The Synthesis and Physical Properties of Several Aromatic Fluorides

Charles J. Basso
THE SYNTHESIS AND

PHYSICAL PROPERTIES OF

SEVERAL AROMATIC FLUORIDES

Since the advent of the hydrogen bomb, more attention
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However, the realm of organic fluorides has not been investi-
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The purpose of this thesis is to give an outline of the
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an aromatic fluoride by one of these methods, namely, the Balz-
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by the use of a new reagent, fluosulfonic acid.

A Thesis Submitted to the
Faculty of the Liberal Arts College
Marquette University
In Partial Fulfillment of the Requirements
for the
Degree of Bachelor of Science
MILWAUKEE, WISCONSIN

January, 1949
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The author wishes to thank Dr. J. R. Koch, his major professor, also Mr. Herman Karl and Dr. John Surak of the Chemistry Department of Marquette University, for their assistance and advice in the composition of this thesis. The author also wishes to thank his wife for her assistance in the preparation of the manuscript.
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Pure fluorine gas, contaminated with hydrofluoric acid vapor, came off at the positive electrode. The fluorine was purified by passing it through a spiral tube at -50°C and then over lumps of sodium fluoride. Fluorine was obtained from this apparatus at a rate of three to four liters per hour. (36)

This, then, was the pioneer method of making fluorine. The rate of production from the Noisemans cell was rather slow, due to the low temperature used, and new cells began to appear.

INTRODUCTION

The Element Fluorine

The element fluorine defied isolation during the first one hundred years of the science of chemistry. The reason lay in its extreme activity. In 1886, Henri Moissan, a French chemist of the Sorbonne, succeeded in obtaining the free element through an electrolytic process. His electrolyzer was a U-tube made of an iridio-platinum alloy with side-arms and electrodes of the same composition. The electrolyte was a mixture of anhydrous hydrofluoric acid and potassium hydrogen fluoride. A bath of liquid methyl chloride (B. P., -23°C) surrounded the U-tube; evaporation of the methyl chloride supplied the low temperature needed for the electrolysis. Finally, twenty-five Bunsen cells, connected in series, supplied the current.

Pure hydrogen came off at the negative electrode. Fluorine gas, contaminated with hydrofluoric acid vapor, came off at the positive electrode. The fluorine was purified by passing it through a spiral tube at -50°C and then over lumps of sodium fluoride. Fluorine was obtained from this apparatus at a rate of three to four liters per hour. (38)

This, then, was the pioneer method of making fluorine. The rate of production from the Moissan cell was rather slow, due to the low temperature used, and new cells began to appear.

During World War I, the Chemical Warfare Service devised a modification of the Moissan apparatus; this new design was capable of producing any desired amount of fluorine.

"The apparatus was constructed of copper and had graphite electrodes. The electrolyte was molten potassium hydrogen fluoride, KF. 2HF (melting point, 217°C). Formation of a protecting layer of metallic fluoride prevented further attack on the inner surfaces of the cell." (46)

The latest development in cells for laboratory scale production of fluorine is a diaphragm-type cell with an anode of copper-impregnated carbon and a cathode of steel. The electrolyte is KF. 2HF with 1.0 to 1.5% lithium fluoride added. The cell operates at 95°C to 115°C and has a production rate of around 35 g. of fluorine per hour. (35)

"Fluorine is a pale-yellow gas with a characteristic odor somewhat resembling a mixture of ozone and chlorine... When liquefied, it boils at -187°C; solid fluorine melts at -223°C." (46)

Due to its activity, fluorine is never found in a free state. It occurs in the combined state as minerals. The main ones are: fluorite, or fluorspar, CaF₂; cryolite, AlF₃· 3 NaF; and fluorapatite, or calcium fluophosphate, Ca₅F(PO₄)₃. Small amounts of fluorine compounds are found in other minerals, in bones, and in the teeth. Drinking water containing soluble fluorides causes an unpleasant discoloration of tooth enamel. However, the dental profession is now interested in waters of

this type as aids in inhibiting tooth deterioration.

