A study of the decomposition of some aromatic diazonium hexafluorophosphate salts.

William A. Redmond

University of Windsor

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A STUDY OF THE DECOMPOSITION OF SOME AROMATIC DIAZONIUM HEXAFLUOROPHOSPHATE SALTS

BY

WILLIAM A. REDMOND

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1964
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ABSTRACT

In order to open new routes to the synthesis of aromatic fluorides many modifications based on the classical Schiemann Reaction have appeared in the literature in the last fifteen years. These methods are discussed and a new modification is presented in this work. The substitution of hexafluorophosphoric acid for fluoboric acid in the Schiemann Reaction was found to lead in almost every case to increased yields of fluoroaromatic. A quite marked improvement was noted in the preparation of ortho and para-fluorobenzoic acids and in the synthesis of o-bromofluorobenzene. A comparison of the yields obtained by the hexafluorophosphate method to those obtained via the normal Schiemann Reaction is included.

In the course of work on the preparation of arylfluorides a new method for the reduction of diazonium compounds was discovered. Tetramethylurea was found to reduce these compounds. Its use has several advantages over the standard methods. The reaction is spontaneous, simple to perform, and one of the few reductions of diazonium compounds that can be carried out in non-aqueous media. Greatly increased yields of reduction product are obtained from ortho and para-aminobenzoic acids over the usual deamination procedures by this method.

ii
A new compound, o-methylphenoxytetramethylamidinium hexafluorophosphate, was isolated from the attempted reduction of o-toluenediazonium hexafluorophosphate in tetramethylurea. The structure of this compound was proved by elemental analysis and hydrolysis to o-cresol and dimethylamine.
ACKNOWLEDGEMENTS

I wish to acknowledge, with thanks, the direction and encouragement given me by Dr. K.G. Rutherford during the course of this work.

Thanks are also due the Ozark-Mahoning Co. of Tulsa, Oklahoma for generous supplies of hexafluorophosphoric acid and other chemicals.

Special thanks are accorded Dr. R.J. Thibert for his generous assistance in the writing of this thesis and for his helpful advice over the years.
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CHAPTER I

INTRODUCTION

1. The Replacement of an Aromatic Amino Group by Fluorine.

Aryldiazonium salts are useful intermediates in the preparation of several classes of organic compounds. Such salts are precursors in the following synthetic procedures:

a) The preparation of phenols by the hydrolysis of a diazonium salt.

b) The preparation of aryliodides, bromides, chlorides, nitriles and thiocyanates by the Sandmeyer Reaction.

c) The replacement of the diazonium group by \(-\text{SH}, \text{N}_3,\) and \(-\text{SCH}_2\text{COOH}.\)

d) The preparation of nitroaromatics.\(^1,2\)

e) The introduction of arsonic or stibonic acid groups by the Bart Reaction.

f) The preparation of fluoroaromatics by the Schiemann Reaction.

---


g) The preparation of arylphosphonic or diarylphosphinic acids.³  

h) The preparation of aromatic compounds of mercury,⁴ tin,⁵ lead,⁶ bismuth,⁷ and antimony.⁸

i) The replacement of the diazonium group by hydrogen.

j) Aryl coupling reactions - the Bachmann-Gomberg Reaction.

k) Arylation reactions - Meerwein Arylation.

l) The preparation of azo compounds by coupling with phenols and aromatic amines.

m) The preparation of anilides.⁹

n) The preparation of organo-thallium compounds.¹⁰

---

⁴ A.N. Nesmeyanov, Ber., 62, 1010 (1929).
The preparation of arylgermanium and arylselenium compounds.

In many of the above reactions the isolation of the intermediate diazonium salt is not a necessary requirement for the realization of good yields of products. In others, however, isolation of the intermediate salt is either desirable or necessary in order to obtain respectable conversion in the overall reaction. Thus in the Schiemann Reaction (Fig. 1) which involves the replacement of a primary amino group with a fluorine atom it is of prime importance to isolate and purify the diazonium fluoborate in order to obtain good yields of the fluorocarbon derivative.

\[
\text{phenyl-N}=\text{N} \quad \text{BF}_4 \quad \Delta \quad \text{phenyl-F} + \text{N}_2 + \text{BF}_3
\]

Fig. 1 The Schiemann Reaction.


The Schiemann Reaction is of great interest in organic chemistry since it is the classical procedure used for the preparation of all types of aromatic fluorocarbons. Indeed, with a few unique exceptions it is the only method available for the incorporation of the fluorine atom into an aromatic nucleus. The reaction is characterized by its simplicity of operation which involves routine diazotization of an aromatic amine followed by the addition of fluoborate ion. Invariably the diazonium fluoborate is relatively insoluble in the reaction medium and is obtained as a crystalline salt. This in itself is quite unique since diazonium compounds in general are unstable even in solution at temperatures slightly above $0^\circ$. The fluoborates, however, can be washed with water and even recrystallized from aqueous solution in order to remove traces of impurities which affect the yield of the final decomposition stage in the overall procedure. The pyrolysis of the fluoborate usually proceeds smoothly to yield the aromatic fluoride, nitrogen, and boron trifluoride.

The success of the latter step in the Schiemann Reaction is very sensitive to traces of impurities. Since the diazotization step usually involves generation of nitrous acid by the action of hydrochloric acid on sodium nitrite, chloride ion is usually a contaminant as a result of coprecipitation of sodium chloride with the fluoborate. Several cases have been reported whereby a chlorine atom has been incorporated into the aromatic nucleus. Thus
Finger\textsuperscript{13} found that 2,5-difluorochlorobenzene and 2,4-difluorochlorobenzene were obtained when 2,4-difluorobenzene-diazonium fluoborate was decomposed. It was found that the chlorine atom originated from sodium chloride that had coprecipitated with the fluoborate. Careful washing of the diazonium salt eliminated this undesirable side reaction. Again, the presence of traces of water reduces the yields of fluoroaromatic by hydrolysis which produces phenolic derivatives.

The purification of diazonium fluoborates usually involves copious washing with cold, distilled water. The salt is usually air-dried followed by drying in vacuo to remove the last traces of moisture. If the diazonium salt is appreciably soluble in water the above purification procedure becomes very limited and total removal of foreign ions is not realized. Overall yields are then decreased substantially.

The mechanism of the thermal decomposition of aryl-diazonium fluoborates has been studied by several workers. However only tentative suggestions for either a free radical or ionic mechanism have thus far been proposed. These are discussed by Roe\textsuperscript{14} in an article on the Schiemann Reaction published in \textit{Organic Reactions}. (See Fig. 2).

\begin{itemize}
\end{itemize}
1. Carbonium ion.
\[
\ar^+ + \text{N}_2 + \left[ \text{F} : \text{BF}_3 \right]^- \xrightarrow{\Delta} \ar^+ \left[ \text{F} : \text{BF}_3 \right]^- \rightarrow \ar \text{F} : + \text{BF}_3
\]

2. Free radical.
\[
\ar^* + \text{N}_2 + \text{BF}_3 + \text{F} : \rightarrow \ar \text{F} : + \text{BF}_3
\]

3. Rearrangement.
\[
\begin{bmatrix}
\ar \xrightarrow{\text{N} \equiv \text{N}} \\
\text{F} : \\
\text{BF}_3
\end{bmatrix}
\rightarrow
\begin{bmatrix}
\ar \text{F} : \\
\text{N} \equiv \text{N} \\
\text{BF}_3
\end{bmatrix}
\rightarrow \ar \text{F} : + \text{N}_2 + \text{BF}_3
\]

Fig. 2. Proposed mechanisms for the decomposition of aryldiazonium fluoborates - from Roe.

Since the time of publication of this article Nesmeyanov, Makarova and their co-workers\(^ {15-18}\) have reported the

\(^{17}\) L.G. Makarova and E.A. Gribchenko, ibid., 693 (1958).
results of decomposition of diazonium fluoborates and diazonium chlorides in nitrobenzene. These authors have found that decomposition of aryldiazonium fluoborates in nitrobenzene yields m-nitrobiphenyl. This is the product that would be expected for an ionic intermediate and they concluded that a phenyl cation was formed during the decomposition. The decomposition of phenyldiazonium chloride in nitrobenzene gave a mixture of ortho, meta, and para-nitrobiphenyl. These results are indicative of a free radical mechanism. Similarly, Olah and Tolgyesi have found that the decomposition of benzenediazonium fluoborates, chloroborates, and bromoborates in fluorobenzene yields ortho and para-fluorobiphenyl (as expected for an ionic mechanism) while the decomposition of the corresponding diazonium chlorides in the same solvent gives a mixture of all isomers (as expected for a free radical mechanism). As is pointed out by Olah, however, the results of his investigations are applicable only to decompositions at low temperatures (less than 85° in all cases) and in the presence of a solvent. Decompositions carried out without solvent and at higher temperatures could well be free radical in nature. In fact, this would probably be the preferred mechanism.

Since the Schiemann Reaction is the only general method available for the preparation of aromatic fluoride

compounds it is not surprising that this procedure has been the object of much research. Several modifications have been reported all of which are directed towards the improvement of yields. The problem is simplified in this respect since the overall reaction is carried out in only two separate stages. A modification which enhances the yield of one of the steps is almost certain to prove general for all classes of compounds.

The first way in which overall yields of the Schiemann Reaction could be improved would involve the use of methods that lead to isolation of greater amounts of the diazonium fluoborates. Several methods have been proposed which have proved quite fruitful. For example, amines which are poorly soluble in aqueous hydrochloric acid solution can often be more readily diazotized in a mixture of sulfuric and glacial acetic acids.²⁰ Lakin and Petrova²¹ recently reported the preparation of anthraquinone-1-diazonium fluoborate in 87.5% yield via the formation of the amino-sulfate followed by diazotization with fluoboric acid and aqueous sodium nitrite.

In some cases an advantage is realized in the preparation of diazonium fluoborates by the use of non-aqueous solvent systems. In these cases the diazonium salt may be


prepared by the use of nitrosyl fluoborate\textsuperscript{22} or the complex of boron trifluoride with dinitrogen trioxide.\textsuperscript{23} A variety of alkyl nitrites have also been used for this purpose. The use of nitrosyl fluoborate has lead to the isolation of phenyldiazonium fluoborate, 2,4-dibromonaphthyl-1-diazonium fluoborate, and 2,6-dibromophenol-4-diazonium fluoborate in yields of 90, 48, and 100% respectively. The use of the dinitrogen trioxide–boron trifluoride complex is particularly advantageous in the conversion of weakly basic amines to the diazonium salt.

Diazotizations carried out in aqueous fluoboric acid and hydrofluoric acid have been found to give increased yields of the aromatic fluoride.\textsuperscript{24} Thus fluorobenzene, p-bromofluorobenzene, o-fluoroanisole, and 1-fluoronaphthalene were prepared in overall yields of 66, 55, 62, and 57%, respectively, by this method. The addition of a solution of nitrosyl chloride dissolved in an excess of hydrofluoric acid to aniline, 2-aminopyridine, and m-toluidine leads to good yields of the corresponding fluoro compounds.\textsuperscript{25}

\textsuperscript{22} U. Wannagat and G. Hohlstein, \textit{Ber.}, \textbf{88}, 1839 (1955).
The preparation of arylfluorides via the decomposition of aryldiazonium fluorides in anhydrous hydrofluoric acid has been investigated by Ferm and VanderWerf. The method involves diazotization of the aromatic amine in cold hydrofluoric acid and subsequent decomposition of the diazonium salt when the solution is warmed to the reflux temperature of hydrofluoric acid. The above workers reported the preparation of the following compounds by this method in the stated yields; fluorobenzene (82%), p-fluorotoluene (78%), m-fluorotoluene (82%), o-fluorotoluene (78%), 4-fluoro-1,3-dimethylbenzene (57%), 2-fluoro-1,4-dimethylbenzene (43%), m-fluorochlorobenzene (81%), p-fluorochlorobenzene (74%), m-nitrofluorobenzene (39%), p-nitrofluorobenzene (62%), m-fluorophenol (46%), o-fluorobenzoic acid (57%), m-fluorobenzoic acid (78%), p-fluorobenzoic acid (98%), and o-fluorobiphenyl (82%). The method failed to give satisfactory results with amines which contained ortho substituents with one or more atoms with unshared electrons. Thus o-chloroaniline, o-aminophenol and o-anisidine failed to give satisfactory yields of the fluoride. The authors suggest this is because the diazonium fluorides derived from these compounds are too stable to decompose readily at the boiling point of hydrofluoric acid at atmospheric pressure. If the pressure was increased and the temperature was raised to a point sufficiently high to decompose

the aryldiazonium fluorides, a complex mixture of high melting solids was obtained instead of the aryfluorides.

