetate gives arylcarboxylic acids. Similarly, according to Jančulev and Podolešov⁽²⁾, the splitting of ethyl arylpyruvates also gives arylcarboxylic acids.

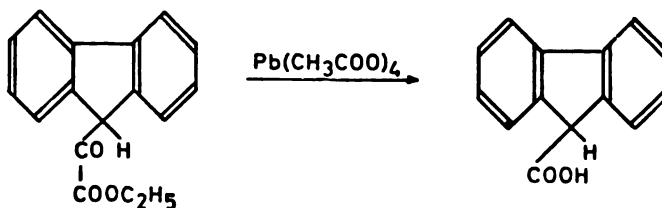
On the basis of these works we assumed that the oxidative splitting of ethyl 9-oxalo-fluorenyl-2-pyruvate would give the hitherto little described fluorene-2,9-dicarboxylic acid. However, the oxidative splitting of ethyl 9-oxalo-fluorenyl-2-pyruvate (I) did not give rise to the expected fluorene-2,9-dicarboxylic acid (II) but to the well-known 9-fluorenone-2-carboxylic acid (IIa) which was determined by the preparation of its methyl ester.

From these results it follows that in the oxidative splitting of ethyl 9-oxalo-fluorenyl-2-pyruvate the $—CO—CH_2—CO—COOC_2H_5$ group in the 2-position is oxidized to the carboxylic group, and the $—CO—COOC_2H_5$ group in the 9-position to the keto group.

In order to explain the unexpected oxidative splitting of the $—CO—COOC_2H_5$ group in the 9-position we have studied the oxidative splitting of ethyl fluorenyl-9-gyoxalate (III).



On the basis of the results obtained in the oxidative splitting of ethyl 9-oxalo-fluorenyl-2-pyruvate, the oxidative splitting of ethyl fluorenyl-9-glyoxalate should give rise to already known fluorenone. However, we were unable to isolate fluorenone from the reaction mixture and we obtained only small amounts of fluorene-9-carboxylic acid.



The oxidative splitting of substituted derivatives of ethyl fluorenyl-9-glyoxalate gave different results. The splitting of ethyl 2-nitrofluorenyl-9-glyoxalate resulted in the formation of 2-nitrofluorenone, and in the oxidation of ethyl 2,7-dibromofluorenyl-9-glyoxalate gave 2,7-dibromofluorenone.



From these results it may be concluded that the $\text{CO}-\text{COOC}_2\text{H}_5$ group in the 9-position is oxidized with lead tetra-acetate to the keto group only in case of substituted derivatives of ethyl fluorenyl-9-glyoxalate.

The results of the oxidative splitting with lead tetraacetate of the compound melting at 114—117°C and of the other substituted derivatives of ethyl fluorenyl-9-glyoxalate prove that the structure ascribed to ethyl 9-oxalo-fluorenyl-2-pyruvate is correct.

The mechanism of the oxidative splitting of the —CO—COOC₂H₅ grouping in the 9-position encountered in substituted derivatives of ethyl fluorenyl-9-glyoxalate will be published later.

EXPERIMENTAL

Condensation of 2-acetylfluorene with diethyl oxalate (ratio 1:2) in the presence of sodium ethylate (ethyl 9-oxalo-fluorenyl-2-pyruvate)

In a 200 ml round-bottomed flask with a condenser and a CaCl₂-tube, sodium ethylate was prepared from 0.69 g of sodium (0.03 mole) and 1.38 g (0.03 mole) of absolute alcohol after N. Lund and J. Bjerrum⁽⁵⁾: Anhydrous ether was added to the reaction mixture until all the sodium was covered. After one hour heating on a water-bath, the reaction mixture was left to stand overnight. To the obtained sodium ethylate solution, with constant stirring, were added first 3:12 g (0.015 mole) of 2-acetylfluorene, and then, 4.38 g (0.03 mole) of freshly distilled diethyl oxalate, slowly and with cooling so that no overheating of the reaction mixture occurred. After standing for three days, the reaction mixture was orange colored.