Fluorine is a member of the halogen family, yet its chemical behavior in certain reactions warrants the statement that fluorine is less closely related to the other halogens than they are to one another. For example, the solubilities of the inorganic fluorides stand in sharp contrast to the solubilities of other salts of the halogens. Silver fluoride is freely soluble whereas the other silver halides are difficultly so. Furthermore, calcium fluoride, unlike the other calcium halides, is sparingly soluble. (46)

Fluorine has great displacing power. Its activity stands in the order

\[ F > Cl > Br > I \]

It will displace halogens from the other ionic halides setting them free. It displaces hydrogen from many compounds. It also can displace halogens from co-valent halides; for example, it liberates chlorine from carbon tetrachloride.

The behavior of fluorine toward tissue shows why the element was so difficult to isolate. It causes severe burns which are painful and slow in healing. At least one investigator died while working on fluorine. (38) The gas attacks water, forming ozone, hydrogen peroxide, and hydrofluoric acid. This acid corrodes glass. Since glass and water are practically inseparable from laboratory work, one can see why the element

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was isolated only recently.

Fluorine reacts with practically every element except members of the rare gas family. To illustrate the extent of its activity:

"In recounting the story of a chemist working on the Manhattan Project at Columbia University who attempted a fluorination in a hot platinum tube only to have the tube catch fire, Cady remembered his own dismay when part of a glass system in which he was working with the gas began to burn. At the Purdue University laboratories, which engaged in fluorination investigations for the Manhattan Project, a favorite method of testing for the presence of fluorine was to place a piece of asbestos cord or glass wool in the stream of the suspected gas; if it burst into flame, the test was positive." (32)

Fluorine combines with hydrogen to form hydrogen fluoride even in the dark, but a trace of moisture must be present. There is divided opinion as to whether an oxide of fluorine exists. The element unites with the other halogens to form halides. (31)

Most metals will combine with fluorine; some require an elevated temperature in order to do so. When the metals copper, gold, silver, platinum, magnesium, and Monel metal are attacked by fluorine, they form protective coatings which resist further action. (50)

INORGANIC COMPOUNDS OF FLUORINE AND THEIR USES

The most important fluorine-bearing mineral, fluorite, has several uses just as it is. First of all, it is the indirect source of all other fluorine compounds. It is used to make hydrogen fluoride, as an optical material, and as an agent for reducing the viscosity of basic slags in metallurgical operations. The gas, hydrogen fluoride, may be prepared by heating a mixture of calcium fluoride and concentrated sulfuric acid or by heating potassium hydrogen fluoride.

\[ \text{CaF}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} \text{CaSO}_4 + \text{HF} \uparrow \]

\[ \text{KHF}_2 \xrightarrow{\Delta} \text{KF} + \text{HF} \uparrow \]

The gas may be dried thoroughly and condensed or it may be led into water to prepare hydrofluoric acid. Both the gas and the acid may be used for the etching of glass. The acid is used in gravimetric analysis, e.g., the determination of silica. Hydrogen fluoride is a good polymerizing agent; it can be used also in reactions where anhydrous aluminum chloride is ordinarily used. Liquid hydrogen fluoride can be used as a solvent for liquid phase oxidations of organic compounds.

"The alkali, ammonium, aluminum, and zinc fluorides are used as preservatives or insecticides, and zinc fluoride is also used as a wood preservative. Antimony and boron fluorides are used in the synthesis of organic fluorine compounds, the former in the manufacture of Freon and the latter as a polymerizing agent. The alkali and ammonium acid fluorides are used as antiseptics and laundry sours and in the etching of glass.

The fluorides of zinc, barium, sodium, magnesium, and aluminum are useful glass and enamel opacifiers. The silicofluorides are used in electrolytic lead refining (Betts process), the sodium, calcium, and aluminum salts in ceramics, and the zinc, magnesium, and aluminum salts to harden concrete. A great number of other inorganic fluorides are useful in many ways." (40)

Certain complex acids containing fluorine are known, such as fluosilicic acid, fluoboric acid, and fluosulfonic acid. Fluosilicic acid, $\text{H}_2\text{SiF}_6$, is unstable and can be kept only in aqueous solutions. Most fluosilicates are soluble in water and have certain uses in industry. (46) Fluoboric acid, $\text{HBF}_4$, results from the action of boron trifluoride on water, thus:

$$\text{BF}_3^{+2} + 2 \text{H}_2\text{O} \rightarrow \text{HBO}_2 + 3 \text{HF}$$

$$\text{BF}_3^{+} + \text{HF} \rightarrow \text{HBF}_4$$

The sodium and potassium salts of fluoboric acid, $\text{NaBF}_4$ and $\text{KBF}_4$, are important in synthesizing various organic fluorides. The other metallic fluoborates are finding more and more use in the electroplating industry. These fluoborates cut down the time required for plating and also do not give off toxic or inflammable fumes from the plating bath. Fluosulfonic acid, $\text{H}_3\text{SO}_3\text{F}$, is the combination of the acid anhydrides, $\text{SO}_3$ and $\text{HF}$. It is now being exploited as a catalyst for aliphatic and aromatic reactions; as a synthesizing agent; and as a polishing agent. (16)