In addition to the above limitations in the scope of the reaction it also suffers from the well known disadvantages involved with the use of hydrofluoric acid. A monel metal flask and a stainless steel stirrer are required for diazotization in hydrofluoric acid. In addition a copper coil must be attached to this flask so that the diazonium fluoride may be heated to the reflux temperature of hydrofluoric acid and thus decomposed. A perhaps greater difficulty encountered in this procedure is the personal danger involved in work with hydrofluoric acid.

Diazonium fluosilicates have been prepared and used as intermediates in the Schiemann Reaction but in general the yields of fluorides obtained through their use are not as high as those obtained by the normal Schiemann conditions.\textsuperscript{27,28} The results of these investigations are summarized in Table 1. As can be seen from the table, p-nitroaniline is the only amine which gives respectable yields of fluorocarbon and in every case except that of p-aminophenol the yield is lower than is obtained by the normal Schiemann Reaction.


Table 1
A Comparison of the use of Fluosilicate versus Fluoborate in the Schiemann Reaction

<table>
<thead>
<tr>
<th>Amine</th>
<th>Percent Yield of Diazonium Fluosilicate</th>
<th>Percent Yield of Fluoroaromatic</th>
<th>Percent Yield of Fluoroaromatic by Schiemann</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>87</td>
<td>39.4</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>m-Nitroaniline</td>
<td>86</td>
<td>22.3</td>
<td>10-19</td>
<td>27</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>85</td>
<td>33.8</td>
<td>40-58</td>
<td>27</td>
</tr>
<tr>
<td>p-Aminophenol</td>
<td>79.2</td>
<td>65</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>Ethyl-p-aminobenzoate</td>
<td>82.5</td>
<td>38.8</td>
<td>71</td>
<td>27</td>
</tr>
<tr>
<td>2-Aminopyridine</td>
<td>0</td>
<td>---,10</td>
<td>34</td>
<td>27,28</td>
</tr>
<tr>
<td>3-Aminopyridine</td>
<td>33</td>
<td></td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>

* Yields reported are taken from A. Roe, Org. Reactions, 5, 193 (1949)
It has been reported by Bergman\textsuperscript{29-31} in a series of papers that diazonium fluoborates can be decomposed in acetone or water in the presence of cuprous chloride. The results of the fairly large number of arylfluorides prepared by this method are summarized in Table 2.

In the second paper of the series (31) yields of 52, 47, and 61\% of arylfluoride are reported from the decomposition of ortho, meta, and para-nitrobenzenediazonium fluoborates, respectively. However, Barben and Suschitzky\textsuperscript{32} in an attempt to prepare 3-fluoro-1-methyl-2-nitrobenzene from the amino precursor by Bergmann's method obtained in 75\% yield o-nitrotoluene instead. They also reported that Bergmann's method failed in the decomposition of the diazonium fluoborates of o-nitrobenzene, 4-methyl-2-nitrobenzene, 2-methyl-6-nitrobenzene, 3-methyl-2-nitrobenzene, and 4-carboxybenzene. In all cases some deamination occurred and some of the chloro compound was formed but none of the desired fluoride could be obtained. Again, Fisher and Joullie\textsuperscript{33} reported that Bergmann's method failed in the


\textsuperscript{30} E.D. Bergmann and M. Bentov, \textit{ibid.}, \textbf{19}, 1594 (1954).


Table 2

Decomposition of Diazonium Fluoborates in Acetone or Water

<table>
<thead>
<tr>
<th>Amine</th>
<th>Percent Yield of Diazonium Fluoborate</th>
<th>Percent Yield of Fluoroaromatic</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Aminoacetanilide</td>
<td>—</td>
<td>82&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>m-Aminoacetanilide</td>
<td>—</td>
<td>75&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>4-Amino-4'-acetamidobiphenyl</td>
<td>—</td>
<td>62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>4-Amino-4'-acetamido-3,3'-dimethoxybiphenyl</td>
<td>—</td>
<td>37&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>4'-Amino-2-acetamidobiphenyl</td>
<td>—</td>
<td>59&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>4-Fluoro-1-acetamidonaphthalene</td>
<td>—</td>
<td>69&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>5-Fluoro-1-acetamidonaphthalene</td>
<td>—</td>
<td>55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>95-98</td>
<td>38</td>
<td>31</td>
</tr>
<tr>
<td>m-Phenylenediamine</td>
<td>96</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>o-Nitroaniline</td>
<td>95</td>
<td>52</td>
<td>31</td>
</tr>
<tr>
<td>m-Nitroaniline</td>
<td>97</td>
<td>47</td>
<td>31</td>
</tr>
</tbody>
</table>
Table 2 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Percent Yield of Diazonium Fluoborate</th>
<th>Percent Yield of Fluoroaromatic</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Nitroaniline</td>
<td>98</td>
<td>61</td>
<td>31</td>
</tr>
<tr>
<td>o-Aminobenzoic acid</td>
<td>51</td>
<td>48</td>
<td>31</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>50</td>
<td>43</td>
<td>31</td>
</tr>
<tr>
<td>p-Aminoacetophenone</td>
<td>88-90</td>
<td>24</td>
<td>31</td>
</tr>
<tr>
<td>Benzidine</td>
<td>90</td>
<td>72</td>
<td>31,29</td>
</tr>
<tr>
<td>p-Aminophenylacetic acid</td>
<td>—</td>
<td>87</td>
<td>31</td>
</tr>
<tr>
<td>p-Aminocinnamic acid</td>
<td>76</td>
<td>48</td>
<td>31</td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>92</td>
<td>46</td>
<td>31,29</td>
</tr>
<tr>
<td>2-Naphthylamine</td>
<td>95</td>
<td>54</td>
<td>31,29</td>
</tr>
<tr>
<td>1-Aminoanthraquinone</td>
<td>88</td>
<td>72</td>
<td>31,29</td>
</tr>
<tr>
<td>2-Aminoanthraquinone</td>
<td>95,84</td>
<td>86,47</td>
<td>31,29</td>
</tr>
<tr>
<td>2-Aminofluorene</td>
<td>77</td>
<td>60</td>
<td>31</td>
</tr>
<tr>
<td>p-Aminophenol</td>
<td>—</td>
<td>71</td>
<td>31</td>
</tr>
<tr>
<td>o-Aminophenol</td>
<td>—</td>
<td>40</td>
<td>31</td>
</tr>
</tbody>
</table>
Table 2 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Percent Yield of Diazonium Fluoborate</th>
<th>Percent Yield of Fluoroaromatic</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Aminoacetanilide</td>
<td>65</td>
<td>55</td>
<td>31</td>
</tr>
<tr>
<td>o-Chloroaniline</td>
<td>—</td>
<td>16(^a)</td>
<td>29</td>
</tr>
<tr>
<td>5-Chloroanthranilic acid</td>
<td>—</td>
<td>36(^a)</td>
<td>29</td>
</tr>
<tr>
<td>p-Bromoaniline</td>
<td>50</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>81</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>m-Toluidine</td>
<td>75</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>82</td>
<td>17</td>
<td>29</td>
</tr>
<tr>
<td>2,3-Dimethylaniline</td>
<td>85</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>2,4-Dimethylaniline</td>
<td>35</td>
<td>17</td>
<td>29</td>
</tr>
<tr>
<td>2,5-Dimethylaniline</td>
<td>82</td>
<td>19</td>
<td>29</td>
</tr>
<tr>
<td>2-Aminobiphenyl</td>
<td>75</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>2,2'-Diamino-6,6'-dimethylbiphenyl</td>
<td>75</td>
<td>20.5</td>
<td>29</td>
</tr>
</tbody>
</table>

\(^a\) Overall yield from the amine
preparation of 5-fluorobenzimidazole from the corresponding diazonium fluoborate. Instead of the expected fluoro compound a compound which contained chlorine was obtained. Bergmann\(^{34}\) has since stated that his method is only possible if the starting arylamine contains no strongly polar substituent on the ring. If this is the case then one would expect the method to fail in the case of nitroarylamines.

It is interesting to note that Hu, Yeh, and Yen\(^{35}\) have reported that the thermal decomposition of diazonium fluoborates can be carried out with better results in a diluent such as sand, sodium fluoride or barium sulfate. This is not unexpected as several diluents have been used in order to better control decomposition of these salts.\(^{36}\) However, they also stated that the decomposition can be conducted at room temperature in a suitable solvent if a catalyst such as powdered copper or iron, cuprous fluoborate, or active carbon is used. They claimed that cuprous fluoborate gave the best results. The use of cuprous fluoborate as a catalyst in the preparation of arylfluorides via the decomposition of diazonium salts in a solvent appears quite similar to Bergmann's use of cuprous chloride.

Roe, in his article on the Schiemann Reaction in Organic Reactions has included tables which list the yields

\(^{34}\) E.D. Bergmann and S. Berkovic, loc. cit.


\(^{36}\) A. Roe, loc. cit.
and references for the preparation of all the aromatic fluorides that were obtained via the Schiemann Procedure prior to 1947. In order to provide a convenient reference to the preparation of all the aromatic prepared via the diazonium salt since that time the following table (Table3) is provided.
Table 3
Yields of Diazonium Fluoborates and Arylfluorides

<table>
<thead>
<tr>
<th>Amines Containing Halogen</th>
<th>Yield of ArN$_2$BF$_4$</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromoaniline</td>
<td>—</td>
<td>54$^a$</td>
<td>38</td>
</tr>
<tr>
<td>2,5-Dibromoaniline</td>
<td>65.7</td>
<td>58.7</td>
<td>39</td>
</tr>
<tr>
<td>2,6-Dibromoaniline</td>
<td>71.4</td>
<td>50.1</td>
<td>39</td>
</tr>
<tr>
<td>3,4-Dibromoaniline</td>
<td>59.8</td>
<td>56.6</td>
<td>39</td>
</tr>
<tr>
<td>2,3,5-Tribromoaniline</td>
<td>52.1</td>
<td>60.6</td>
<td>39</td>
</tr>
<tr>
<td>2,4,5-Tribromoaniline</td>
<td>57.7</td>
<td>46.8</td>
<td>39</td>
</tr>
<tr>
<td>2,4,6-Tribromoaniline</td>
<td>70.2</td>
<td>53.4</td>
<td>39</td>
</tr>
<tr>
<td>3,4,5-Tribromoaniline</td>
<td>60.2</td>
<td>62.6</td>
<td>39</td>
</tr>
<tr>
<td>2,4-Dichloroaniline</td>
<td>—</td>
<td>68.7</td>
<td>39</td>
</tr>
<tr>
<td>2,5-Dichloroaniline</td>
<td>69</td>
<td>68.5</td>
<td>39</td>
</tr>
<tr>
<td>2,6-Dichloroaniline</td>
<td>53.6</td>
<td>72.7</td>
<td>39</td>
</tr>
<tr>
<td>3,4-Dichloroaniline</td>
<td>61.2</td>
<td>59.8</td>
<td>39</td>
</tr>
<tr>
<td>3,5-Dichloroaniline</td>
<td>78.6</td>
<td>65.4</td>
<td>39,40</td>
</tr>
<tr>
<td>Amine</td>
<td>Yield of $\text{ArN}_2\text{BF}_4$</td>
<td>Yield of ArF</td>
<td>Reference</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>2,3,5-Trichloroaniline</td>
<td>---</td>
<td>56.9</td>
<td>39</td>
</tr>
<tr>
<td>2,4,5-Trichloroaniline</td>
<td>60.7</td>
<td>56.9</td>
<td>39</td>
</tr>
<tr>
<td>3,4,5-Trichloroaniline</td>
<td>67.4</td>
<td>56.6</td>
<td>39</td>
</tr>
<tr>
<td>2-Fluoroaniline</td>
<td>83</td>
<td>51</td>
<td>41,42</td>
</tr>
<tr>
<td>4-Fluoroaniline</td>
<td>---</td>
<td>44</td>
<td>43</td>
</tr>
<tr>
<td>2,4,5-Trifluoroaniline</td>
<td>quant.</td>
<td>38-40</td>
<td>44</td>
</tr>
<tr>
<td>2,4-Difluoroaniline</td>
<td>---</td>
<td>45,46</td>
<td></td>
</tr>
<tr>
<td>2,3,5-Trifluoroaniline</td>
<td>89</td>
<td>43</td>
<td>47</td>
</tr>
<tr>
<td>3,5-Difluoroaniline</td>
<td>98</td>
<td>62.8</td>
<td>48</td>
</tr>
<tr>
<td>2-Chloro-4-fluoroaniline</td>
<td>---</td>
<td>---</td>
<td>46</td>
</tr>
<tr>
<td>2-Fluoro-5-bromoaniline</td>
<td>84</td>
<td>8</td>
<td>49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amines Containing Alkyl Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Benzylaniline</td>
</tr>
<tr>
<td>Aminonitrodurene</td>
</tr>
<tr>
<td>Aminonitroisodurene</td>
</tr>
<tr>
<td>Amine</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>Nitromesidine</td>
</tr>
<tr>
<td>Fluoromesidine</td>
</tr>
<tr>
<td>Difluoromesidine</td>
</tr>
<tr>
<td>cis-2-Aminostilbene</td>
</tr>
<tr>
<td>trans-2-Aminostilbene</td>
</tr>
<tr>
<td>p-t-Butylaniline</td>
</tr>
<tr>
<td>4-(2-chloroethyl)aniline</td>
</tr>
<tr>
<td>o-Toluidine</td>
</tr>
<tr>
<td><strong>Phenols and Ethers</strong></td>
</tr>
<tr>
<td>2-Aminodiphenyl ether</td>
</tr>
<tr>
<td>4-Amino-2,6-diethylanisole</td>
</tr>
<tr>
<td>p-Anisidine</td>
</tr>
<tr>
<td>o-Anisidine</td>
</tr>
<tr>
<td>2,6-Dibromo-4-aminophenol</td>
</tr>
<tr>
<td>Amine</td>
</tr>
<tr>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>p-Aminophenol</td>
</tr>
<tr>
<td>4-Chloro-2,5-diethoxyaniline</td>
</tr>
<tr>
<td>m-Aminophenol</td>
</tr>
<tr>
<td>2-Aminophenylbenzyl ether</td>
</tr>
<tr>
<td>o-Trifluoromethoxyaniline</td>
</tr>
<tr>
<td>m-Trifluoromethoxyaniline</td>
</tr>
<tr>
<td>o-((1,1,2-Trifluoro-2-chloroethoxy)aniline</td>
</tr>
<tr>
<td>m-((1,1,2-Trifluoro-2-chloroethoxy)aniline</td>
</tr>
<tr>
<td>p-((1,1,2-Trifluoro-2-chloroethoxy)aniline</td>
</tr>
<tr>
<td>p-Aminodiphenyl ether</td>
</tr>
<tr>
<td><strong>Esters and Acids</strong></td>
</tr>
<tr>
<td>5-Amino-2-chlorobenzoic acid</td>
</tr>
<tr>
<td>6-Nitroanthranilic acid</td>
</tr>
</tbody>
</table>
Table 3 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield of ArN₂BF₄</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl anthranilate</td>
<td>—</td>
<td>46ᵃ</td>
<td>42</td>
</tr>
<tr>
<td>Methyl-2-aminoveratrate</td>
<td>—</td>
<td>—</td>
<td>67</td>
</tr>
<tr>
<td>p-Aminosalicylic acid methyl ester</td>
<td>—</td>
<td>31ᵃ</td>
<td>68</td>
</tr>
<tr>
<td>o-Aminobenzoic acid</td>
<td>51</td>
<td>—</td>
<td>69</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>50</td>
<td>—</td>
<td>69</td>
</tr>
</tbody>
</table>