The reaction product was filtered off, washed with ether and dried in air. The obtained 7.7 g of orange colored sodium derivative was treated with ice cold hydrochloric acid (1:1). 6.6 g of brown-red condensation product was obtained after drying in air. It was readily soluble in alcohol, acetone, glacial acetic acid and ethyl acetate. It was then treated with 200 ml of benzene whereby a dark red colored deposit was left undissolved. The benzene solution was filtered and left to crystallize.

After standing two days the benzene solution yielded about 1.5 g of a dark red precipitate which melted at 100°C. After some time the concentrated filtrate gave an additional 3 g of a yellow precipitate which melted at 110°C. Further standing of the filtrate resulted in the formation of a yellow deposit which melted at 150°C. The crystals melting at 100—110°C, after two further crystallizations, gave yellow needles of m. p. 114°C (Kofler block m. p. 117°C). The results of the elementary analysis corresponded to ethyl 9-oxalo-fluorenyl-2-pyruvate (Ia).

Analysis

Found : C 67.45%; H 4.90%
 Calculated for C₂₃H₇₀O₇: C 67.74%; H 4.94%.

The recrystallization of the yellow needles melting at 150°C from benzene or acetone gave crystalline plates melting at 168—169°C (Ib).

Analysis:

Found : C 71.10%; H 4.34%
 Calculated for $C_{40}H_{30}O_{10}$: C 71.63%; H 4.51%

Oxidative splitting of ethyl 9-oxalo-fluorenyl-2-pyruvate with lead tetraacetate (9-Fluorenone-2-carboxylic acid) (IIa).

To a suspension of 1 g of ethyl 9-oxalo-fluorenyl-2-pyruvate (m. p. 114—117°C) in 48 ml of 98% acetic acid, 8 g of powdered lead tetraacetate was added. In the course of 30 minutes the suspension turned to a yellow colored solution and its temperature rose about 6°C. The reaction mixture was stirred for a further 6 hours and a yellow precipitate separated. The stirring was continued for 15 hours whereby lead tetraacetate completely disappeared from the solution. To remove any traces of unreacted lead tetraacetate a few ml of ethylene glycol were added to the reaction mixture. The separated yellow reaction product was filtered off and dried. The yield was about 0.25 g. By adding water to the filtrate an additional 2 g of the reaction product was obtained. Recrystallization from glacial acetic acid gave yellow needles melting at 333°.

The mixed melting point determination with an authentic sample of 9-fluorenone-2-carboxylic acid showed no depression.

Analysis:

Found : C 74.78%; H 3.85%;
 Calculated for $C_{14}H_8O_3$: C 74.99%; H 3.60%

Methyl ester of 9-fluorenone-2-carboxylic (IIb)

The product of the oxidative splitting of 9-oxalo-fluorenyl-2-pyruvate was determined by the preparation of its methyl ester in the following way:

By heating 0.15 g of the oxidation product (IIa), m. p. 333°C, with 5 ml of thionyl chloride on a water bath for 90 minutes a clear solution was obtained. The excess thionyl chloride was removed in vacuo and the solid residue was heated on a water-bath with 30 ml of methanol for 90 minutes. Then active charcoal was added to the solution, the mixture was boiled for 5 minutes and filtered hot. On cooling the methanolic solution yielded long shiny needles melting at 182°C. Repeated recrystallization yielded crystals of m. p. 182—184°C. The mixed melting point with an authentic specimen of 9-fluorenone-2-carboxylic acid (m. p. 180—185°C, prepared according to Fortner⁽⁶⁾) gave no depression.