ORGANIC FLUORINE COMPOUNDS AND THEIR PROPERTIES

Before discussing the properties of organic fluorides, it is well to indicate how these fluorides should be named. The symposium on fluorine chemistry in the Industrial and Engineering Chemistry contains two articles suggesting systems of nomenclature. The first article lists some 26 compounds and their names according to (1) Chemical Abstracts; (2) International Union of Chemistry; and (3) the so-called "per" system. (30) The "per" system of nomenclature denotes complete substitution by fluorine of all positions attached to the carbon skeleton. This is accomplished by attacking the prefix "perfluoro-" to the name of the proper parent compound. The second article mentioned above contains a modification of all the "per" system. This can be called the "phi," or $\phi$ system. These authors substitute the prefix "phi" for the prefix "perfluoro." (21) Some representative compounds according to the four systems of nomenclature are presented in Table I.

It will be noticed that both the "per" and the "phi" system cannot be applied except to compounds where all skeletal hydrogens are replaced by fluorine. Thus, compounds which contain halogens or hydrogens still attached to carbon cannot be named by this system. See numbers (2) and (7) below.

TABLE I
NOMENCLATURE OF FLUORINE CONTAINING COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>C. A.</th>
<th>I.V.C.</th>
<th>&quot;Per&quot; System</th>
<th>&quot;Phi&quot; System</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\ce{C7F16}$</td>
<td>Hexadeca Fluoroheptane</td>
<td>Hexadeca Fluoroheptane</td>
<td>per Fluoro-</td>
<td>$\Phi$-heptane</td>
</tr>
<tr>
<td>(2) $\ce{C7F11}$</td>
<td>Chloropenta deca Fluoro heptane</td>
<td>Chloropenta deca Fluoro heptane</td>
<td>per Fluoro-</td>
<td>$\Phi$-naphthalene</td>
</tr>
<tr>
<td>(3) $\ce{F3}$</td>
<td>Octa Fluoronaphthalene</td>
<td>Octa Fluoronaphthalene</td>
<td>per Fluoro-</td>
<td>$\Phi$-acetic acid</td>
</tr>
<tr>
<td>(4) $\ce{C\ 2\ H02F3}$</td>
<td>Tri Fluoroacetic acid</td>
<td>Tri Fluoroethanoic acid</td>
<td>per Fluoro-</td>
<td>$\Phi$-benzene</td>
</tr>
<tr>
<td>(5) $\ce{C\ 3\ F2}$</td>
<td>Hexa Fluorobenzene</td>
<td>Hexa Fluorobenzene</td>
<td>per Fluoro-</td>
<td>$\Phi$-tolvene</td>
</tr>
<tr>
<td>(6) $\ce{C\ 3\ F2}$</td>
<td>Octa Fluorotolvene</td>
<td>(Tri-Fluoro-methyl) - penta Fluorobenzene</td>
<td>per Fluoro-</td>
<td>$\Phi$-tolvene</td>
</tr>
<tr>
<td>(7) $\ce{C\ 3\ F2}$</td>
<td>$\lambda,\lambda,\lambda,\lambda,\lambda,\lambda$ - Hexa Fluoro-m-xylene</td>
<td>1,3 Bis (tri Fluoro-methyl) benzene</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>(8) $\ce{C\ 2\ F5}$</td>
<td>Hexa Fluoropropanone</td>
<td>Hexa Fluoropropanone</td>
<td>per Fluoro-</td>
<td>$\Phi$-acetone</td>
</tr>
<tr>
<td>(9) $\ce{C\ 2\ F5}$</td>
<td>Penta Fluoroethyl pentafluoro propionate</td>
<td>Penta Fluoroethyl pentafluoro propionate</td>
<td>per Fluoro-</td>
<td>$\Phi$-ethyl-propionate</td>
</tr>
</tbody>
</table>
The properties of organic fluorides may be divided into three classes: physical, chemical, and physiological. Physically,