Amines, Anilides and Azo Compounds

<table>
<thead>
<tr>
<th>Structure</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>failed</td>
<td>70</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>quant.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1-Amino-N-diethylamino-2-ethoxybenzene</td>
<td>90</td>
<td>n.d.</td>
</tr>
<tr>
<td>o-Amino-N-methylbenzanilide</td>
<td>—</td>
<td>n.d.</td>
</tr>
</tbody>
</table>
Table 3 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of $\text{ArF}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Amino-4-fluoroacetanilide</td>
<td>failed</td>
<td>failed, 5</td>
<td>41,49</td>
</tr>
<tr>
<td>2-Amino-N-methylbenzo-1'-naphthalide</td>
<td>n.d.</td>
<td>n.d.</td>
<td>74</td>
</tr>
<tr>
<td>2-Amino-N-methylbenzo-2'-naphthalide</td>
<td>n.d.</td>
<td>n.d.</td>
<td>74</td>
</tr>
</tbody>
</table>

<p>| Ketones                               |                                     |                        |           |
|---------------------------------------|                                     |                        |           |
| 2-Aminobenzophenone                   | 60                                   | n.d.                   | 75        |
| o-Aminopropiophenone                  | 79                                   | n.d.                   | 76        |
| m-Aminopropiophenone                  | 88                                   | n.d.                   | 76        |
| 2-($4'$-Methylbenzoyl)aniline         | 56                                   | n.d.                   | 75        |
| 2-($4'$-Methylbenzoyl)aniline         | 70                                   | n.d.                   | 75        |
| 2-($3'$-Nitrobenzoyl)aniline          | 90                                   | n.d.                   | 75        |</p>
<table>
<thead>
<tr>
<th>Amines</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nitro Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Dinitroaniline</td>
<td>92</td>
<td>trace</td>
<td>77</td>
</tr>
<tr>
<td>2-Fluoro-5-nitroaniline</td>
<td>—</td>
<td>failed</td>
<td>41</td>
</tr>
<tr>
<td>4-Nitroaniline</td>
<td>97.7, 51</td>
<td>48.6, 43.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>70, 91</td>
</tr>
<tr>
<td>3-Chloro-4-Nitroaniline</td>
<td>74.2</td>
<td>n.d.</td>
<td>78</td>
</tr>
<tr>
<td>2-Iodo-5-nitroaniline</td>
<td>92.5</td>
<td>44</td>
<td>78</td>
</tr>
<tr>
<td>1-Fluoro-2-amino-4-nitrobenzene</td>
<td>—</td>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>4-Chloro-3-nitroaniline</td>
<td>81</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td><strong>Naphthalene Derivatives</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>—</td>
<td>57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>38</td>
</tr>
<tr>
<td>2,4-Dibromo-1-naphthylamine</td>
<td>48</td>
<td>62</td>
<td>59</td>
</tr>
<tr>
<td>2-Nitro-1-naphthylamine</td>
<td>—</td>
<td>n.d.</td>
<td>81</td>
</tr>
<tr>
<td>3-Nitro-2-naphthylamine</td>
<td>—</td>
<td>n.d.</td>
<td>81</td>
</tr>
</tbody>
</table>
Table 3 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polynuclear Hydrocarbon Derivatives</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Aminofluorenone</td>
<td>98.5</td>
<td>67(^a)</td>
<td>79</td>
</tr>
<tr>
<td>1-Aminofluorenone</td>
<td>100</td>
<td>78.5</td>
<td>79</td>
</tr>
<tr>
<td>2-NN-Dimethylamino-1-fluorenamine</td>
<td>80</td>
<td>31(^a)</td>
<td>79</td>
</tr>
<tr>
<td>1-Aminoanthraquinone</td>
<td>87.5</td>
<td>n.d.</td>
<td>82</td>
</tr>
<tr>
<td><strong>Heterocyclic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfathiazole</td>
<td>76</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>5-((p-Aminophenyl)thiazole</td>
<td>90</td>
<td>13</td>
<td>68</td>
</tr>
<tr>
<td>5(6) Aminobenzimidazole</td>
<td>86</td>
<td>38</td>
<td>83</td>
</tr>
<tr>
<td>4(7) Aminobenzimidazole</td>
<td>61</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>2-Aminoquinoline</td>
<td>n.i.</td>
<td>28(^a)</td>
<td>84</td>
</tr>
<tr>
<td>3-Aminoquinoline</td>
<td>80</td>
<td>91.5</td>
<td>84</td>
</tr>
<tr>
<td>4-Aminoquinoline</td>
<td>—</td>
<td>—</td>
<td>84</td>
</tr>
<tr>
<td>5-Aminoquinoline</td>
<td>94</td>
<td>59</td>
<td>84</td>
</tr>
</tbody>
</table>
Table 3 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-Aminoquinoline</td>
<td>95.5</td>
<td>60</td>
<td>84</td>
</tr>
<tr>
<td>7-Aminoquinoline</td>
<td>100</td>
<td>$27^a$</td>
<td>84</td>
</tr>
<tr>
<td>8-Aminoquinoline</td>
<td>74</td>
<td>33</td>
<td>84</td>
</tr>
<tr>
<td>1-Aminoisoquinoline</td>
<td>—</td>
<td>$15^a$</td>
<td>84</td>
</tr>
<tr>
<td>3-Aminoisoquinoline</td>
<td>—</td>
<td>$49^a$</td>
<td>85</td>
</tr>
<tr>
<td>4-Aminoisoquinoline</td>
<td>—</td>
<td>$36^a$</td>
<td>85</td>
</tr>
<tr>
<td>5-Aminoisoquinoline</td>
<td>—</td>
<td>$67^a$</td>
<td>86</td>
</tr>
<tr>
<td>2-Amino-4-methylthiazole</td>
<td>—</td>
<td>$5^a$</td>
<td>86</td>
</tr>
</tbody>
</table>

Compounds with more than one Amino Group

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of ArF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Phenylenediamine</td>
<td>95,80</td>
<td>—</td>
<td>69,64</td>
</tr>
<tr>
<td>m-Phenylenediamine</td>
<td>96,54</td>
<td>—</td>
<td>69,50</td>
</tr>
<tr>
<td>2-Amino-sym-diphenylethane</td>
<td>50</td>
<td>n.d.</td>
<td>57</td>
</tr>
<tr>
<td>$(4-H_2NC_6H_4)_2$CMeAc</td>
<td>76</td>
<td>$27^a$</td>
<td>87</td>
</tr>
<tr>
<td>$(p-H_2NC_6H_4)_2$CH_2</td>
<td>—</td>
<td>—</td>
<td>50</td>
</tr>
</tbody>
</table>
## Table 3 (contd.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Yield of $\text{ArN}_2\text{BF}_4$</th>
<th>Yield of $\text{ArF}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Miscellaneous Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Chemical Structure Image]</td>
<td>---</td>
<td>50(^b)</td>
<td>88</td>
</tr>
<tr>
<td>p-Sulfonamidoaniline</td>
<td>7(^a)</td>
<td>n.d.</td>
<td>89</td>
</tr>
<tr>
<td>3-(p-Aminophenyl)-DL-alanine</td>
<td>73</td>
<td>n.d.</td>
<td>90</td>
</tr>
<tr>
<td>3-(m-Aminophenyl)-DL-alanine</td>
<td>81</td>
<td>n.d.</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\) Overall yield from the amine

\(^b\) Yield after hydrolysis of ester and decarboxylation to p-fluoro-\(\beta\)-alanine

n.i. - not isolated

n.d. - not decomposed by Schiemann Method
References For Table 3


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2. The Replacement of an Aromatic Amino Group with a Hydrogen Atom.

Several methods are known for the replacement of a primary aromatic amino group with a hydrogen atom by reduction of its intermediate diazonium compound. The more generally used of these procedures involve the use of ethanol, hypophosphorous acid, or alkaline formaldehyde as the reducing agents. Sodium stannite, stannous chloride and sodium sulfite have also been used but only in a limited number of cases. The ethanol procedure involves diazotization of the amine most commonly in sulfuric acid and the addition of the diazonium sulfate to hot ethanol. As an alternative the diazotization may be carried out in ethanol and the reaction mixture held at reflux temperature until no more gas is evolved. The isolation of the product is determined by its own properties and hence depends on the specific compound involved. In the hypophosphorous acid method the amine is diazotized in a cold solution of hydrochloric acid. A large excess of a cold solution of

93 J. Mai, Ber., 35, 163 (1902).
95 P. Friedlander, Ber., 22, 587 (1889).
96 A. Haller, Ber., 18, 90 (1885).
hypophosphorous acid is added with stirring to the diazo- 
nium chloride. The cold mixture is stirred for an addi- 
tional hour and finally placed in a refrigerator for 24 hours. 
The product is then isolated in a suitable manner. The 
alkaline formaldehyde procedure also involves the decomp- 
osition of a diazoniunm chloride. Here the solution of the 
diazonium chloride is poured into an aqueous solution of 
formalin and sodium hydroxide. Nitrogen is evolved and the 
product separated according to its own nature. These pro- 
cedures are discussed in more detail by Kornblum98 in Organic 
Reactions.

Several modifications of these standard methods have 
been developed which give increased yields of the reduced 
product. Roe and Graham99 obtained better results with the 
ethanol deamination procedure through the use of diazoniunm 
fluoborates rather than the usual chlorides or sulfates and 
by carrying out the reduction in the presence of zinc. This 
procedure was much more successful than the usual ethanolic 
deamination method in the preparation of benzene from anil- 
line and toluene from any one of the three isomeric methyl- 
anilines. A yield of 46.5% of benzene was obtained from 
benzenediazonium fluoborate and toluene was prepared in 
yields of 82.2, 73.7, and 84.8% from the diazoniunm fluobor- 

98 W. Kornblum, in Organic Reactions, (New York, 1944), 

(1952).
ates derived from ortho, meta, and para-toluidine, respectively. These results are in contrast to a yield of only 5% in the preparation of benzene from aniline by the usual procedure. In the deamination of the diazonium salts derived from ortho, meta, and para-toluidine via the ethanol method ether formation, which is always a problem in this procedure becomes predominant and only the corresponding methylphenetoles are isolated. The modified ethanol deamination method has also been extended to the reduction of some heterocyclic amines. For example, the above authors have obtained quinoline in 34% yield by the reduction of quinoline-6-diazenium fluoborate and pyridine in 26.3% yield from the reduction of pyridine-3-diazenium fluoborate.

