THE INTRODUCTION OF FLUORINE INTO AROMATIC NUCLEI BY MEANS OF AMMONIUM FLUOBORATE*

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Fluorine is most conveniently introduced into the aromatic nucleus by means of the diazonium fluoborate synthesis discovered by Bart[1], and developed by Schiemann[2]. In brief, the reaction involves the diazotization of an aromatic amine, conversion to the insoluble diazonium fluoborate, and subsequent thermal decomposition to the aromatic fluoride. It is illustrated as follows:

$$ArNH_2^* \rightarrow ArN_2^+ \rightarrow ArN_2BF_4$$
$$\rightarrow ArF + N_2 + BF_3$$

The diazonium fluoborates in a relatively pure state have characteristic and definite decomposition temperatures below which they are stable, and, in many cases, can be stored for indefinite periods of time.

Fluoboric acid was originally used to form the diazonium salt. The resulting acid medium was exceedingly corrosive to glass or metal equipment. Due to the commercial significance of this reaction, it was improved upon by the use of sodium fluoborate[3, 4] thus avoiding the use of corrosive hydrofluoric and fluoboric acids. This improvement has made it possible to prepare many aromatic fluorine compounds in the laboratory at a reasonable cost in ordinary glass apparatus.

Ammonium fluoborate has become available and can be prepared in a much purer form on an industrial scale than the sodium salt due to its lower solubility. This study was made to determine whether ammonium fluoborate can be used in place of the sodium salt.

Aniline, *o*-toluidine, *α*-naphthylamine, and benzidine were converted to the corresponding diazonium chlorides. Each diazonium chloride solution was then divided into two equal portions, one was treated with a calculated excess of sodium fluoborate, and the other with an equal excess of ammonium fluoborate. Since the ammonium salt is less soluble than the sodium salt its molar solution volume was larger. Each precipitate pair was then filtered, washed, dried, and weighed in the usual manner under identical conditions. The results are semi-quantitative in nature and are based on the diazonium fluoborates. The data in this form are interesting not only from the standpoint that the diazonium fluoborates can be used to form dyes[5] but the $-N_2BF_4$ group can be replaced by acetoxy[6], mercury[7], nitro[8], and arsonic acid[9] groups. Thermal decomposition in all cases gave the corresponding nucleated fluorine compound.

Table I.—Yield of Aryl Diazonium Fluoborates With Sodium Fluoborate and Ammonium Fluoborate

Amine	Moles of Amine	Moles of MBF_4	$NaBF_4$			NH_4BF_4		
			Grams of ArN_2BF_4	Yield in %	Avg. %	Grams of ArN_2BF_4	Yield in %	Avg.
Aniline	0.25	0.3	33	69		28	58	
	0.5	0.6	69.5	72.5	70.7	56	58	58
o-Toluidine	0.25	0.3	31	60		34	65	
	0.5	0.6	59.5	58.8	59.4	54	52.5	58.7
α-Naphthylamine	0.25	0.3	40	66		37.5	62	
	0.25	0.3	45	73	69.5	47.7	78	70
Benzidine	0.15	0.34	49	85		43	75	
	0.15	0.34	47	82	83.5	53.5	93	84

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The data in Table I indicate that the ammonium salt gives yields as satisfactory as the sodium salt except with aniline. Since the solubility of the diazonium fluoborate is an important factor, the decreased yield in the case of aniline may be due to the larger volume necessary with the ammonium salt.

Since this study is preliminary in nature, other amines will be studied as well as some of the factors involved. The authors wish to express their appreciation to the Aluminum Ore Co. of East St. Louis for furnishing the commercial samples of the sodium and ammonium fluoborates.

Conclusions.—Ammonium fluoborate can be used satisfactorily in the preparation of some aromatic fluorine compounds by means of the Schiemann reaction.

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* Ar represents an aromatic radical.

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