[CONTRIBUTION FROM THE LABORATORY OF RADIOCHEMISTRY, UNIVERSITY OF CINCINNATI]

9,9-Difluorofluorene

BY FRANCIS EARL RAY AND CLARENCE E. ALBERTSON

Only the following fluorine derivatives of fluorene have been prepared: 4-fluoro-5-nitro-1-methylfluorene,[1] 2-fluorofluorenone and its oxime,[2,3] 2-fluoro-9,9-dichlorofluorene and several 9,9- condensation products, and perfluorofluorane ($C_{13}F_{22}$).[4]

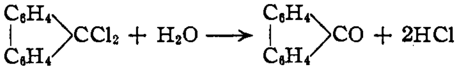
Since the 9-position in fluorene has aliphatic properties and has never been fluorinated independently of the rest of the molecule, it seemed of interest to attempt the preparation of 9,9-difluorofluorene. The difluoro compound was selected because it seemed doubtful if the allylic character of the 9-carbon[5] would permit the preparation of 9-monofluorofluorene.

Little difficulty was expected in the preparation of 9,9-difluorofluorene because Henne and Leicester[6] had reported the preparation of diphenyldifluoromethane in yields of 60%.

We treated 9,9-dichlorofluorene with hydrogen fluoride in the presence of mercuric oxide. To reduce the violence of the reaction, toluene or chlorobenzene was used as a diluent. The products that were obtained from the reaction were fluorenone, tolylmercuric chloride and mercuric chloride.

It is not clear whether the formation of fluorenone is the primary reaction. It is possible that hydrogen fluoride reacted with mercuric oxide to produce water and that 9,9-dichlorofluorene was subsequently hydrolyzed to fluorenone.

$$2HF + HgO \longrightarrow H_2O + HgF_2$$



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>\!CCl_2 + H_2O \longrightarrow \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>\!CO + 2HCl$$

Other catalysts such as antimony tri- and pentafluoride and zinc fluoride also gave fluorenone or intractable tars as did the use of uncatalyzed hydrogen fluoride.

Impure 9,9-fluorochlorofluorene may have been present in some of these products. The monofluorochloro derivatives are generally less stable than the difluoro compounds.[7]

Despite the fact that hydrous mercuric fluoride was entirely unsuitable as a catalyst, Henne[8] later found that it was not necessary to isolate mercuric fluoride but simply passed a stream of hydrogen fluoride into the mixture of mercuric oxide and the substance. This was the first method tried and it led to the formation of fluorenone.

The inconvenient preparation of mercuric fluoride from mercuric chloride and fluorine and the bad effects of mercuric oxide in the second method might both be avoided by passing hydrogen fluoride into a mixture of mercuric chloride and the substance to be fluorinated. Daudt and Youker, U. S. Patent 2,005,707, disclose the use of mercuric chloride in vapor phase hydrofluorination at elevated temperatures but give no experimental details.

On carrying out this experiment at 70°, we obtained the desired 9,9-difluorofluorene in addition to some of the unstable material obtained previously and thought to be 9,9-fluorochlorofluorene.

An attempt to increase the yield by operating at 100 pounds pressure produced a sponge-like rubbery hydrocarbon mass of approximately 2800 molecular weight.

9,9-Difluorofluorene formed white crystals that melted at 47–48° and analyzed correctly for fluorine and had the required molecular weight. After standing for two weeks in a desiccator evidence of decomposition was apparent.

It is thus seen that mercuric chloride and hydrogen fluoride form a fluorinating agent that is especially useful in the conversion of the less stable halides to fluorides or in the preparation of the less stable fluorides.

Experimental

9,9-Dichlorofluorene.—Fluorenone was prepared by the method of Huntress, Hershberger and Cliff[9] except that the acetic acid was reduced from 20 moles to 13 moles. This makes the preparation of large amounts more convenient and slightly improves the yields. From 200 g. of fluorene there was obtained some 148 g., 68%, melting at 82.8 to 83.1°. Fluorenone was converted to 9,9-dichlorofluorene by the following modification of Smedley's[10] method.