An interesting modification of the hypophosphorous acid-cuprous oxide deamination procedure enabled Finger and White\textsuperscript{100} to reduce a nitro substituent to an amino group while reduction of the diazo group was carried out. Usually in hypophosphorous acid-cuprous oxide reductions of diazonium salts the cuprous oxide is thought of as a catalyst and hence a small and arbitrary quantity is added to the reaction mixture. The above authors, however, discovered that a nitro group could be simultaneously reduced during hypophosphorous acid deaminations if a three fold excess of cuprous oxide was used and if the reaction mixture was heated at 90-100° on a steam bath for four hours. Through the

use of this method they were able to prepare 3, 5-difluoro-
4-chloroaniline from 4, 6-difluoro-5-chloro-2-nitroaniline.
Similarly 4-fluoroaniline and 3, 5-dichloroaniline were
prepared from the corresponding nitroamines in yields of
55 and 59%, respectively.

Kornblum and Iffland have shown that it is possible
to reduce an aromatic amino group in the presence of an
aliphatic amino group by conducting the diazotization at a
pH less than three. These authors used hypophosphorous
acid both to set the proper pH for the diazotization and to
reduce the diazonium salts obtained. The overall reaction
scheme is shown in Figure 3. The selective deamination of

\[
\begin{align*}
\text{CH}_2\text{NH}_2 & \quad \text{H}^+\text{N} \equiv \text{NO}_2 \
\text{NH}_2 & \quad \text{pH} < 3
\end{align*}
\]

![Fig. 3. The selective deamination of an aromatic amino group.](image)

m-aminobenzylamine, p-aminobenzylamine, 2-(o-aminophenyl)ethylamine, 2-(m-aminophenyl)ethylamine, and 2-(p-aminophenyl)ethylamine gave the corresponding aliphatic monoa-
mines in yields of 87, 84, 52, 70, and 71%, respectively.

Several other diamines were treated in the same manner and in all cases the aromatic amino group was replaced by a hydrogen atom and a good yield of the aliphatic amine was obtained. Hughes, Ingold, and Ridd\textsuperscript{102} have shown in a series of papers that diazotization takes place by attack of the nitrosating agent on the free amino group and not on the protonated form of the amine. This fact offers an explanation for the observation that an aromatic amino group may be diazotized without affecting an aliphatic amino group since it would be expected that the aliphatic group would be protonated more readily than the aromatic group. Indeed Gillis\textsuperscript{103} calculated the relative amounts of each of the three species derived from p-aminobenzylamine that would be present at various pH values based on the assumption that the dissociation constant for the aliphatic amino group is of the same order of magnitude as that of benzylamine and that the dissociation constant for the aromatic amino group is of the same order of magnitude as that of p-toluidine. These calculations (see Figure 4) show that no appreciable proportion of free aliphatic amino groups is present at a pH less than three. Since there is such a small proportion of free aliphatic group present it cannot be diazotized while at the same pH the aromatic amino group remains to a great extent in the free form and hence is

\textsuperscript{102} E.D. Hughes, C.K. Ingold, and J.H. Ridd, \textit{J. Chem. Soc.}, 58 (1958) and following papers.


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Fig. 4. The relative amounts of each protonated form of p-aminobenzylamine at various pH levels.

Several methods have been reported for the reduction of diazonium salts in non-aqueous media. The first of these was reported in a German Patent by Zerweek, Schubert, and Fleischhauer.\textsuperscript{104} They found that the diazotization of aromatic amines with N oxides, nitrosyl chloride, or butyl nitrite in the presence of a salt, ester, or amide of formic acid led to replacement of the diazo group by a hydrogen atom. Thus, diazotization of 2,5-dichloroaniline with butyl nitrite in dimethylformamide produced p-dichlorobenzene.

Another non-aqueous reduction of aromatic amines was

recently reported by Hendrickson. His method involves the diazotization of the amine and the formation of the diazonium fluoborate. The diazonium fluoborate is then isolated and dried prior to its reduction with sodium borohydride in either cold tetrahydrofuran or methanol. The method appears to be simple to carry out and good yields of reduced product were obtained in the examples he reported. Nitro and carboxylic acid substituents were not simultaneously reduced by the sodium borohydride and therefore the method appears to have many advantages. However, only a very few examples were given and further work will be required before the actual scope and limitations of this reaction are known.

Meerwein has reported the use of dioxane, dioxolane, diglyme, and tetrahydrofuran as hydride transfer agents in the reduction of aryl diazonium chlorides. The yield of reduction product in each case with the limited number of examples chosen was good. The authors' attempts to reduce diazonium fluoborates in tertiary amines apparently did not show promise even though p-chlorobenzenediazonium fluoborate and 2,4,6-trichlorobenzenediazonium fluoborate gave yields of 45% and 65%, respectively, of reduction product. In


more recent work on diazonium fluoborates Meerwein\textsuperscript{107} has shown that 4-trimethylammonium-2,6-dichlorobenzenediazonium chloride fluoborate, which is formed by the reaction of trimethylamine with 2,4,6-trichlorobenzenediazonium fluoborate in acetonitrile (see Figure 5) may be reduced to 1,3,5-trichlorobenzene by the action of 1,3 dioxolane.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{N=N} & \quad \text{BF}_4^- \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\quad + \quad (\text{CH}_3)_3\text{N}
\xrightarrow{\text{CH}_3\text{CN}}
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{C} & \quad \text{H}_3\text{N}-\text{C} & \quad \text{H}_3 \\
\text{C} & \quad \text{Cl} \\
\text{N=N}
\end{align*}
\quad \text{BF}_4^-
\]

**Fig. 5.** The preparation of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate chloride.

Since Meerwein was primarily interested in the mechanism of ionic hydrogenation and dehydrogenation and in ionic transfer mechanisms he has done little work to extend this method as a general reaction. However, from the limited number of compounds with which he has worked it appears as though the reaction has good possibilities as a general deamination procedure.

CHAPTER II

DISCUSSION OF EXPERIMENTAL RESULTS

1. The Preparation of Arylfluorides.

The literature of Organic Chemistry contains a great number of references with respect to the study of reactions and their use. A modification or an innovation which can broaden the scope of an organic reaction is of fundamental significance since the route to new compounds which might have biological or industrial importance may be realized as a result. Workers are continually trying to find new reactions and to improve existing ones. In this latter respect the Schiemann Reaction is no exception. Indeed, interest in the past fifteen years in fluorine containing compounds in general has been manifested in the literature by the appearance of several papers dealing with the uses and modifications of this useful reaction.

Our interest in the Schiemann Reaction stemmed from the observation that of several cases reported in the literature the yields of the Schiemann Reaction are low because of the relatively high solubility of some diazonium fluoborates. This is particularly glaring with aromatic amino acids. Thus the yield of diazonium fluoborate obtained from ortho and para-aminobenzoic acids are 0-46 and 76-84%,
respectively.\textsuperscript{1} It is reasonable to expect that a method which results in the precipitation of a larger amount of some intermediate diazonium salt will give greater yields overall of the fluoroaromatic if the decomposition of the salt proceeds as well as it does in the normal Schiemann Reaction. Accordingly, the possibility of using hexafluorophosphoric acid instead of fluoboric acid to precipitate the diazonium salts for use in the preparation of arylfluorides was investigated. The overall reaction sequence is shown in Figure 6.

\[
\begin{align*}
\text{C}_{6} \text{H}_{5} & \equiv \text{N} \text{PF}_{6}^{-} \xrightarrow{\Delta} \text{C}_{6} \text{H}_{6}^{-} \text{F} + \text{N}_{2} + \text{PF}_{5}
\end{align*}
\]

Fig. 6. The preparation of arylfluorides via the diazonium hexafluorophosphate method.

It was expected that diazonium hexafluorophosphates should be less soluble in aqueous solutions than the corresponding fluoborates because of their larger size. It has been shown that the larger the anion in the diazonium salt the more insoluble the salt will be if other factors

are approximately equal. In addition to the increased yields of intermediate salt that would be expected by the use of the hexafluorophosphate anion one would also expect that its thermal decomposition would give greater yields than with the diazonium fluoborate. Thermal decomposition of aryldiazonium hexafluorophosphates yields phosphorous pentafluoride which is a weaker Lewis acid than the boron trifluoride that is produced in the normal Schiemann Reaction. Therefore the use of the hexafluorophosphate salt should minimize any undesirable side reactions and lead to a greater yield of arylfluoride.

The first report of the preparation and decomposition of aryldiazonium hexafluorophosphates in the literature is that of Lange and Mueller in 1930. They obtained a low yield of 4,4'-difluorobiphenyl and an unstated yield of fluorobenzene via the thermal decomposition of the corresponding diazonium hexafluorophosphates. This reaction was given no further consideration in the literature until the report by Newman and Galt of the conversion of 6-bromo-2-naphthylamine and 1-bromo-3-naphthylamine to the fluoroanalogs via the diazonium hexafluorophosphate method.

In general, the hexafluorophosphate method is a con-


3 W. Lange and E. Mueller, Ber., 63, 1058 (1930).

venient procedure for the preparation of arylfluorides. A polypropylene (Nalgene) graduated cylinder was used to measure the hexafluorophosphoric acid solution and rubber gloves were used to protect the hands but it was not found necessary to use copper or monel ware for either the preparation or decomposition of the diazonium hexafluorophosphates. Since the aqueous solution of hexafluorophosphoric acid does contain a small amount of free hydrofluoric acid the glassware used for the preparation and decomposition of the diazonium hexafluorophosphates did become etched. However, a large number of preparations could be carried out in the same equipment before the glass was seriously weakened by etching. Contamination of the diazonium salt by dissolved silicates from the glassware does not appear to have any appreciable effect on the yield of arylfluoride produced during the decomposition. The only equipment beyond the usual laboratory glassware that is required for the reaction is an efficient fume hood which is capable of removing the large volume of phosphorous pentafluoride that is produced during the decomposition of the diazonium salt. The simplicity of the equipment that is required for this reaction is in marked contrast to that required for the use of anhydrous hydrofluoric acid in the diazonium fluoride method.

In contrast to most other diazonium salts none of the diazonium hexafluorophosphates that were prepared in this laboratory showed any evidence of explosion hazard. M. Paul-
schock and B.C. McKusick, the checkers on a submission to *Organic Synthesis* for the preparation of 1-bromo-2-fluoro-5 benzene examined o-bromobenzenediazonium hexafluorophosphate in laboratories of the Dupont Co. Explosives Department. They found it to be sensitive to neither shock nor static electricity and to decompose rapidly but not detonate when heated to 250°. Thus these salts may be handled readily with no danger. However, they should be isolated from heat, particularly when in closed containers, since slow decomposition liberates nitrogen and phosphorous pentafluoride which build up a considerable pressure and could conceivably fracture a container. In addition open samples should probably be kept in a fume hood in order to avoid contamination of the laboratory with small quantities of phosphorous pentafluoride gas from the slow decomposition of the salt even at room temperature.

It has been found that in almost all cases the yield of aryldiazonium hexafluorophosphate by our method was quantitative or very nearly so. With the exception of p-carboxybenzenediazonium hexafluorophosphate all the salts could be liberally washed with cold water without any appreciable loss. Hence any coprecipitated sodium chloride could be removed from the diazonium compound before thermal decomposition. Any organic impurities were removed by washing with a solution of eighty parts ether and twenty

parts methanol. In addition to the removal of organic impurities this washing also facilitated drying of the salt.

In general the decomposition points of the diazonium hexafluorophosphates investigated were sharp and were slightly higher than those reported for the diazonium fluoroborates. A comparison of the decomposition points of the corresponding diazonium salts can be seen in Table 4.

In most cases the thermal decomposition of the aryl-diazonium hexafluorophosphates was smooth and easily controlled. However, a more violent reaction was noted when o-nitrobenzenediazonium hexafluorophosphate was heated and considerable charring of the reaction mixture occurred. This is also noted in the decomposition of the corresponding fluoroborate and in both cases the yield of o-fluoronitrobenzene is low.

