[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Decomposition of 2-Fluorenediazonium Chloride and 2-Fluorenonediazonium Chloride in Acetic Acid

BY H. V. CLABORN AND H. L. HALLER

In preparing derivatives of fluorene to be tested for their insecticidal action, it became desirable to prepare 2-acetoxyfluorene and 2-acetoxyfluorenone. These compounds are not described in the literature, but it was found that they could be obtained readily by the acetylation of the corresponding hydroxy compounds. The latter compounds were first prepared by Diels,[1] who obtained them by the decomposition of the corresponding diazonium chlorides with water in the usual manner. The yield of the 2-hydroxyfluorene was reported to vary considerably, and this observation has been confirmed by us. When, however, the decomposition of the diazonium chloride was carried out in 3% sulfuric acid, as suggested by Ruiz,[2] an 80% yield of the 2-hydroxyfluorene was obtained.

The decomposition of 2-fluorenonediazonium chloride in water gave 2-hydroxyfluorenone in a yield of 55%, whereas in dilute acetic acid, as suggested by Patrizietti,[3] an 80% yield of the same compound was obtained.

The replacement of the amino group by the acetoxy group through the diazo reaction has been accomplished by the decomposition of a dry diazonitrate or sulfate with glacial acetic acid;[4] by the interaction of a diazo bromide and acetic anhydride;[5] by the diazotization of an amine in glacial acetic acid;[6] and more recently by the interaction of solid aryl diazonium borofluorides and acetic acid.[7,8] In the last reaction the acetates of phenols are obtained in good yield, and this reaction is particularly useful when the normal decomposition does not take place readily. Since 2-fluorenediazonium chloride and 2-fluorenonediazonium chloride are fairly stable solids, it seemed of interest to attempt the preparation of the acetoxy compounds directly from the diazonium chlorides and acetic acid. When the experiment was carried out with 2-fluorenediazonium chloride, three compounds were obtained, with the following yields: 2-chlorofluorene, 10%; 2-acetoxyfluorene, 46.7%; and 2-hydroxyfluorene, 11%. The last-named compound separated readily from the reaction mixture by extraction with alkali. Although a partial separation of the chloro and the acetoxyfluorenes could be effected by recrystallization from methanol, it was found expedient to separate the two by saponifying the acetate with alkali to the phenol and removing the chloro compound by filtration from the alkaline solution.

The interaction of 2-fluorenonediazonium chloride and acetic acid gave a 60% yield of 2-acetoxyfluorenone.

Experimental

Interaction of 2-Fluorenediazonium Chloride and Acetic Acid.—A solution of 10 g. of 2-fluorenediazonium chloride in 50 cc. of glacial acetic acid was heated gently under a reflux condenser until nitrogen began to be evolved. After the vigorous reaction had subsided, the solution was boiled for five minutes and then concentrated under reduced pressure until most of the acetic acid was removed. The concentrated solution was poured into ice water; the separated product was removed by filtration and dried; yield 7.6 g.; m. p. 85–100°. The product was dissolved in ether and extracted twice with 5% potassium hydroxide solution. The combined alkaline solutions were acidified with dilute hydrochloric acid, and the precipitated phenol was separated by filtration. It was recrystallized from 50% acetic acid; yield 1.1 g.; m. p. 168°. When mixed with an equal quantity of authentic 2-fluorenol, there was no depression of the melting point.

From the ether solution there was obtained, after drying over sodium sulfate and removal of the ether, 5.8 g. of a mixture of the chlorofluorene and acetoxyfluorene. This mixture was best separated by heating it to boiling for thirty minutes with 30 cc. of 10% potassium hydroxide solution, cooling, and then removing the chloro compound by filtration. The chloro compound was then purified by steam distillation; yield 1 g.; m. p. 168°. It was identified as 2-chlorofluorene by a mixed melting point determination with authentic material prepared according to the method of Chanussot.[9]

2-Acetoxyfluorene.—One gram of 2-fluorenol was refluxed for thirty minutes with 5 cc. of acetic anhydride and 0.5 g. of anhydrous sodium acetate. The solution was cooled and a small volume of methanol added to decompose the acetic anhydride. The solution was poured slowly, with stirring, into ice water. The acetate sepa-

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(1) O. Diels, *Ber.*, **34**, 1758 (1901).

(2) C. Ruiz, *Anal. asoc. quim. argentina*, **16**, 170 (1928).

(3) R. Patrizietti, *ibid.*, **22**, 24 (1934).

(4) W. R. Orndorff, *Am. Chem. J.*, **10**, 368 (1888).

(5) O. Wallach, *Ann.*, **235**, 233 (1886).