"the per-fluorocarbons have nearly the same freezing and boiling points as hydrocarbons of the same structure and number of carbon atoms. The boiling points are extremely low relative to the molecular weight, coming closer in this respect to the inert gases than any other type of chemical compounds. The per-fluorocarbons have relatively high fluidities and low surface tensions. They appear to be substances with a minimum of attractive force between molecules. Their liquid densities are somewhere between 50 and 100% greater than corresponding hydrocarbons." (45)

The chemical nature of organic fluorides varies from the extremes of inertness to the extremes of reactivity. Thus, fluorobenzene, $C_6H_5F$, is an inert material while tri-fluoroacetic acid, $CF_3 - COOH$, is reported to be even stronger than tri-chloro-acetic acid. The per-fluorocarbons are characterized by great thermal stability and resistance to chemical action. In general, fluorine imparts inertness to the substance. Fluorine (single atoms) in the aromatic nucleus is quite unreactive, and fluorine in all organic compounds seems more resistant to hydrolysis than chlorine. Compared to hydrocarbons, per-fluorocarbons are completely resistant to oxidation and do not burn. They resist the action of most chemical reagents, even the alkali metals, up to relatively high temperatures.

Henne prefaces his article on alephatic fluorides with this interesting remark:

"(His) presentation is almost completely limited to aliphatic compounds, because aromatic fluorides have chemical, physiological, and physical properties which are more or less predictable from the known trends of the other aromatic halides, whereas aliphatic compounds may or may not show the characteristics to be expected by analogy." (24)

"In order satisfactorily to account for the chemical behavior of aliphatic organic fluorides, it is convenient to divide them sharply into two classes, monofluorides and polyfluorides. Monofluorides are characterized by their instability and their tendency to lose hydrogen fluoride, which automatically generates an unsaturated residue and therefore gives rise to olefins, polymers, or condensation products. By contrast, polyfluorides are exceedingly stable and often physiologically inert; chemically, they are indifferent or sluggish and resist oxidation particularly well. These properties are so marked that they place the aliphatic polyfluorides in a class by themselves.... It should be emphasized that a polyfluoride is stable only when the various fluorine atoms (or at least halogen atoms) are grouped together. In this respect CH₂CHF₂ is a typical polyfluoride and is stable, while CH₂FCH₂F is better regarded as a double monofluoride, and is therefore particularly likely to lose hydrogen fluoride." (24)

Again,

"as- di-fluoroethylene, CH₂=CF₂, is completely stable to air oxidation, in contrast to the corresponding di-chloro compound, which under the same conditions is rapidly attacked. The stabilizing effect of fluorine atoms extends to other halogen atoms situated on the same or adjacent carbon atoms, for di-chloro-di-fluoro-methane, CCl₂F₂, is completely impervious to hydrolysis and to molten sodium." (9)

This stabilizing influence is also illustrated by the fact that the chlorine atom in 1-chloro-2-, 2-difluoropropane is far more stable to heat and chemical reagents than the one in 1-chloro-propane. (22)

"Per-fluorocarbons are not attacked by nitric acid, concentrated (96%) and fuming sulfuric acid, nitration mixture, acid chromate, and permanganate solutions. ... Per-fluorocarbons are stable toward air and do not burn by themselves. They crack, however, in the flame of a Bunsen burner. They do not decolorize bromine water and are stable against bromine and iodine." (20)

"Polyfluoride groups have a marked directing influence. In sharp contrast with CH₃, a CF₃ side chain is a powerful agent to direct substitution into the meta position. A single fluorine atom in the ring, however, directs a substituent to the ortho and para positions, and favors para over ortho replacement." (24)

The physiological properties of organic fluorides need explanation. The degree of toxicity (or harmlessness, on the other hand) varies.