It is generally preferable to decompose the diazonium hexafluorophosphate in a diluent such as mineral oil in those cases in which the arylfluoride can be readily isolated by distillation with steam. This technique gives better control over the temperature of the decomposition than does the application of direct heat to the salt in the absence of a diluent. Slightly improved yields were also obtained when the decomposition of the diazonium hexafluorophosphate was effected at the greatest possible rate. Care must be exercised, however, that the reaction does not become too violent under these conditions.

Some increase in yield of arylfluoride was noted in
nearly every case through the substitution of hexafluoro-
phosphoric acid for fluoboric acid in the Schiemann Reaction. 
Although in some cases no appreciable advantage in the use of 
the hexafluorophosphate salt was noted, several amines were 
converted in greatly increased yields to their fluoro ana-
logs. Outstanding in this respect are the increased yields 
of o-fluorobenzoic acid, p-fluorobenzoic acid, o-fluoro-
bromobenzene, p-fluoroanisole, and p-fluorophenol. Increa-
ses in yields of the above compounds were 52, 49, 35, 27, 
23, and about 15% respectively. A comparison of the yields 
obtained by the two methods can be seen in Table 4.
### Table 4

Hexafluorophosphoric Acid versus Fluoboric Acid in the Schiemann Reaction

<table>
<thead>
<tr>
<th>Aromatic Amine</th>
<th>Fluoboric Acid Method</th>
<th>Hexafluorophosphoric Acid Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Yield of $\text{ArN}_2\text{BF}_4$</td>
<td>Decomp. Temp.</td>
</tr>
<tr>
<td>o-Aminobenzoic acid</td>
<td>0.46</td>
<td>125</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>76-84</td>
<td>-</td>
</tr>
<tr>
<td>o-Bromoaniline</td>
<td>50</td>
<td>156</td>
</tr>
<tr>
<td>p-Bromoaniline</td>
<td>64</td>
<td>133</td>
</tr>
<tr>
<td>p-Aminophenol</td>
<td>Failed</td>
<td>-</td>
</tr>
<tr>
<td>p-Chloroaniline</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>o-Aminoanisole</td>
<td>52-91</td>
<td>125</td>
</tr>
<tr>
<td>p-Aminoanisole</td>
<td>85</td>
<td>139</td>
</tr>
</tbody>
</table>
Table 4 (contd.)

<table>
<thead>
<tr>
<th>Aromatic Amine</th>
<th>Fluoboric Acid Method</th>
<th>Hexafluorophosphoric Acid Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Yield of ArF</td>
<td>Decompos. Temp.</td>
</tr>
<tr>
<td></td>
<td>ArN₂BF₄</td>
<td></td>
</tr>
<tr>
<td>o-Nitroaniline</td>
<td>63-92</td>
<td>133</td>
</tr>
<tr>
<td>m-Nitroaniline</td>
<td>79-99</td>
<td>170-178</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>80-100</td>
<td>156</td>
</tr>
<tr>
<td>o-Aminotoluene</td>
<td>59-90</td>
<td>106</td>
</tr>
<tr>
<td>m-Aminotoluene</td>
<td>79-90</td>
<td>108</td>
</tr>
<tr>
<td>p-Aminotoluene</td>
<td>67-90</td>
<td>110</td>
</tr>
<tr>
<td>2-Aminopyridine</td>
<td>Not isolated</td>
<td>0</td>
</tr>
</tbody>
</table>

a Data from A. Roe, loc. cit.

b Numbers in parentheses represent over-all yields.
2. The Reduction of Diazonium Hexafluorophosphates in Tetramethylurea.

A diazonium fluoborate which reacts too violently when heated by itself may decompose quite smoothly in the presence of a diluent. Hence, improved yields of fluoroaromatic are often obtained via the Schiemann Reaction when the intermediate salt is thermally decomposed in a diluent. Accordingly, heavy mineral oil and xylene were tried for this purpose in an attempt to increase the yields obtained via the hexafluorophosphate method. However, it was considered likely that decomposition would occur at a lower temperature and would be even more readily controlled if a suitable solvent could be found for these salts. Attempts to use tetrahydrofuran and dimethylformamide as media for the decomposition met with little success. In an effort to find a better solvent the diazonium hexafluorophosphate derived from anthranilic acid was added to tetramethylurea. Immediate evolution of a gas was noted and the temperature of the reaction mixture rose. After the evolution of nitrogen had ceased the reaction mixture was poured over an ice-hydrochloric acid mixture and a red precipitate formed. Treatment with Norit and recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave a colourless precipitate which on further examination proved to be benzoic acid. Thus the diazonium salt was reduced and little or no o-fluorobenzoic acid was formed. A yield of 80-85% of reduced product was obtained in several runs.
in marked contrast to the yields obtained by reductions with ethanol (ethyl benzoate, 53%) and with alkaline formaldehyde (benzoic acid, 25%). Because of the greatly increased yield of benzoic acid that was obtained by this procedure several other diazonium hexafluorophosphates were similarly treated in an effort to ascertain the scope of the reaction.

All of the aryldiazonium hexafluorophosphates conveniently decomposed spontaneously and exothermally in tetramethylurea. Decomposition was slow with some of the salts unless the reaction mixture was warmed to about 50° at which temperature a much more rapid evolution of nitrogen began.

Reduction of diazonium hexafluorophosphates with tetramethylurea shows many points in common with reductions of diazonium salts with ethanol. In both cases very good yields of reduction product are obtained when electron withdrawing groups are present on the aromatic nucleus. Poor yields of reduction product are obtained by both methods when they are applied to the reduction of diazonium salts derived from amines which contain electron donating groups. In these cases the hypophosphorous acid and alkaline formaldehyde procedures show a distinct advantage over the other methods. In fact, the hypophosphorous acid method appears to be the most widely applicable of these methods and to be quite independent of other substituents on the aromatic nucleus of the parent amine. A comparison of the tetramethylurea method with the more commonly used deamination
procedures can be seen in Table 5.

The mechanism of reduction by tetramethylurea is still a matter of speculation. It could quite easily be either a free radical or an ionic reaction. However, an ionic reaction pathway appears more likely in view of the work of Meerwein and DeTar. Meerwein has obtained very good evidence of hydride transfer in the reaction of 2,4,6-trichlorobenzenediazonium fluoborate with 2-phenyl-1,3-dioxolane to give a 55% yield of trichlorobenzene and an 80% yield of 2-phenyl-1,3-dioxolenium fluoborate.

![Chemical structure](image)

Fig. 7. The reaction of 2,4,6-trichlorobenzenediazonium fluoborate with 2-phenyl-1,3-dioxolane.


Table 5
Comparison of Yield of Reduction Product via Common Procedures

<table>
<thead>
<tr>
<th>Amine</th>
<th>Ethanol</th>
<th>Hypophosphorous Acid</th>
<th>Alkaline Formaldehyde</th>
<th>Tetramethylurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>5</td>
<td>60</td>
<td>60</td>
<td>25-30</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>o-Methylphenetole, ca. 50</td>
<td>70-75</td>
<td>80</td>
<td>25-30</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>o-Methylphenetole, ca. 50</td>
<td>77-83</td>
<td>80</td>
<td>25-30</td>
</tr>
<tr>
<td>o-Anisidine</td>
<td>Amount unstated</td>
<td></td>
<td>75</td>
<td>33</td>
</tr>
<tr>
<td>Anthranilic acid</td>
<td>Ethyl benzoate, 53</td>
<td></td>
<td>25</td>
<td>80-85</td>
</tr>
<tr>
<td>p-Aminobenzoic acid</td>
<td>p-Ethoxybenzoic acid, 50 + ethyl benzoate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Nitroaniline</td>
<td>82</td>
<td>75-80</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>70</td>
<td>55-60</td>
<td>10</td>
<td>62</td>
</tr>
<tr>
<td>p-Chloroaniline</td>
<td>87</td>
<td>50</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>o-Bromoaniline</td>
<td>72-80</td>
<td></td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>p-Bromoaniline</td>
<td>68-80</td>
<td></td>
<td></td>
<td>72</td>
</tr>
<tr>
<td>p-Aminoacetophenone</td>
<td></td>
<td></td>
<td></td>
<td>43</td>
</tr>
</tbody>
</table>

a Unless otherwise specified, the amino group has been replaced by hydrogen.

b Data taken from Nathan Kornblum, Org. Reactions, 2, 262 (1944)
More recently Meerwein has reported the reaction of triphenylmethyl fluoborate with various 1,3-dioxolanes to produce triphenylmethane and 1,3-dioxolenium fluoborate in good yields. These reactions would almost certainly be ionic in mechanism and because of their similarity to the reduction of the diazonium fluoborate may be taken as supporting evidence for the hydride transfer mechanism.

Finally he has reported that the reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate, chloride with 1,3-dioxolane gave a yield of 82% of 1,3,5-trichlorobenzene. On the other hand if the reduction was carried out with 2-methyl-1,3-dioxolane in the presence of copper bronze a mixture which consisted mainly of trimethyl-3,5-dichlorophenylammonium fluoborate was obtained. The 2-methyl-1,3-dioxolane was converted to 2-chloroethyl acetate in this reaction. It is apparent from this reaction that if conditions are set to favour a free radical mechanism over an ionic one products which differ from those formed in the normal reduction reaction are isolated. The following reaction sequences were given by Meerwein to explain how the products were obtained.


Fig. 8. The reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate chloride with substituted dioxolanes.
In the above reaction sequence an ionic mechanism is in force. Both a hydride ion and a proton are lost from the substituted 1,3-dioxolane in order to reduce the diazo-compound and form trichlorobenzene.

When copper bronze is added to the reaction in order to encourage free radical reduction the following sequence occurs.
Fig. 9. The free radical reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate chloride.

All of this work by Meerwein points very strongly to a hydride transfer mechanism for the reduction of diazonium fluoborates with 1,3-dioxolanes. DeTar has given strong evidence for a hydride transfer mechanism in ethanolic deaminations. Inductive effects noted in tetramethylurea deaminations closely parallel those of the ethanolic reaction. This tends to indicate that a similar mechanism might be operative.

In tetramethylurea deaminations the aryldiazonium hexafluorophosphate presumably breaks down ionically into an aryl cation, nitrogen, and hexafluorophosphate anion. The aryl cation, depending on its reactivity, can either abstract hydride from the solvent (Fig. 10), couple with it to form a salt (Fig. 11), or react with hexafluorophosphate anion to yield the fluoroaromatic and phosphorous pentafluoride (Fig. 12). If the aryl cation abstracts hydride from the solvent as in Figure 10 the solvent ion formed
Ar$^+$ + \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\] \rightarrow \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\] + \[
\begin{array}{c}
\text{H}_2\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\] + \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\]

a) PF$_6^-$ \quad b) PF$_6^-$

PF$_5$ + \[
\begin{array}{c}
\text{F} \\
\text{H}_2\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{H}_3
\end{array}
\] \rightarrow \[
\begin{array}{c}
\text{F} \\
\text{H}_2\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\] + \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\]

Fig. 10. The aryl cation abstracts a hydride ion from the solvent.

PF$_5$ + \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{H}_3
\end{array}
\] \rightarrow \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{H}_3
\end{array}
\] + \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{H}_3
\end{array}
\]

Fig. 11. The aryl cation forms a salt with the solvent.
\[ \text{Ar}^+ + \text{PF}_6^- \rightarrow \text{ArF} + \text{PF}_5 \]

Fig. 12. The aryl cation reacts with hexafluorophosphate anion.

\[
\begin{align*}
\text{CH}_3^+ &-\text{N}-\text{CH}_3 \quad \text{Cl}^- \\
\text{CH}_3\text{N}=\text{N} \quad \text{BF}_4^- \\
\text{CH}_3^+ &-\text{N}-\text{CH}_3
\end{align*}
\]

Fig. 13. The reduction of 4-trimethylammonium-2,6-dichlorobenzenediazonium fluoborate chloride with trimethylamine.

may then further react either with hexafluorophosphate anion to form phosphorous pentafluoride and a fluorinated solvent molecule (Fig. 10a) or it may form a salt (Fig. 10b). The formation of a salt seems more likely since no evidence
for the evolution of phosphorous pentafluoride gas in anything but trace amounts during the reaction was obtained and because of the similarity of this pathway to that shown by Meerwein\textsuperscript{10} in the decomposition of 4-trimethylammonium-3,5-dichlorobenzenediazonium fluoborate chloride in trimethylamine. This reaction is shown in Figure 13.

