Preparation of Aromatic Fluorine Compounds Using Diazonium Fluosilicates

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The Schiemann reaction[1] is a convenient method of preparing many aromatic and heterocyclic[2] fluorine compounds. In some cases, however, the yields are low; this is true of many nitrofluoro and hydroxyfluoro compounds. The preparation of *p*-fluorobenzoic acid from ethyl *p*-aminobenzoate using the diazonium fluosilicate instead of the diazonium fluoborate has been reported recently.[3] It was of interest to see how this method of preparing fluorine compounds would compare with the Schiemann method, and if it would give better results with those types of compounds for which the Schiemann reaction is not too satisfactory.

The results are shown in the accompanying table. In every case but one—*p*-fluorophenol—the Schiemann reaction gave a better yield than the diazonium fluosilicate method. In another instance, the preparation of methyl 5-fluoronicotinate,[4] the diazonium fluosilicate method has been successful where all other methods failed.

TABLE I

Fluorine compound	% Yield diazonium fluosilicate	% Yield F cmpd. from amine	% Yield F cmpd. Schiemann reacn.
Fluorobenzene	87	30.4	51–97[1,5,6,7]
m-Nitrofluorobenzene	86	22.3	43–54[8,9,10,11]
p-Nitrofluorobenzene	85	33.8	40–60[9,11,12,13]
p-Fluorophenol	79.2	6.5	0[9]
Ethyl *p*-fluorobenzoate	82.5	38.8	71[14]
2-Fluoropyridine	0	..	34[2]

Experimental

Preparation of the Amine Fluosilicates.—This was usually accomplished by dissolving the amine in the minimum quantity of 95% ethanol, warming if necessary to keep the volume of ethanol down, and adding slightly more than the theoretical amount of 27% fluosilicic acid. The solution was then cooled in an ice-bath and the precipitated salt washed with ether and dried in a desiccator or by warming to 30–40° in an oven for a short time. Methanol was tried as a solvent in the case of *p*-nitroaniline; the yield was lower (72%) than with ethanol (89.5%). With *p*-aminophenol, methanol and ethanol gave similar results.

Preparation of the Diazonium Fluosilicates.—A typical procedure was as follows: 134 g. of *p*-nitroaniline fluosilicate was suspended in 500 ml. of glacial acetic acid, and ethyl nitrite was passed into the mixture with stirring until all the solid had dissolved. The temperature was allowed to rise to about 40°, and kept there by an ice-bath. The solution was then cooled to room temperature, 600 ml. of absolute ether added, and the solution then cooled to 0° and allowed to stand tightly covered in the ice-box overnight. The oil which appeared upon addition of the ether slowly changed to a solid. The product was filtered, washed twice with 150 ml. of absolute ethanol, twice with 150 ml. of absolute ether, and dried at 40°. The yield was 114–120 g.

All of the compounds tried gave lower yields at temperatures much above 40°; with aniline fluosilicate, at 50° for instance, the yield dropped to 67% although with the *p*-hydroxyaniline fluosilicate the yield was 89% at 40° and 88% at 60°.

Decomposition of the Diazonium Fluosilicates.—In most cases the diazonium salt was diluted with an inert material, such as sodium fluoride, to make the decomposition less vigorous. A typical example: 108 g. of *p*-nitrobenzenediazonium fluosilicate (dried overnight over phosphorus pentoxide) was mixed with an equal weight of sodium fluoride (dried overnight at 107° in an oven). The decomposition was carried out in a 2-liter flask connected to a series of traps; this consisted of five eight-inch test-tubes each fitted with a two-holed rubber stopper carrying an inlet and outlet tube, and filled about two-thirds full of broken glass tubing; all were immersed in an ice–salt-bath. The diluted diazonium salt was decomposed in eight separate lots of approximately 27 g. each. The initial lot was set off by heating gently with a bunsen burner; the others started to decompose shortly after being added to the flask warm from the previous decomposition. Decomposition was smooth, but rapid.

Steam was blown through the traps to remove any product in them; the material so collected was added to the decomposition flask, more water was added, and the mixture steam distilled. The oil was extracted from the distillate with ether, the ether dried, and the *p*-fluoronitrobenzene recovered by distillation; yield, 27.5 g., b. p. 203°.

All the fluorine compounds reported in this investigation had been prepared previously, as indicated in the table. The boiling points and refractive indices of our compounds checked the literature values.

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Sodium Hydride and Alkyl Halides[1]

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The recent report of the lack of reaction of sodium hydride with diethyldichlorosilane[2] prompts us to report at this time our results on the attempted reaction of sodium hydride with certain alkyl halides. In the course of this investigation it was found that sodium hydride did not react with any of the eight halides studied. The com-

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[1] This work was conducted as part of a program of research under a contract between the Office of Naval Research and the University of Colorado.

[2] Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947).