"The physiological inertness of the aliphatic polyfluorides has been illustrated already by di-chloro-di-fluoro-methane, CCl₂F₂. Before being placed on the market as refrigeration agents other chlorofluorides have been thoroughly investigated to establish their lack of toxicity. Methylene fluoride can be administered in large doses without ill effect, although it is not so thoroughly inert as CCl₂F₂. Fluorocarbon is completely inert and has no soporific effect, in complete contrast to chloroform." (24)

"The per-fluorocarbons are probably the most non-toxic organic compounds possible, but the

A new rat poison known as 1080 (monofluoroacet-ic acid) is an extremely toxic substance. The fluoride ion is well known for its toxicity, and this has been the basis of the use of inorganic fluorides as insecticides. The toxicity of monofluoroacetate acid, however, can hardly be based on fluoride ion, because it is much more toxic." (45)

Mention may also be made once more of the function of fluoride ion in the health of the teeth. The possibilities and properties of these compounds indicate their eventual use as heat transfer and dielectric media, fire extinguishers, fireproofing compounds, turbine impellants, high-temperature lubricants, thermal and chemical resistant plastics, etc. The inertness of fluorine in certain compounds has led them to be used as dyes because of their stability and light fastness.

Two broad methods of introducing fluorine into an organic molecule. The first, or indirect, method consists of the use of reagents such as antimony fluorides (Swarts reaction), hydrogen fluoride in the presence of antimony or other metallic halides as catalysts, fluoboric acid (Schiamann reaction), or in other ways. The second method consists in the direct reaction of the gaseous element with organic compounds under a variety of conditions.

"The powerful reactions actually observed can, in general, be moderated and caused to take place in an orderly fashion, first, by breaking up the reaction chains, and second, by dissipating the heat. The more common means for moderating direct fluorinating reactions are as follows:

FLUORINATION PROCESSES: DIRECT FLUORINATION

The element fluorine has been avoided in chemical synthesis up to this time, since many of its reactions are explosive. Besides this, it is a costly reagent; the prewar price of fluorine was about $75 a pound. It has been predicted that the price will drop to 25¢ a pound soon. There has not been too good a dissemination of techniques involving this substance. It took a war emergency as a catalyst to get concerted action on solving the problems connected with the use of elementary fluorine. The opinion now is that when the lower price prevails, fluorine will become increasingly more useful in chemical industry.

There are, in general, two broad methods of introducing fluorine into an organic molecule. The first, or indirect, method consists of the use of reagents such as antimony fluorides (Swarts reaction), hydrogen fluoride in the presence of antimony or other metallic halides as catalysts, fluoboric acid (Schiemann reaction), or in other ways. The second method consists in the direct reaction of the gaseous element with organic compounds under a variety of conditions.

"The powerful reactions actually observed can, in general, be moderated and caused to take place in an orderly fashion, first, by breaking up the reaction chains, and second, by dissipating the heat. The more common means for moderating direct fluorinations are as follows:

1. Diluting the fluorine by an inert gas.
2. Conducting the reaction in an inert solvent.

3. Fluorinating by means of compounds which easily release fluorine atoms or molecules, such as C6H5IF2, SbF5, PbF4, MnF3, CeF4, AgF2, CoF3, and others.

4. Carrying out the reaction in the vapor phase, within the meshes of a metal packing, with or without other catalyst.

5. Reacting the fluorine with a relatively inert compound.

6. Various combinations of the preceding."

The number 3 process above is in reality a type of indirect fluorination because it does not involve a reaction of the gaseous element itself. In reactions of this type, the metallic element is reduced to a lower valence state when the fluorine atom or molecule is given up. Fluorine gas is afterwards used to restore the metal to its original higher valence. In this sense, the process might be called a variety of direct fluorination.

"This procedure leads readily to the formation of completely fluorinated organic molecules, as the result of substitution, addition, polymerization, or cleavage, which possess valuable properties and cannot in general be prepared successfully in any other way. The direct method...has certain obvious disadvantages, all of which are being greatly reduced by recent developments. Elementary fluorine is still relatively costly and its reactions are energetic and must be adequately controlled, while in substitution reactions only half of the fluorine is directly available, although the remainder may easily be recovered as hydrogen fluoride and used again." (2)