With highly reactive aryl cations, the activation energy for hydride transfer would be met more readily and the resultant urea carbonium ion could conceivably then react further according to either equation shown in Figure 10\textsuperscript{a} or b. However, no direct evidence has been obtained in this laboratory for either course. No attempt was made to isolate and characterize the products that would be obtained from either pathway even though this would give a strong indication of the reaction mechanism. The less reactive cations would not be sufficiently energetic for predominant hydride transfer and competing reactions seen in Figures 11 and 12 become more likely. No evidence for reaction as in Figure 12 has been obtained in this laboratory although it is quite possible that small quantities of the fluoroaromatic may be formed in this reaction. DeTar\textsuperscript{11} found that small amounts of fluoroaromatic were obtained in the decomposition of diazonium fluoborates in methanol but no attempt was made to show if some were formed by the decomposition

\textsuperscript{10} H. Meerwein, K. Wunderlich, and K. F. Zenner, \textit{op. cit.}

\textsuperscript{11} D.F. DeTar and T. Kosuge, \textit{op. cit.}
of diazonium hexafluorophosphates in tetramethylurea. Again this reaction could not have occurred to any large extent as no evidence of a substantial evolution of phosphorous pentafluoride was obtained.

Evidence for reaction as in Figure 11, however, is concrete in the decomposition of o-toluenediazonium hexafluorophosphate. Decomposition of this diazonium salt in tetramethylurea gave a 61% yield of o-methylphenoxytetramethylamidinium hexafluorophosphate. The structure of this salt (Fig. 14) was proved by elemental analysis and vigorous base hydrolysis to o-cresol and dimethylamine. The hexa-

![Fig. 14. o-Methylphenoxytetramethylamidinium hexafluorophosphate.](image)

fluorophosphate anion was determined quantitatively by tetraphenylarsonium chloride reagent.

The presence of hexafluorophosphate anion in this salt renders a free radical reaction highly unlikely. A free radical breakdown of the aryldiazenium hexafluorophosphate would occur according to the equation shown in Figure 15.

To explain the evolution of nitrogen (97% of the theoretical
amount) one must envisage at least in part an electron transfer from the hexafluorophosphate anion to the positively charged nitrogen species. This would leave phosphorous pentafluoride and a fluorine atom. Regardless of the fate of the fluorine atom, reformation of the hexafluorophosphate anion would be highly unlikely. Again, an electron transfer from the solvent to the positively charged nitrogen species would render the solvent positively charged. This charged species would have a stronger tendency to react with the hexafluorophosphate anion than with the aromatic free radical. Again this would produce phosphorous pentafluoride or the hexafluorophosphate salt with the solvent.

\[ \text{ArN}_2\text{PF}_6 \rightarrow \text{Ar}^+ + :\text{N} = \text{N}^+ + \text{PF}_6^- \]

Fig. 15. Free radical breakdown of aryldiazonium hexafluorophosphates.

Similar salts as well as reduction product have been isolated from the decomposition of the diazonium hexafluorophosphate salts derived from p-nitroaniline, aniline, and p-toluidine. It is interesting to note that Meerwein\(^\text{12}\) decomposed the diazonium fluoborates derived from p-nitroaniline and p-chloroaniline in tetramethylthiourea. No reduc-

-tion product was reported - instead there were obtained in high yields tetramethylthiocuronium fluoborate salts of the following structure.

\[
\begin{align*}
X = \text{NO}_2, \text{Cl} \\
\text{Fig. 16. Tetramethylthiocuronium fluoborates.}
\end{align*}
\]

Evidently the much higher nucleophilic property of the sulfur atom over oxygen as well as its greater size makes it more susceptible to attack by the aryl cation and hence a reaction analogous to the equation shown in Figure 11 is predominant.
CHAPTER III

EXPERIMENTAL

1. The Preparation of Aryldiazonium Hexafluorophosphates.

In all cases diazotization was carried out in the usual manner. That is, the amine was dissolved in an aqueous solution of hydrochloric acid and diazotization effected in the cold (less than 0\(^\circ\)) by the stepwise addition of an aqueous solution of sodium nitrite. In a few cases it was necessary to heat the amine in the hydrochloric acid solution before it would dissolve. The amine hydrochloride would then reprecipitate on cooling to diazotization temperature but as long as the hydrochloride was initially formed this had no effect on the diazotization reaction.

When an excess of nitrous acid was formed, as shown by a test with potassium iodide-starch test paper, hexafluorophosphoric acid\(^1\) was added to precipitate the diazonium hexafluorophosphate. The precipitate was separated by filtration over suction, air dried for several hours, washed with a solution of 80 parts ether and 20 parts methanol and dried over suction. In some cases the diazonium salt was

1. A 65\% aqueous solution of hexafluorophosphoric acid (sp. gr. 1.8) obtained from Ozark-Mahoning Co. of Tulsa, Oklahoma was used.
further dried overnight in a vacuum desiccator. The product was then weighed and its decomposition temperature was recorded.

The general method is illustrated by the following example for the preparation of o-toluenediazonium hexafluorophosphate. For the remaining compounds only the differences in method from this example along with the quantities of reagents used, yield, decomposition temperature etc. will be given.

**Toluene-2-diazonium Hexafluorophosphate.**—The addition of toluidine (50 g., 0.47 mole) to a solution of concentrated hydrochloric acid (100 ml., 37%) in one liter of water contained in a two-liter, wide-mouthed Erlenmeyer flask resulted in the complete formation of o-toluidine hydrochloride. The contents of the flask were cooled to -5° in an acetone-dry ice bath and diazotization effected by the addition of sodium nitrite (35 g., 0.51 mole) dissolved in 100 ml of water. The addition of the sodium nitrite solution was carried out at such a rate that the temperature of the reaction mixture did not rise above -3°. When all the sodium nitrite had been added, the presence of an excess of nitrous acid was indicated by the formation of an immediate blue colouration when potassium iodide-starch paper was wetted with the solution. While the o-toluenediazonium chloride solution was still cold hexafluorophosphoric acid (110 ml., 0.9 mole) measured in a polypropylene container was added in one portion while the reaction flask was vigorously swirled.
A white precipitate was immediately formed and the temperature of the reaction mixture rose several degrees. The mixture was again cooled to \(-5^\circ\text{C}\), the solid was separated by suction filtration, and washed with 500 ml. of cold water. Most of the water was removed by compacting the filter cake while it was still in the Buchner funnel. (A large ground glass stopper was found to be quite effective for this purpose). The precipitate was air dried for several hours over suction and then washed with a solution which contained 80 parts ether and 20 parts methanol to aid further drying and to effect the removal of organic impurities. After it was air dried over suction for an additional hour the filter cake was powdered and weighed. A yield of 119.3 g. (97\%) was obtained, m.p. 110\(^\circ\text{C}\) dec.

**Toluene-4-diazonium Hexafluorophosphate.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-toluidine</td>
<td>(50 g., 0.47 mole)</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>100 ml.</td>
</tr>
<tr>
<td>water</td>
<td>1000 ml.</td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>35 g., 0.51 mole</td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>120 ml., 0.97 mole</td>
</tr>
<tr>
<td>diazotization temperature</td>
<td>(-5^\circ\text{C})</td>
</tr>
<tr>
<td>yield</td>
<td>119.7 g.</td>
</tr>
<tr>
<td>percent yield</td>
<td>97</td>
</tr>
<tr>
<td>melting point</td>
<td>112(^\circ\text{C}) dec.</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Nitrobenzene-4-diazonium Hexafluorophosphate.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nitroaniline</td>
<td>27.6 g., 0.2 mole</td>
<td></td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>176 ml.</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>300 ml.</td>
<td></td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>15 g., 0.22 mole</td>
<td></td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>45 ml., 0.36 mole</td>
<td></td>
</tr>
<tr>
<td>diazotization temperature</td>
<td>-15°</td>
<td></td>
</tr>
<tr>
<td>yield</td>
<td>55 g.</td>
<td></td>
</tr>
<tr>
<td>percent yield</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>melting point</td>
<td>156° dec.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrobenzene-3-diazonium Hexafluorophosphate.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m-nitroaniline</td>
<td>50 g., 0.36 mole</td>
<td></td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>300 ml.</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>500 ml.</td>
<td></td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>29 g., 0.42 mole</td>
<td></td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>75 ml., 0.61 mole</td>
<td></td>
</tr>
<tr>
<td>diazotization temperature</td>
<td>-10°</td>
<td></td>
</tr>
<tr>
<td>yield</td>
<td>106.9 g.</td>
<td></td>
</tr>
<tr>
<td>percent yield</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>melting point</td>
<td>170-178° dec.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrobenzene-2-diazonium Hexafluorophosphate.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>o-nitroaniline</td>
<td>100 g., 0.72 mole</td>
<td></td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>700 ml.</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>1000 ml.</td>
<td></td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>54 g., 0.78 mole</td>
<td></td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>150 ml., 1.22 mole</td>
<td></td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Diazotization temperature</td>
<td>-20°</td>
<td></td>
</tr>
<tr>
<td>Yield</td>
<td>200 g.</td>
<td></td>
</tr>
<tr>
<td>Percent yield</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>133° dec.</td>
<td></td>
</tr>
</tbody>
</table>

**Bromobenzene-2-diazonium Hexafluorophosphate**

- o-bromoaniline: 60 g., 0.34 mole
- Hydrochloric acid: 95 ml.
- Water: 650 ml.
- Sodium nitrite: 29 g., 0.42 mole
- Hexafluorophosphoric acid: 74 ml., 0.60 mole
- Diazotization temperature: -5°
- Yield: 120 g.
- Percent yield: 100%
- Melting point: 156° dec.

**Bromobenzene-4-diazonium Hexafluorophosphate**

- p-bromoaniline: 60 g., 0.34 mole
- Hydrochloric acid: 95 ml.
- Water: 650 ml.
- Sodium nitrite: 29 g., 0.42 mole
- Hexafluorophosphoric acid: 74 ml., 0.60 mole
- Diazotization temperature: -5°
- Yield: 115.4 g.
- Percent yield: 97%
- Melting point: 143° dec.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Components</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Toluene-3-diazonium Hexafluorophosphate</strong></td>
<td>m-toluidine 50 g., 0.47 mole</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hydrochloric acid 100 ml.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>water 1000 ml.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sodium nitrite 35 g., 0.51 mole</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hexafluorophosphoric acid 120 ml., 0.97 mole</td>
<td></td>
</tr>
<tr>
<td></td>
<td>diazotization temperature -3°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>yield 123 g.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>percent yield 100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>melting point 110° dec</td>
<td></td>
</tr>
</tbody>
</table>

| **Chlorobenzene-4-diazonium Hexafluorophosphate** | p-chloroaniline 45 g., 0.35 mole |                          |
|                                                    | hydrochloric acid 95 ml.            |                          |
|                                                    | water 650 ml.                       |                          |
|                                                    | sodium nitrite 29 g., 0.42 mole     |                          |
|                                                    | hexafluorophosphoric acid 74 ml., 0.60 mole |                |
|                                                    | diazotization temperature -5°       |                          |
|                                                    | yield 97 g.                         |                          |
|                                                    | percent yield 97                    |                          |
|                                                    | melting point 137° dec              |                          |

| **Anisole-2-diazonium Hexafluorophosphate**      | o-anisidine 62 g., 0.50 mole         |                          |
|                                                 | hydrochloric acid 120 ml.            |                          |
|                                                 | water 360 ml.                        |                          |
|                                                 | sodium nitrite 39.6 g., 0.57 mole    |                          |
|                                                 | hexafluorophosphoric acid 75 ml., 0.61 mole |                |
diazotization temperature  $-10^\circ$
yield  140 g.
percent yield  100
melting point  $121^\circ$ dec.

Anisole-4-diazonium Hexafluorophosphate.-

- p- anisidine  60 g., 0.49 mole
- hydrochloric acid  120 ml.
- water  360 ml.
- sodium nitrite  39.6 g., 0.57 mole
- hexafluorophosphoric acid  75 ml.
- diazotization temperature  $-10^\circ$
- yield  136 g.
- percent yield  100
- melting point  $149^\circ$ dec.