To 15 g. (0.1 mole) of phosphorus oxychloride in 60 cc. of toluene are added 90 g. (0.5 mole) of fluorenone and 114 g. (0.55 mole) of phosphorus pentachloride. The mixture was heated for three hours on the water-bath and agitated intermittently. The phosphorus pentachloride had disappeared at the end of the first hour and the mixture became dark brown in color. The reaction mass was subjected to vacuum distillation (25 mm.) to remove most of the phosphorus compounds. The residue was dissolved in benzene, washed twice with ice water and dried over calcium chloride. The benzene was removed under reduced pressure and the residue recrystallized from glacial acetic acid. A 66% yield of almost colorless crystals melting at 102.9 to 103.1° was obtained. Smedley[10] gives m. p. 103°. The pure product is quite stable if protected from moisture. Samples of impure material decomposed within a week to give a sticky green-yellow mass with the sharp odor of hydrogen chloride.

9,9-Difluorofluorene.—Most of the experiments were carried out in a stirred copper reactor with a thermometer well and a copper inlet tube. In general runs using about 0.5 mole of 9,9-dichlorofluorene were made. An excess

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[1] Stoughton and Adams, THIS JOURNAL, **54**, 4426 (1932).

[2] Bergman, Hoffman and Winter, *Ber.*, **66**, 48 (1933).

[3] Balz and Schiemann, *ibid.*, **60**, 1186 (1927).

[4] McBee and Bechtol, *Ind. Eng. Chem.*, **39**, 380 (1947).

[5] Weissgerber, *Ber.*, **34**, 1659 (1901); Sampey and Reid, THIS JOURNAL, **69**, 234 (1947); Jaeger, U. S. Patent 1,764,023 (1930).

[6] Henne and Leicester, *ibid.*, **60**, 864 (1938).

[7] Henne and Midgley, Jr., *ibid.*, **58**, 884 (1936).

[8] Henne, *ibid.*, **60**, 1569 (1938).

[9] Huntress, Hershberger and Cliff, *ibid.*, **53**, 2720 (1931).

[10] Smedley, *J. Chem. Soc.*, **87**, 1249 (1905).

of 10–28% of mercury salt and 50–60% of hydrofluoric acid was used. Some runs employed 0.25 mole of the chloride and as much as 200% excess hydrofluoric acid. The successful preparation of 9,9-difluorofluorene is described in detail below.

Five-tenths mole (117 g.) of 9,9-dichlorofluorene was dissolved in 200 cc. of chlorobenzene and 0.37 mole (100 g.) of mercuric chloride was now added. Hydrogen fluoride next was bubbled into the stirred solution at a temperature of 30°. After thirty minutes no apparent reaction had occurred so the temperature was raised. At 70° the solution turned a very dark green but in contrast to the large amount of heat liberated when mercuric oxide and hydrofluoric acid are used this reaction showed little evidence of heat evolution. The temperature did not exceed 81° and the time of reaction was one and one-half hours.

The solution was washed with water and sodium carbonate solution, treated with Darco and distilled at 1–5 mm. The first fraction 55–115° (5 mm.), weighed 6 g. and was chlorobenzene. The second fraction, 115–130° (3 mm.), weighed 20 g. It was a light yellow, viscous oil. The third fraction, 125–135° (3 mm.), weighed 13 g. and came over as a yellow oil that solidified in the receiver. On standing overnight fraction 2 had changed to a thick tarry mass with gas bubbles and yellow crystals held in suspension. Some pressure was evidenced and fumes of hydrogen chloride and hydrogen fluoride were evolved when the container was unstoppered. A somewhat similar but much less pronounced effect was observed in fraction 3.

The yellow crystals were separated and recrystallized from ligroin, m. p. 47–48°. They contained fluorine but no chlorine.

