

Synthesis of 7-Nitrofluorenone-2-Carboxylic Acid¹

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The synthesis of 7-nitrofluorenone-2-carboxylic acid was first attempted by nitrating fluorenone-2-carboxylic acid. A yellow product resulted which melted above 300° C. In order to prove the structure of this product, it was decided to decarboxylate it and identify the resulting nitrofluorenone by comparing its properties with those nitrofluorenes described in the literature. All attempts at decarboxylation ended in failure. The yellow product obtained at the direct nitration of fluorenone-2-carboxylic acid later proved to be a complex of a mono-nitro- and a dinitro-fluorenone-2-carboxylic acid.

It was then decided to synthesize 7-nitrofluorenone-2-carboxylic acid from fluorene by a series of reactions which would leave no doubt as to its structure.

Fluorene was first converted to 2-nitrofluorene by the method given in *Organic Syntheses* (6) using concentrated nitric acid with glacial acetic acid as a solvent. The 2-nitrofluorene was then added to a mixture of equal volumes of glacial acetic acid and fuming nitric acid forming 2,7-dinitrofluorene (4). The literature gives three different melting points for 2,7-dinitrofluorene: Morgan and Thomason (5) give the melting point as vigorous decomposition at 269° C; Anantakrishnan and Hughes (1) state that their compound melted with vigorous decomposition at 295-300° C; Courtot (2) obtained a melting point of 334° C after he had recrystallized his compound from nitrobenzene.

Each time we prepared 2,7-dinitrofluorene our product consistently melted at 269° C in agreement with the melting point given by Morgan and Thomason. Repeated recrystallizations from acetic anhydride of a small sample, however, gave long, almost colorless, glistening needles melting sharply at 299° C. This melting point agrees with that given by Anantakrishnan and Hughes (1).

Crude 2,7-dinitrofluorene was oxidized to 2,7-dinitrofluorenone with sodium dichromate, using 3:1 mixture of glacial acetic acid and acetic anhydride as a solvent. The product melted over a range 240-270° C which was not in accordance with the melting point given by Anantakrishnan and Hughes, 292° C (1). By fractional extraction the supposed 2,7-dinitrofluorenone was separated into almost equal parts of 2,5-dinitrofluorenone melting at 239° C and 2,7-dinitrofluorenone melting at 293° C. When, however, the crude 2,7-dinitrofluorenone was completely dissolved in glacial acetic acid, the crystalline product which precipitated on cooling melted at 268° C. From this it is evident that the 2,5- and 2,7-dinitro-isomers can best be separated by fractional extraction.

¹This research was done at the University of Cincinnati under the direction of Dr. Francis E. Ray, now Director of Research at the Cancer Research Laboratory, University of Florida, Gainesville, Florida.

The reduction of the pure 2,7-dinitrofluorenone to 2-amino-7-nitrofluorenone with ammonium sulfide resulted after two recrystallizations from monochlorobenzene in beautiful glistening black needles which melted at 281-282° C. Eckert and Langecker (3) report a melting point of 279° C for 2-amino-7-nitrofluorenone.

2-Amino-7-nitrofluorenone was converted to the nitrile by the Sandmeyer reaction. It was difficult to extract the 2-cyano-7-nitrofluorenone from the reaction mixture. The final sublimation product was orange needles melting at 245-247° C. A nitrogen analysis gave 11.21% whereas the calculated nitrogen content for the compound is 11.20%.

2-Cyano-7-nitrofluorenone was refluxed with a solution of five percent potassium hydroxide in which the nitrile gradually dissolved, giving a red solution. The evolution of ammonia showed that hydrolysis was taking place. The 7-nitrofluorenone-2-carboxylic acid was precipitated from the alkaline solution with 1:1 hydrochloric acid and on sublimation gave an orange product melting at 210-213° C.

Literature Cited

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