We might well begin our discussion of direct fluorination methods with the fluorination of carbon, although it was not the first material to be fluorinated. Humiston in 1920 brought fluorine, at times diluted with nitrogen, into direct contact with carbon; he found that the carbon burned to a mixture of fluorocarbons, but no pure products were isolated. (2) In 1926, Lebeau and Damiens reacted fluorine with wood charcoal, isolated carbon tetrafluoride, and described a few of its reactions. (2) Ruff and Keim in 1930 passed a current of fluorine over purified wood charcoal contained in a glass tube. They also obtained carbon tetrafluoride and completely characterized it. (2) A few years later Ruff and Bretschneider showed that Norite or graphite will absorb fluorine progressively until the product had the composition required by the formula \((\text{CF})_x\). (2) The existence of such a compound seems well-confirmed. Simons and Block passed fluorine over different varieties of finely divided carbon contained in a copper tube. About one per cent of mercurous or mercuric chloride was added to the charge in order to inhibit the violent explosions which otherwise took place. Most of the yield was \(\text{CF}_4\), \(\text{C}_2\text{F}_6\), and \(\text{C}_3\text{F}_8\), together with small amounts of other per-fluorocarbons. (41, 42)

(2) Bigelow, L. A., ibid., 56.
(2) Bigelow, L. A., ibid., 58.
The saturated hydrocarbons can be considered next.

"Moissan and Chavanne in 1905 attempted to react solid methane (m. p. -184°C) with liquid fluorine at -187°C, but even at this very low temperature the reactivity of the halogen was so great that the only result was a powerful explosion." (2)

Since most organic substances burn or explode when introduced into an atmosphere of fluorine, means had to be found to moderate the reaction; in combustion, the product is mainly carbon tetrafluoride. The authors Bigelow, Pearson, Calfee, Young, Hadley, and Fukuhara (6, 7, 21, 51) did much work on the fluorination of ethane and methane, not to mention other substances. They found that these compounds could be fluorinated in the gaseous form over copper gauze; the fluorine used was diluted with nitrogen. Many different products were obtained; in addition, it was observed that such vapor-phase fluorinations could be used to build up a carbon chain.

The action of fluorine upon unsaturated compounds has been studied, but with inconclusive results. "The addition of fluorine to double bonds has been observed in only few cases, and is very impractical because the large amount of heat evolved breaks down the organic molecule." (29) In most instances it is best to avoid the use of elementary fluorine for the saturation of olefins with fluorine.

The fluorination of benzene has provided much room for speculation. Bancroft and Jones reported in 1929 that when benzene vapor and fluorine were mixed, there was a short induction period followed by an explosive reaction. (2) Bockemuller found evidence that the primary attack on the aromatic nucleus is one of addition rather than substitution. In an exploratory paper by Fredenhagen and Cadenbach, a relatively easy fluorination of benzene is described. No pure fluorine compounds were isolated, however. (12) In 1941, Fukuhara and Bigelow fluorinated benzene. They obtained a very complex mixture of compounds, with $C_6F_{12}$ predominating, but no aromatic fluoro compounds could be found. (14) Aromatic fluorides cannot be prepared by direct substitution with fluorine.

The fluorination of halogen-containing compounds has been well investigated, but it also has its limitations in lack of prediction of results. Humiston in 1920 fluorinated phosgene, chloroform, and some chlorocarbons, but did not isolate any pure products. (2) Ruff and Keim

"attempted to fluorinate carbon tetrachloride by passing fluorine through it, but found that while at room temperature little reaction occurred, at reflex temperatures dangerous explosions took place frequently, caused perhaps by the presence of chlorine fluoride in the gas."

In seeking to overcome this danger, they discovered that direct fluorination over a metal halide catalyst was a much safer process; this type of reaction has been very fully exploited recently. These authors also showed that "direct combination of fluorine with fluoriform (CHF₂) led to ignition and the formation of not only carbon tetrafluoride but also hexafluoroethane. This represents the first instance of the building up of a carbon chain by direct vapor-phase fluorination, a phenomenon which has since become of increasing importance." (2)

Simons fluorinated carbon tetrachloride to yield mainly carbon tetrafluoride and some chlorotrifluoroformethane. By reacting fluorine and dichlorodifluoromethane over a mercury catalyst at 340°C - 370°C, he obtained a good yield of chlorotrifluoroformethane. (43)

The fluorination of chloro-ethanes and -ethylenes has been studied by Miller and his co-workers. In 1937, Miller fluorinated tetrachloroethylene, C₂Cl₄, and hexachloroethane, C₂Cl₆, to yield s-difluorotetrachloroethane. (33) Ethyl chloride was fluorinated by Calfee to yield a variety of products. (8)

In 1940, Miller brought out a new procedure for fluorination of organic liquids. Undiluted fluorine was run in counter-current flow to the sample in a brass U-tube. Chloroform and various two-carbon chlorine compounds were fluorinated and the results described. (34)