Anal. Calcd. for $C_{13}H_8F_2$: F, 18.8; mol. wt., 202.2. Found: F, 17.9; mol. wt., 195.

From the decomposed material, fluorenone was isolated. Probably unstable 9,9-fluorochlorofluorene was the principal product in fraction 2.

Summary

9,9-Difluorofluorene has been prepared by treating 9,9-dichlorofluorene with hydrogen fluoride in the presence of mercuric chloride. It is somewhat unstable. Evidence has been found for the transitory existence of 9-chloro-9-fluorofluorene.

Mercuric chloride and hydrogen fluoride form a fluorinating agent that is especially useful in the preparation of the less stable fluorides.

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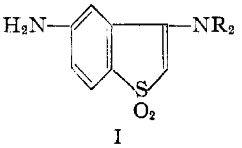
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies in the Thianaphthene Series.[1] II. Aminothianaphthene-1-dioxides[2]

BY F. G. BORDWELL AND C. J. ALBISETTI, JR.[3]

In a previous paper[4] the synthesis of a sulfanilamide vinylog in which the sulfamyl group was separated from the aromatic ring by a vinyl group was described. As an extension in our synthesis of molecules with chemical characteristics similar to sulfanilamide, but with different stereochemical relationships of the functional groups, the synthesis of 3,5-diaminothianaphthene-1-dioxide (I, R = H) was undertaken. This molecule is a vinylog of sulfanilamide in which the sulfonyl and amino portions of the sulfamyl group have been separated by a vinyl group. It is also noteworthy because of its relationship to bis-(4-aminophenyl) sulfone, a compound which has aroused considerable interest because of its high bacteriostatic activity. Recently 2,8-diaminodibenzothiophene-5-dioxide and 2,8-diaminothiaxanthene-5-dioxide, which are closely related to I, have been synthesized for pharmacological testing.[5]



I

The simplest approach to I appeared to be nitration of 5-nitrothianaphthene, oxidation of the sulfur atom and reduction of the nitro groups.

The preparation of 5-nitrothianaphthene by decarboxylation of 5-nitro-2-thianaphthenecarboxylic acid[6] has been described by Fieser and Kennelly.[7] Our yields of 5-nitro-2-thianaphthenecarboxylic acid from crude 2-chloro-5-nitrobenzaldehyde were about 25%; which compares well with the 28% yield reported by Fieser and Kennelly[7] using pure 2-chloro-5-nitrobenzaldehyde, but is considerably lower than the maximum yield of 45% reported by Fries and his co-workers.[6] The decarboxylation was carried out by a slight modification of the method of Fieser and Kennelly,[7] which was found to be more convenient.

Nitration of 5-nitrothianaphthene to give a pure dinitrothianaphthene was not easy, since it was found that a third nitro group entered the molecule almost as readily as did the second nitro group. By carrying out the nitration with an equivalent amount of potassium nitrate in sulfuric acid at 0–5° for one hour a dinitrothianaphthene, m. p. 171°, was isolated in 46% yield. This compound is very probably 3,5-dinitrothianaphthene since the 3-position is known to be the most active

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[1] For the first paper in this series see Bordwell and Albisetti, THIS JOURNAL, **70**, 1558 (1948).

[2] A preliminary account of this work was given at the One Day Technical Meeting of the Chicago Section of the American Chemical Society, January 24, 1947.

[3] Du Pont Predoctoral Fellow, 1946–1947. Present address: du Pont Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Abstracted from the Ph.D. dissertation of C. J. Albisetti, Jr., August, 1947.

[4] Bordwell, Colbert and Alan, THIS JOURNAL, **68**, 1778 (1946).

[5] Neumoyer and Amstutz, *ibid.*, **69**, 1920, 1925 (1947).

[6] Hemmecke, Dissertation, Braunschweig, 1929; Fries, Heering, Hemmecke and Siebert, *Ann.*, **527**, 83 (1936).

[7] Fieser and Kennelly, THIS JOURNAL, **57**, 1611 (1935).