Analysis:

Found : C 75.38%; H 4.30%;
 Calculated for $C_{15}H_{10}O_3$: C 75.62% H 4.23%

From the elementary analysis of the oxidation product (IIa) and its melting point and from the melting point of the corresponding methyl ester, it may be concluded that its structure corresponds to 9-fluorenone-2-carboxylic acid.

Oxidative splitting of ethyl fluorenyl-9-glyoxalate (III) with lead tetraacetate

Ten grams of ethyl fluorenyl-9-glyoxalate prepared by the method of Wislicenus⁽⁸⁾ was dissolved in 100 ml of 99% acetic acid with an addition of 2—3 ml of water. 30 g of lead tetraacetate was added to the solution and the reaction mixture was kept at 60°C with warming and constant stirring for about 30 hours. Then a small amount of ethylene glycol was added in order to remove the unreacted lead tetraacetate. The reaction mixture was diluted with water, the separated flaky precipitate was collected and the filtrate was extracted with ether. The sticky yellow precipitate was dissolved in benzene and from the cooled solution an almost white product was deposited. It was recrystallized from benzene-petroleum ether, yielding about 0.1 g of a substance melting at 210—230°C. Recrystallization from a mixture of glacial acetic acid and water yielded white needles melting at 321°C (lit. 325°C⁽⁹⁾). The mixed melting point with fluorene-9-carboxylic acid remained unchanged.

On removal of the solvents, ethereal extract and the benzene solution gave a yellow-red residue from which fluorene was obtained.

Distillation of the residue furnished no fluorenone but only fluorene, which was probably formed by the decomposition of ethyl fluorenyl-9-carboxylic acid.

The oxidative splitting of ethyl 2-nitrofluorenyl-9-glyoxalate (IV) with lead tetraacetate

To a solution of 0.84 g of powdered ethyl 2-nitrofluorenyl-9-glyoxylate (m. p. 140—144°C)⁽¹⁰⁾ in 70 ml of acetic acid, 4 g of powdered lead tetraacetate were added. The reaction mixture was heated at 50—60°C with constant stirring for about 20 hours. After some time a yellow crystalline precipitate appeared. Some ml of ethylene glycol were added in order to remove the unreacted lead tetraacetate, and the separated product was filtered off, giving 0.35 g of compound melting at 210°C. Recrystallization from glacial acetic acid with the addition of active charcoal gave long shiny needles of m. p. 216—217° (lit. 218.5°C)⁽¹¹⁾.

Analysis:

Found : C 69.15%; H 3.20%;
 Calculated for C₁₃H₇NO₃: C 69.33%; H 3.13%.

The mixed melting point with 2-nitrofluorenone obtained by the oxidation of 2-nitrofluorene with dichromate showed no depression. All these data show that the obtained product is 2-nitrofluorenone.

Oxidative splitting of ethyl 2,7-dibromofluorenyl-9-glyoxalate (V) with lead tetraacetate

To a mixture of 0.8 g of ethyl 2,7-dibromofluorenyl-9-glyoxalate⁽¹²⁾ and 50 ml of 98% acetic acid 5 g of powdered lead tetraacetate was added. The reaction mixture was kept at 55—60°C. with constant stirring for 20 hours. Then some ml of ethylene glycol were added in order to remove the unreacted lead tetraacetate, and the reaction mixture was diluted with water. The separated precipitate was recrystallized from 96% alcohol, yielding about 0.25g of a crystalline product in the form of yellow needles which melted at 202° (lit 202°C)⁽¹³⁾.

Analysis:

Found : C 46.30%; H 1.95%;

Calculated for C₁₃H₆OBr₂: C 46.19%; H 1.95%.

The mixed melting point with 2,7-dibromofluorenone prepared by the oxidation of 2,7-dibromofluorene showed no depression.

The obtained oxidation product was determined in the form of its oxime which crystallized as light yellow needles of m. p. 236—237° (lit. 235°C)⁽¹³⁾.

From the above data it is evident that the obtained product is 2,7-dibromofluorenone-9.

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