(6) R. Mendola and F. J. East, *J. Chem. Soc.*, **53**, 460 (1888).

(7) H. L. Haller and P. S. Schaffer, THIS JOURNAL, **55**, 4954 (1933).

(8) L. E. Smith and H. L. Haller, *ibid.*, **56**, 237 (1934).

(9) P. Chanussot, *Anal. asoc. quim. argentina*, **15**, 216 (1927).

rated as colorless crystals, which were removed by filtration. These were washed with water and dried; yield 1.1 g. After recrystallization from dilute methanol the compound melted at 128°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.40. Found: C, 80.16; H, 5.46.

2-Acetoxyfluorenone.—One gram of 2-fluorenonediazonium chloride in 5 cc. of glacial acetic acid was heated gently until the evolution of nitrogen began. After the initial reaction subsided, the solution was again heated carefully until the evolution of nitrogen ceased and then boiled for five minutes. Fifteen cubic centimeters of ethanol was then added and the solution chilled in ice. The product which separated consisted of large yellow plates; yield 0.6 g.; m. p. 154°. After recrystallization from 95% ethanol, it melted at 157°. The compound was identified as 2-acetoxyfluorenone by a mixed melting point determination with an authentic sample of 2-acetoxyfluorenone. The latter was obtained by acetylation of 2-hydroxyfluorenone (1 g.) according to the method described for the preparation of 2-acetoxyfluorene. The yield was 1.15 g. On recrystallization from 95% ethanol it melted at 157°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.60; H, 4.23. Found: C, 75.43; H, 4.28.

On saponification with 5% potassium hydroxide solution 2-acetoxyfluorenone (1.9 g.) was converted into 2-hydroxyfluorenone (1.5 g.), which after recrystallization from 50% acetic acid melted at 204°. Diels[1] reports this compound as sintering at 200° and melting at 206.7°.

Summary

The interaction of 2-fluorenediazonium chloride and acetic acid gives three compounds in the following yields: 2-chlorofluorene, 10%; 2-acetoxyfluorene, 46.7%; and 2-hydroxyfluorene, 11%.

From 2-fluorenonediazonium chloride and acetic acid there was obtained a 60% yield of 2-acetoxyfluorenone.

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Identification of Alkylbenzenes. I. Identification of Monoalkylbenzenes by Means of the Acetamino Derivative[1]

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In the course of the study of the alkylation,[2] depolyalkylation,[3] and destructive alkylation[4] of aromatic hydrocarbons, the need for a simple method for the identification of alkylbenzenes became apparent. The boiling points and other physical constants are fairly satisfactory for distinguishing the homologous compounds but are inadequate in the case of isomers. Oxidation to benzoic acid or to one of the phthalic acids may be used to differentiate between mono- and dialkylbenzenes but is of no aid in the determination of the structure of the alkyl groups.

In the present investigation, the characterization of monoalkylbenzenes by means of their mono- and diacetamino derivatives was studied. Although there was nothing inherently new in the preparation of such derivatives by nitration, followed by reduction of the nitro compound and subsequent acetylation of the amine, there had been no previous study of the nitration of a series of alkylbenzenes under a single set of conditions; furthermore, it was not possible to predict whether the solid derivative would be a single compound or a mixture. If the nitration yielded a mixture of ortho and para isomers, the reaction would not be applicable. On the other hand, the preparation of a dinitro derivative would eliminate this difficulty since there is ample evidence[5] to show that only the 2,4-dinitro compound would be obtained.

The problem, then, consisted essentially in determining the conditions necessary for the formation either of a mononitro derivative, unadmixed with isomers, or of the dinitro derivative. This was less difficult than had been anticipated, and a procedure was developed by means of which monoalkylbenzenes may be identified easily and quickly using small amounts of material. It was found that under the prescribed conditions pure 4-nitroalkylbenzenes may be obtained by use of a nitrating mixture consisting of equal volumes of concentrated nitric and sulfuric acids. The ortho-substituted isomers are present in such small amount, if at all, that they do not interfere. It

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(1) Presented before the Division of Organic Chemistry at the Chapel Hill meeting of the American Chemical Society, April, 1937.

(2) Ipatieff, Corson and Pines, THIS JOURNAL, 58, 919 (1936).

(3) Ipatieff and Pines, *ibid.*, 58, 1056 (1936).

(4) Grosse and Ipatieff, *ibid.*, 57, 2415 (1935); Ipatieff, Komarewsky and Pines, *ibid.*, 58, 918 (1936).

(5) Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928); Brady and Cunningham, *ibid.*, 121 (1934).