Quinoline-8-diazonium Hexafluorophosphate.-

- 8-aminoquinoline  50 g., 0.35 mole
- hydrochloric acid  150 ml.
- water  300 ml.
- sodium nitrite  24 g., 0.35 mole
- hexafluorophosphoric acid  60 ml., 0.49 mole
- diazotization temperature  $-5^\circ$
- yield  102.5 g.
- percent yield  99
- melting point  $144^\circ$ dec.
<table>
<thead>
<tr>
<th>Compound</th>
<th>p-aminophenol</th>
<th>27.3 g., 0.25 mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p-aminophenol</td>
<td>27.3 g., 0.25 mole</td>
</tr>
<tr>
<td></td>
<td>hydrochloric</td>
<td>75 ml.</td>
</tr>
<tr>
<td></td>
<td>acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>150 ml.</td>
</tr>
<tr>
<td></td>
<td>sodium nitrite</td>
<td>19 g., 0.28 mole</td>
</tr>
<tr>
<td></td>
<td>hexafluorophosphoric acid</td>
<td>37.5 ml., 0.30 mole</td>
</tr>
<tr>
<td></td>
<td>diazotization temperature</td>
<td>0°</td>
</tr>
<tr>
<td></td>
<td>yield</td>
<td>45.2 g.</td>
</tr>
<tr>
<td></td>
<td>percent yield</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>melting point</td>
<td>45-46° dec.</td>
</tr>
</tbody>
</table>

**Acetophenone-4-diazonium Hexafluorophosphate.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>p-aminoacetophenone</th>
<th>50 g., 0.37 mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hydrochloric acid</td>
<td>150 ml.</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>350 ml.</td>
</tr>
<tr>
<td></td>
<td>sodium nitrite</td>
<td>25.3 g., 0.37 mole</td>
</tr>
<tr>
<td></td>
<td>hexafluorophosphoric acid</td>
<td>70 ml., 0.57 mole</td>
</tr>
<tr>
<td></td>
<td>diazotization temperature</td>
<td>-10°</td>
</tr>
<tr>
<td></td>
<td>yield</td>
<td>106.4 g.</td>
</tr>
<tr>
<td></td>
<td>percent yield</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>melting point</td>
<td>109° dec.</td>
</tr>
</tbody>
</table>

**Phenol-4-diazonium Hexafluorophosphate.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>o-aminobiphenyl</th>
<th>50 g., 0.30 mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hydrochloric</td>
<td>150 ml.</td>
</tr>
<tr>
<td></td>
<td>acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>700 ml.</td>
</tr>
<tr>
<td></td>
<td>sodium nitrite</td>
<td>23 g., 0.33 mole</td>
</tr>
<tr>
<td></td>
<td>hexafluorophosphoric acid</td>
<td>60 ml., 0.49 mole</td>
</tr>
</tbody>
</table>

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diazotization temperature  -5°
yield  86.8 g.
percent yield  89
melting point  94-95° dec.

Benzoic Acid-2-diazonium Hexafluorophosphate.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthranilic acid</td>
<td>100 g., 0.73 mole</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>72 ml.</td>
</tr>
<tr>
<td>water</td>
<td>500 ml.</td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>60 g., 0.87 mole</td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>240 ml., 1.94 mole</td>
</tr>
<tr>
<td>yield</td>
<td>159 g.</td>
</tr>
<tr>
<td>percent yield</td>
<td>75</td>
</tr>
<tr>
<td>melting point</td>
<td>--</td>
</tr>
</tbody>
</table>

Benzoic Acid-4-diazonium Hexafluorophosphate.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-aminobenzoic acid</td>
<td>20 g., 0.15 mole</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>100 ml.</td>
</tr>
<tr>
<td>water</td>
<td>240 ml.</td>
</tr>
<tr>
<td>sodium nitrite</td>
<td>12 g., 0.18 mole</td>
</tr>
<tr>
<td>hexafluorophosphoric acid</td>
<td>20 ml., 0.16 mole</td>
</tr>
<tr>
<td>yield</td>
<td>33 g.</td>
</tr>
<tr>
<td>percent yield</td>
<td>77</td>
</tr>
<tr>
<td>melting point</td>
<td>128-129° dec.</td>
</tr>
</tbody>
</table>

Pyridine-2-diazonium Hexafluorophosphate. - This diazonium
compound is very unstable and decomposes at a temperature lower than 
-10°. It was not isolated since it decomposed as formed to the corresponding fluoropyridine.

Diazotization was carried out by the portionwise addition of dry sodium nitrite (27 g., 0.39 mole) to 2-aminopyridine (35 g., 0.37 mole) suspended in cold (-5°) hexafluorophosphoric acid (120 ml., 0.97 mole). The reaction mixture solidified during the addition of sodium nitrite hence water (200 ml.) was added so that diazotization could be completed. The diazonium salt decomposed as formed with the evolution of phosphorous pentafluoride gas and no diazonium hexafluorophosphate was isolated. The reaction mixture was then allowed to warm up to room temperature to complete the decomposition of the diazonium salt.

2. The Preparation of Arylfluorides by the Decomposition of Diazonium Hexafluorophosphates.

In all cases except that for the preparation of 2-fluoropyridine, an identical apparatus was used for the decomposition of the aryldiazonium hexafluorophosphates. A one-liter, three-necked, round-bottomed flask was outfitted with a 500-mm. condenser or two 200-mm. condensers in series. A 300-ml. Erlenmeyer flask was attached to the other neck by means of a short length of gooch rubber tubing. A mechanical stirrer could also be inserted into the flask but in most cases no advantage was gained by its use. The apparatus was vented to an efficient fumehood to remove the
large volume of phosphorous pentafluoride that was evolved during the decomposition. In cases in which the fluoro-aromatic that was formed could be conveniently isolated by distillation with steam, heavy mineral oil (Nujol, 200 ml.) was added to the reaction flask and heated in an oil bath to several degrees above the decomposition temperature of the diazonium hexafluorophosphate prior to the addition of the salt. In several cases the salt was decomposed without a diluent. The reaction flask was heated in an oil bath to a few degrees above the decomposition point of the salt and the salt was added in small portions to the hot flask. Whether or not a diluent was used the diazonium salt was placed initially in the Erlenmeyer flask. From this flask it could be easily added in small portions through the connecting tubing to the reaction vessel. The decomposition was carried out at a rate sufficient to evolve phosphorous pentafluoride rapidly yet without explosiveness. This technique resulted in slightly higher yields of the fluoro-aromatic.

When the evolution of phosphorous pentafluoride had ceased the oil bath was removed and the reaction vessel was cooled rapidly with cold water. A five percent solution of sodium carbonate was poured through the condenser in order to wash down any condensed fluoroaromatic and neutralize the acidic reaction mixture.

The product was separated by distillation with steam. The organic layer was separated from the aqueous solution.
by means of a separatory funnel and was dried over anhydrous sodium sulfate. Finally the product was distilled from a Claisen-Vigreux flask and weighed.

The diazonium hexafluorophosphate obtained from anthranillic acid was decomposed in xylene while those from p-aminobenzoic acid and p-aminophenol were decomposed without the use of a solvent medium.

The following detailed description of the decomposition of p-toluenediazonium hexafluorophosphate illustrates the general method used. For all cases in which the general procedure is the same only the pertinent data will be given.

**Preparation of p-Fluorotoluene.** Toluene-4-diazonium hexafluorophosphate (119.6 g., 0.45 mole) was placed in a 300-ml. Erlenmeyer flask which was attached by means of a short length of gooch rubber tubing to a one-liter, three-necked, round-bottomed flask which contained 200 ml. of heavy mineral oil (Nujol). A 500-mm. reflux condenser was fitted to the flask and the third neck stoppered with a glass stopper. The apparatus was set up in an efficient fumehood and gently lowered into an oil bath maintained at 125-130°. After a ten minute wait to allow the mineral oil in the reaction flask to reach the bath temperature the diazonium salt was added in small portions to the reaction flask through the rubber connecting tubing. After the last portion of the salt was added the heating was maintained for an additional five minutes to ensure complete decomposition. The heating
bath was then removed and the reaction vessel cooled in a cold water bath. When the flask had cooled to room temperature a saturated solution of sodium carbonate (400 ml.) was added through the condenser. The condenser and Erlenmeyer flask were removed from the reaction flask and a still head and condenser set for distillation were attached. The product was separated by distillation with steam, separated from the aqueous layer of the distillate by means of a separatory funnel, dried over anhydrous sodium sulfate, and distilled from a Claisen-Vigreux flask. A yield of 36.3 g. (71%) of p-fluorotoluene, b.p. 117°, n_D^26 1.4657, was obtained.

Important data for the preparation of the other fluoro-compounds are given below. In all cases the general method described above was followed.

**o-Fluorotoluene.**—o-Toluenediazonium hexafluorophosphate (119 g., 0.45 mole) was decomposed in mineral oil at 115-120°. The product was separated by distillation with steam, the two layers separated and the organic layer dried over anhydrous sodium sulfate. Distillation from a Claisen-Vigreux flask gave 28.8 g. (58%) of o-fluorotoluene, b.p. 115-117°, n_D^24 1.4728.

**p-Fluoronitrobenzene.**—p-Nitrobenzenediazonium hexafluorophosphate (50 g., 0.17 mole) was decomposed in heavy mineral oil at 170°. The product was isolated by distillation with steam and separation from the aqueous layer. The
organic layer was dried over anhydrous sodium sulfate and
distilled from a Claisen-Vigreux flask. The product (15.1
g., 63%) was collected at 202-204°.

m-Fluoronitrobenzene. m-Nitrobenzenediazonium hexafluoro-
phosphate (50 g., 0.17 mole) was decomposed in heavy min-
eral oil at 190°. The product was isolated by distillation
with steam and separation from the aqueous layer. The
organic layer was dried over anhydrous sodium sulfate and
distilled from a Claisen-Vigreux flask. The product (13.8
g., 57%) was collected at 198-202°.

m-Fluorotoluene. The decomposition of m-toluenediazonium
hexafluorophosphate (123 g., 0.47 mole) was carried out in
heavy mineral oil at 135°. The fluorotoluene produced was
separated by distillation with steam and separation from
the aqueous layer. The organic layer was distilled from a
Claisen-Vigreux flask and the fraction which boiled at 114-
118° collected. This gave a yield of 29.3 g. (58%) of m-
fluorotoluene.

p-Chlorofluorobenzene. p-Chlorobzenediazonium hexafluo-
orophosphate (97 g., 0.34 mole) was decomposed in heavy
mineral oil at 160°. The product was separated by distill-
ation with steam and separation from the aqueous layer.
The organic layer was dried over anhydrous sodium sulfate
and distilled from a Claisen-Vigreux flask. The yield of
p-chlorofluorobenzene was 31.8 g. (69%), b.p. 128-131°,
o-Fluoronitrobenzene.- The decomposition of o-nitrobenzene-
diazonium hexafluorophosphate (95 g., 0.32 mole) was carried
out in heavy mineral oil at 190°. The product was isolated
by distillation with steam and separation from the aqueous
layer. The organic layer was dried over anhydrous sodium
sulfate and distilled from a Claisen-Vigreux flask. The
yield of o-fluoronitrobenzene was 5 g. (ca. 10%), b.p. 210-
216°.

o-Bromofluorobenzene.- o-Bromobenzenediazonium hexafluoro-
phosphate (119 g., 0.41 mole) was decomposed in heavy
mineral oil at 165°. The product was separated by distil-
lation with steam and separation from the aqueous layer.
The organic layer was dried over anhydrous sodium sulfate
and distilled from a Claisen-Vigreux flask. The yield of
o-bromofluorobenzene was 46.1 g. (76%), b.p. 155-158°,
$\text{n}_D^{22} 1.5336$.

p-Bromofluorobenzene.- The decomposition of p-bromobenzene-
diazonium hexafluorophosphate (115 g., 0.40 mole) was
carried out in heavy mineral oil at 160-170°. The product
was isolated by distillation with steam and separation from
the aqueous layer. The organic layer was dried over anhy-
drous sodium sulfate and distilled from a Claisen-Vigreux
flask. The yield of p-bromofluorobenzene was 48 g. (79%),
b.p. 150-153°, $\text{n}_D^{22.5} 1.5283$.
o-Fluoroanisole.- o-Methoxybenzenediazonium hexafluorophosphate (70 g., 0.25 mole) was decomposed in heavy mineral oil at 170-175°. The product was separated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of o-fluoroanisole was 19 g. (61%), b.p. 158-160°, n_D^26 1.4940.

p-Fluoroanisole.- The decomposition of p-methoxybenzenediazonium hexafluorophosphate (84 g., 0.30 mole) was carried out in heavy mineral oil at 170-180°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of p-fluoroanisole was 26.5 g. (70%), b.p. 154-156°, n_D^22 1.4853.

8-Fluoroquinoline.- Quinoline-8-diazonium hexafluorophosphate (102.5 g., 0.34 mole) was decomposed in heavy mineral oil at 165-170°. The product was extracted with a dilute solution of hydrochloric acid, the extract neutralized with sodium carbonate and re-extracted with ether. After the ether solution was dried over anhydrous sodium sulfate the solvent was removed and the product distilled under reduced pressure (30 mm.). The fraction (5.9 g., 11.5%) which boiled at 147-149° was collected, n_D^26 1.5970.

p-Fluoroacetophenone.- The decomposition of p-acetophenone-
diazonium hexafluorophosphate (106 g., 0.36 mole) was carried out in heavy mineral oil at 125°. The product was isolated by distillation with steam and separation from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate and distilled from a Claisen-Vigreux flask. The yield of p-fluoroacetophenone was 5.8 g. (11.5%), b.p. 194-198°, n_D^20 1.5060.

p-Fluorophenol.- p-Hydroxybenzenediazonium hexafluorophosphate (51.4 g., 0.19 mole.) was decomposed without solvent at 120-130°. The dark red tars that were formed were extracted with ether and the ether solution dried over anhydrous sodium sulfate. The ether was removed by evaporation and a rapid distillation carried out in an apparatus which consisted of a distilling flask and a receiving flask connected by a U tube of 15 mm. diameter. The U tube was heated by passing a current, which was controlled by an autotransformer, through nichrome wire wound around the tube. The system was evacuated through a side arm from the U tube to a vacuum pump and the receiving flask was cooled in an ice-water bath. The contents of the distilling flask were heated rapidly with an open flame and the product solidified in the receiving flask. Very crude p-fluorophenol (5.2 g., 18.5%) was collected.

