[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, XAVIER UNIVERSITY]

NITRATION OF FLUORENONE-1-CARBOXYLIC ACID

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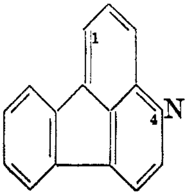
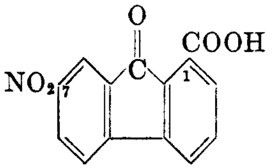
In the course of preparation of some new fluorene compounds, the nitration of fluorenone-1-carboxylic acid was investigated. Fittig and Liepmann (1) in 1880, reported the preparation of a mononitro derivative of fluorenone-1-carboxylic acid by direct nitration with mixed acid. The compound melted at 245–246°. No proof of structure was given. The suggestion has been made (2) that the compound obtained by Fittig might be 2-nitrofluorenone-1-carboxylic acid, but this is unlikely in view of the orientation effect present. The presence of a *meta*-directing group in the 1-position would certainly deactivate that ring system, and consideration of analogous cases will suggest that the in-coming nitro group would largely take the 7-position along with the possible formation of some 5-nitro compound. Thus, in the nitration of fluorenone-4-carboxylic acid (3) the chief product is 7-nitrofluorenone-4-carboxylic acid. A smaller yield of 5-nitrofluorenone-4-carboxylic acid is simultaneously produced.

Furthermore, 2-nitrofluorenone-1-carboxylic acid has unequivocally been prepared by the oxidation of 4-nitrofluoranthene (I) (4, 5). The melting point of the compound was given as 233–235° with decomposition. The disparity of ten degrees between the melting points of the two nitro acids would seem to suggest that they are not the same.

Consequently, the synthesis of Fittig's nitro compound was repeated using a modification of the original procedure designed to improve the yield. Fluorenone-1-carboxylic acid was nitrated with mixed acid to give a crude material representing a yield of 85%. Recrystallization from glacial acetic acid gave golden yellow crystals of the supposed 7-nitrofluorenone-1-carboxylic acid (II) melting at 245–246°. Repeated recrystallizations failed to elevate the melting point of the material. Dilution of the acetic acid mother-liquor from the initial crystallization with water gave a precipitate which, when dry, melted at 199–201°, and probably represented a mixture. It is likely that this fraction contains some 5-nitrofluorenone-1-carboxylic acid. The supposed 7-nitrofluorenone-1-carboxylic acid was found to be reasonably stable and could be sublimed unchanged under a vacuum.



I



II

The preparation of 2-nitrofluorenone-1-carboxylic acid was more difficult, and again improvements were made on the literature procedures. Fluoranthene was nitrated in glacial acetic acid solution with concentrated nitric acid. The yield of crude product was 58%. Recrystallization from acetic acid gave a yellow crystalline product, 4-nitrofluoranthene, melting at 162–163°. Oxidation to 2-nitrofluorenone-1-carboxylic acid was accomplished by chromic anhydride in acetic acid solution, and extraction of the crude product with barium carbonate ultimately yielded a light-yellow compound which melted at 229–230°. Recrystallization from glacial acetic acid raised the melting point to 234–235°. The poor yield in this oxidation step can be ascribed to the rigor of the reaction and the appreciable thermal instability of the product which readily decarboxylates.

The dissimilarity of 2-nitrofluorenone-1-carboxylic acid and the supposed 7-nitrofluorenone-1-carboxylic acid is seen in the disparity of their melting points as well as in the obvious differences in thermal stability. The mixture melting point of the two compounds was 218–222°.

The final step in the structure proof for the supposed 7-nitrofluorenone-1-carboxylic acid involved decarboxylation to give 2-nitrofluorenone. The compound was surprisingly difficult to decarboxylate, and several procedures proved ineffectual. Decarboxylation was finally accomplished by treatment with hot quinoline and copper followed by sublimation. The sublimate, recrystallized from alcohol, gave beautiful yellow needles melting at 217–218°. A mixture melting point with an authentic sample of 2-nitrofluorenone showed no depression. This indicated the 7-position as the point of attachment of the nitro group, since the possibility of the 2-position had been excluded.

Incidentally, decarboxylation of 2-nitrofluorenone-1-carboxylic acid was readily accomplished by sublimation of the free acid. The facility of decarboxylation is explained by the presence of an *ortho*-nitro group. The sublimate, recrystallized from alcohol, melted at 217–218°, and a mixture melting point with 2-nitrofluorenone showed no depression.

EXPERIMENTAL

Melting points. An aluminum block was used throughout with a thermometer calibrated against samples of pure compounds.