2-Fluorobiphenyl.- The decomposition of biphenyl-2-diazonium hexafluorophosphate (87 g., 0.27 mole) was carried out in heavy mineral oil at 100°. The product was isolated by
distillation with steam and separation from the aqueous layer by filtration. The precipitate was air dried and weighed. A yield of 35 g. (69%) of 2-fluorobiphenyl, m.p. 71°, was obtained.

**o-Fluorobenzoic acid.**- o-Carboxybenzenediazonium hexafluorophosphate (70 g., 0.24 mole) was decomposed in xylene at 135-140°. The product was extracted with a saturated solution of sodium carbonate. After treatment with Norite the solution of sodium carbonate was poured slowly with stirring onto an excess of ice and hydrochloric acid whereupon the o-fluorobenzoic acid precipitated. A crude yield of 26 g. (78%) was obtained, m.p. 110-115°. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair yielded the pure acid, m.p. 124-125° (recorded m.p. 120-122°) neut. equiv., 138.5.

**p-Fluorobenzoic acid.**- p-Carboxybenzenediazonium hexafluorophosphate (33 g., 0.11 mole) was decomposed without solvent at a bath temperature of 145-155°. The product was extracted with a five percent solution of sodium carbonate and re-precipitated when the basic solution was poured slowly onto a mixture of ice and hydrochloric acid. The acid was separated by suction filtration and air dried. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair yielded 10 g. (64%) of p-fluorobenzoic acid, m.p. 180-182°. A slight coloration of the acid was removed by treatment of a chloroform solution with Norite.
3. The Decomposition of Aryldiazonium Hexafluorophosphates in Tetramethylurea.

The dry aryldiazonium hexafluorophosphates prepared as previously described were decomposed by the stepwise addition of 50 g. to a beaker which contained tetramethylurea (200 ml.) at room temperature. Usually a rapid evolution of nitrogen was noted and the temperature of the reaction mixture rose quite rapidly. In cases where the reaction was only moderately exothermic the mixture was warmed to increase the rate of decomposition. The temperature was not allowed to rise above 65° in any of the cases. When all sign of reaction had ceased as evidenced by the lack of nitrogen evolution (about 1 1/2 hours in most cases) the solution was poured into one liter of water. The reduction product was normally recovered by distillation with steam followed by separation from the water layer and distillation.

In the case of the reduction of the aminobenzoic acids the reaction mixture was poured onto a mixture of cracked ice and hydrochloric acid. The benzoic acid which precipitated was then recovered by filtration.

*Benzoic Acid from Anthranilic Acid.* - o-Carboxybenzenediazonium hexafluorophosphate (20 g., 0.068 mole) was decomposed in 50 ml. tetramethylurea. The temperature of the reaction mixture was maintained between fifty and sixty degrees until nitrogen ceased to be evolved. The mixture was then poured onto ice and hydrochloric acid and the precipitate
separated by filtration. After it was dried in a vacuum desiccator a yield of 7.3 g. of crude benzoic acid was obtained. The filtrate from above was neutralized with sodium carbonate, extracted with ether in order to remove excess tetramethylurea and concentrated to a volume of 100 ml. This solution was acidified with hydrochloric acid and cooled in a refrigerator for one-half hour. The crystals which formed were separated by filtration and dried. This treatment yielded an additional gram of benzoic acid. The combined crude yield was 8.3 g. (87%), m.p. 110-118°. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave pure benzoic acid, m.p. 122°. The possibility that this product was actually o-fluorobenzoic acid was eliminated when a mixture melting point with an authentic sample of benzoic acid showed no depression.

Benzoic Acid from p-Aminobenzoic Acid.- p-Carboxybenzenediazonium hexafluorophosphate (20 g., 0.068 mole) was added portionwise to tetramethylurea (80 ml.) in a 150-ml. beaker. No spontaneous decomposition occurred until the temperature of the mixture was raised to 58-60°. The temperature was maintained between 60-70° for three hours until no more nitrogen was evolved. The solution was then poured over one liter of crushed ice which contained 50 ml. of concentrated hydrochloric acid. The yellow crystalline solid which precipitated was separated by filtration and air-dried. A yield of 7.1 g. (86%) of crude benzoic acid
was obtained, m.p. 110-120°. Recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave colourless crystals of benzoic acid, m.p. 119-121°.

Nitrobenzene from o-Aminonitrobenzene.- The diazonium salt hexafluorophosphate (80 g., 0.27 mole) obtained from o-aminonitrobenzene was added portionwise to tetramethylurea (200 ml.). The temperature of the reacting mixture immediately rose but was held at or slightly below 70° by means of an ice bath. When nitrogen ceased to be evolved the reaction mixture was poured over one liter of ice which contained 50 ml. of concentrated hydrochloric acid. The nitrobenzene was separated by distillation with steam. The distillate was extracted three times with 100-ml. portions of ether, the ether solution dried over anhydrous sodium sulfate, and the ether removed by evaporation. The product was distilled from a Claisen-Vigreux flask under reduced pressure and the fraction which boiled at 60-66° at 10 mm. was collected. This gave a very crude product in greater than quantitative yield. Therefore this impure product was redissolved in ether and extracted three times with 50-ml. portions of water to remove any tetramethylurea that may have been entrained in the distillation. The ether layer was again dried over anhydrous sodium sulfate and after removal of the ether the product was distilled from a Claisen-Vigreux flask. This treatment gave a yield of 25.3 g. (76%) of nitrobenzene. The m-dinitroderivative was
prepared according to standard procedures. Its melting point was 88-90° and no depression of the melting point was shown when a mixture melting point determination was made with an authentic sample of m-dinitrobenzene.

Another run was made in which 50 g. of the diazonium hexafluorophosphate was decomposed in tetramethylurea (200 ml.). Separation of the nitrobenzene was effected by distillation with steam of the mixture which resulted from addition of the reaction mixture to 1500 ml. of water. The distillate was extracted three times with 25-ml. portions of ether, the ether solution dried over anhydrous sodium sulfate and nitrobenzene separated by distillation from a Claisen-Vigreux flask. This technique yielded 18 g. (86%) of nitrobenzene, b.p. 204-208°, n_D^20 1.5510 (recorded n_D^20 1.5529).

Nitrobenzene from p-Aminonitrobenzene.—p-Nitrobenzenediazonium hexafluorophosphate (50 g., 0.17 mole) was added portionwise to tetramethylurea (200 ml.) contained in a 400-ml. beaker. The temperature of the mixture rose to 36° and nitrogen was evolved. After all the diazonium salt had been added the reaction mixture was warmed to 50-60° by means of a warm water bath and held in this temperature range until no more nitrogen was evolved. The reaction mixture was then poured into 1500 ml. of water and the nitrobenzene layer separated by distillation with steam. The organic layer was separated, dried over anhydrous...
sodium sulfate and distilled from a Claisen-Vigreux flask. The fraction which boiled at 204-206° was collected. This gave a yield of 12.9 g. (61.7%) of nitrobenzene, $n_d^{20} 1.5510$.

The m-dinitroderivative was prepared. Its melting point was 91.5-92.5° and showed no depression when a mixture melting point determination was taken with an authentic sample.

Bromobenzene from o-Bromoaniline.— The decomposition of the diazonium hexafluorophosphate derived from o-bromoaniline was effected exactly as described in the general procedure outlined above. A yield of 19.5 g. (82%) of bromobenzene, b.p. 154-158°, $n_d^{20} 1.5598$, was obtained.

Bromobenzene from p-Bromoaniline.— The decomposition of the diazonium salt derived from p-bromoaniline was carried out as in the general method. A yield of 17.3 g. (72.4%) of bromobenzene, b.p. 154-158°, $n_d^{20} 1.5574$, was obtained.

Chlorobenzene from p-Chloroaniline.— p-Chlorobenzenediazo- nium hexafluorophosphate was decomposed in the same manner as outlined above. A yield of 14 g. (70%) of chlorobenzene was obtained, b.p. 128-134°, $n_d^{20} 1.5223$.

Acetophenone from p-Aminoacetophenone.— The method given above was followed for the decomposition of the diazonium salt derived from p-aminoacetophenone. Three washings with water (25 ml.) of the crude product obtained from distillation with steam were necessary in order to remove all
trace of tetramethylurea. The yield of acetophenone was 7 g. (34%) b.p. 198-202°, n_D^{20} 1.5318.

Benzene from Aniline.— The decomposition of the diazonium salt prepared from aniline was carried out in the same manner as was described previously. A yield of 4.9 g. (33%) of benzene, b.p. 78-80°, n_D^{21.5} 1.4995, was obtained.

Toluene from p-Toluidine.— The method described previously was followed for the decomposition of the diazonium salt derived from p-toluidine. A yield of 7 g. (30%) of toluene was obtained, b.p. 108-112°.

Anisole from o-Anisidine.— The decomposition of the diazonium salt derived from o-anisidine was carried out according to the procedure outlined above. A yield of 6.5 g. (33%) of anisole, b.p. 153-156°, n_D^{20} 1.5163, was obtained.

o-Methylphenoxytetramethylamidinium Hexafluorophosphate.— o-Toluendiazonium hexafluorophosphate (20 g., 0.076 mole) was added in small portions to tetramethylurea (60 ml.) contained in a 150-ml. beaker at such a rate that the temperature of the reacting mixture did not rise above 65°. In order to prevent a very rapid decomposition it was sometimes necessary to cool the reaction mixture in an ice-water bath. When evolution of nitrogen had ceased the deep red reaction mixture was poured over a mixture of ice (150 g.) and concentrated hydrochloric acid (25 ml.). The deep red precipitate which was obtained was recovered by filtra-
tion and air dried. Treatment of a chloroform solution of the product with Norite removed the red colour. Recrystal-
lization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair gave 14.5 g. (60%) of colourless o-methylphen-
oxytetramethylamidinium hexafluorophosphate, m.p. 144-145°.

**Anal.** Calc'd for C_{12}H_{19}ON_{2}PF_{6}: C, 40.90; H, 5.44; N, 7.95; PF_{6}, 41.16.

Found: C, 40.57; H, 5.24; N, 7.75; PF_{6}, 41.04.

**Hydrolysis of o-Methylphenoxytetramethylamidinium Hexafluoro-
phosphate.*** - The hydrolysis of o-methylphenoxytetramethyl-
amidinium hexafluorophosphate was accomplished in 100 ml. of 4N sodium hydroxide in a 250-ml. round-bottomed flask fitted with a reflux condenser. A rubber connecting tube was led from the top of the condenser into a gas washing bottle which was fitted with a sintered glass disc. To the washing bottle was added 150 ml. of anhydrous ether. While heating the flask at reflux temperature a gas was evolved which dissolved in the ether. After four hours the apparatus was disassembled and dry hydrogen chloride gas was bubbled through the ethereal solution. The precipitate which formed was isolated by rapid filtration and dried in vacuo. A yield of 3.2 g. (48.4%) of dimethylamine hydro-
chloride, m.p. 168-171°, was obtained.

Addition of dry ice to the reaction mixture resulted in the formation of a pink organic layer which when separ-
ated yielded 7.5 g. (83%) of o-cresol. The p-bromobenzene sulfonate derivative melted at 78°. A mixture melting
point determination with an authentic sample showed no depression. The dibromo derivative (m.p. 56°) likewise showed no depression in melting point when mixed with an equal portion of an authentic sample.

Analysis of o-Methylphenoxytetramethylamidinium Hexafluorophosphate for the Hexafluorophosphate Anion. Three samples of 0.30-0.35 g. of the title compound were each dissolved in a solution of water (25 ml.) and acetone (10 ml.) by gentle warming on a steam bath. When all had dissolved tetraphenylarsenium chloride (35 ml., 4 g./250 ml.) was added to each solution. Hydrochloric acid (5 ml.) was added in order to help coagulate the precipitates. The precipitate was allowed to stand in contact with the mother liquor for one half hour and then separated by filtration through weighed, medium pore, sintered glass funnels. The samples were dried in an oven at 110° for one day, their weights were determined and the percentage of $PF_6$ was calculated. The average of the three determinations was 41.04%. The calculated value for the title compound is 41.16%.
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