Nitration of fluorenone-1-carboxylic acid. Finely divided fluorenone-1-carboxylic acid (m.p. 192–193°) (20 g., 0.090 mole) was added in small portions with constant stirring at room temperature to a mixture of 100 ml. of concentrated sulfuric acid and 100 ml. of concentrated nitric acid (*d.* 1.42) over a period of 20 minutes. During the addition, the temperature increased to 35–37°; the mixture was stirred an additional hour at 35°, cooled, and poured into ice-water. The precipitated product was filtered off, washed with water, and dried. The yield of crude 7-nitrofluorenone-1-carboxylic acid was 20–22 g. (83–92%). Recrystallization from glacial acetic acid gave 15 g. (63% over-all yield) of golden-yellow crystals, melting at 245–246° with decomposition.

4-Nitrofluoranthene. Fluoranthene (20 g., 0.10 mole) was dissolved in 150 ml. of glacial acetic acid, and, with constant stirring, 27 ml. of concentrated nitric acid (*d.* 1.42, 0.43 mole) was added at 75° during the course of about 15 minutes. Stirring was continued for another ten minutes at the same temperature during which time a yellow precipitate formed. The mixture was filtered hot and the solid product was washed with glacial acetic acid and water, and then dried. The crude nitro compound (14 g., 57% yield) melted at 158.5–160°. After recrystallization from acetic acid, the melting point was 162–163° with some decomposition.

2-Nitrofluorenone-1-carboxylic acid. A solution of 15 g. (0.15 mole) of chromic anhydride in 25 ml. of glacial acetic acid and 25 ml. of water was added slowly with stirring to 5 g. (0.021 mole) of 4-nitrofluoranthene in 100 ml. of glacial acetic acid, maintaining the temperature at 90–95°. Stirring was continued at this temperature for an additional hour. The solution was cooled, diluted with four volumes of water, and let stand overnight. The separated solid material was filtered off and washed with dilute sulfuric acid and with water. The crude nitro acid was then added to a suspension of 3 g. of barium carbonate in 200 ml. of water and stirred on the water-bath for 30 minutes. The suspension was filtered hot and the residue was submitted to a second extraction. The combined filtrates were acidified with hydrochloric acid to give a yellow precipitate. After cooling, the solid was filtered, washed, and dried to yield 1.6 g. of product (29%) melting at 229–230°. Recrystallization from acetic acid gave a material melting at 234–235° with decomposition (evolution of a gas).

A mixture melting point of 2-nitrofluorenone-1-carboxylic acid with the supposed 7-nitrofluorenone-1-carboxylic acid gave a value of 218–221°.

Decarboxylation of 7-nitrofluorenone-1-carboxylic acid. 7-Nitrofluorenone-1-carboxylic acid (2 g.) was dissolved in 10 ml. of quinoline and 0.2 g. of copper powder was added. The solution was stirred in an oil-bath for 30 minutes at 175–180° and filtered hot. The quinoline was removed by treatment with dilute hydrochloric acid and the separated solid, contaminated with tars, was filtered, washed with water and dried. The material was decolorized with charcoal in hot glacial acetic acid, and the product crystallizing from the cooled filtrate was filtered and washed with water. It was then stirred with 50 ml. of warm, dilute sodium hydroxide, filtered, washed with water and dried. The dried product was then submitted to sublimation, using two 125-ml. Erlenmeyer flasks connected by a short bend of 10 mm. glass tubing. The flask containing the sample was heated in a sand-bath while a small current of air was aspirated through the system. The receiving flask was cooled by immersion in cold water. The yellow sublimate was recrystallized from ethanol to give bright yellow crystals of 2-nitrofluorenone melting at 217–218°. A mixture melting point with an authentic sample of 2-nitrofluorenone (m.p. 217–218°) showed no depression.

Decarboxylation of 2-nitrofluorenone-1-carboxylic acid. 2-Nitrofluorenone-1-carboxylic acid (1 g.) was mixed intimately with 0.2 g. of copper powder. The material was sublimed in a small evaporating dish covered with a watch glass containing some water for cooling. Heating was accomplished by a sand-bath. The yellow sublimate was recrystallized from ethanol to give yellow crystals of 2-nitrofluorenone melting at 217–218°. A mixture melting point with an authentic sample of 2-nitrofluorenone showed no depression.

SUMMARY

The product formed by the direct nitration of fluorenone-1-carboxylic acid has been shown to be largely 7-nitrofluorenone-1-carboxylic acid since it is not 2-nitrofluorenone-1-carboxylic acid and it decarboxylates to give 2-nitrofluorenone.

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