Herachlorobenzene and fluorine give different compounds under different conditions. A liquid phase fluorination yields mainly C₆F₄Cl₆ and C₆F₆Cl₆. (4) By using sublimed hexachlorobenzene and fluorine at atmospheric pressure over copper gauze, no less than ten liquid and two crystalline products were isolated; however, no molecular weights or structures for these compounds were reported. (13)

Many other substances have been directly fluorinated but this type of fluorination needs much study in regard to control of products. Precision fractional distillation has been employed to good advantage in separating the various products of a direct fluorination. Other direct fluorinations are as follows: silver cyanide, (2); n- and iso-butyric acids, crotonic acids, oleic acid, and benzoic acid, (2); acetone, (15); and acetophenone, (44).

THE USE OF HYDROGEN FLUORIDE IN FLUORINATIONS

Liquid hydrogen fluoride can be used as a solvent for direct fluorinations. The best solvents for this reaction are the commercial refrigerants, \( \text{CCl}_2\text{F}_2 \) and \( \text{C}_2\text{F}_4\text{Cl}_2 \), and liquid hydrogen fluoride, which cannot react with fluorine and which dissolve it readily.

"A process has been described by Du Pont in which the substance to be fluorinated is dissolved or suspended in hydrogen fluoride, and fluorine is introduced into the mixture. The temperature at which the reaction mixture is maintained depends on the particular compounds involved (\(-70^\circ\text{C} \text{ to } 70^\circ\text{C}\)), and a pressure great enough to keep the products in the liquid state is applied. Catalysts may be added in proportions of 0.1 to 5%." (49)

Various aliphatics and aromatics have been fluorinated by this method.

Hydrogen fluoride adds to both double bonds and triple bonds. Grosse and Linn in 1938 studied the addition of anhydrous hydrogen fluoride to ethylene, propylene, cyclohexene, and cyclopropane. No catalyst was necessary for this reaction. (18) Henne and co-workers synthesized various chloro-fluoropropanes by adding hydrogen fluoride to the chloro-olefins. (23, 25, 27, 28, 36). Grosse and Linn added hydrogen fluoride to various

alkynes in 1942. (19) Acetylene and hydrogen fluoride react
to give a mixture of vinyl fluoride and 1, 1-difluoroethane.
The reactions are very violent and uneven.

"Hydrogen fluoride converts compounds of the
type RCl₂ to RCF₃. The simplest example of
this reaction, which proceeds without a cata-
lyst, is the conversion of methyl chloroform
stepwise at 150°C to methyl fluoroform, CH₃CF₂,
with the liberation of hydrogen chlor-
ide. The reaction of benzotrichloride with
hydrogen fluoride is of considerable technical
importance. The reaction is carried out at
110°C under pressure. Derivatives of benzotri-
chloride are also converted by the action of
hydrogen fluoride to the corresponding tri-
fluorides. A trichloromethyl group ortho or
para to a chlorine atom does not react. If
there are two trichloromethyl groups ortho or
para to each other, they are converted simulta-
neously to trifluoromethyl groups; with mesit-
ylene, the final product is sym- C₆H₃-(CF₃)₃...

The presence of a -COC₁ group meta or para to
a -CCl₃ group does not hinder the exchange with
hydrogen fluoride; the corresponding trifluoro-
methylbenzoyl fluoride is formed." (5)

The use of hydrogen fluoride in connection with other substances
as a fluorinating agent is discussed later.

Swarts in 1890 discovered a procedure which has proved to
be a very important means of synthesizing organic fluorides.
He discovered that saturated polyhalides of the types R₂Cl₃
and RCl₄ can be transformed to the corresponding polyfluorides
RCF₂R and RCF₃ by long refluxing with antimony trifluoride or
hydrogen fluoride. The reaction is so slow, however, that it

(19) Grosse, A. V. and Linn, C. B., J. Am. Chem. Soc., 64,
2289 (1942).
(5) Bockemuller, W., "Organic Fluorine Compounds," in Newer
Methods of Organic Preparative Chemistry, New York,
THE USE OF METALLIC FLUORIDES IN FLUORINATIONS

"The replacement of a halogen atom in an aliphatic organic compound by fluorine may be affected by treatment with any of several inorganic fluorides. The most important are mercury, silver, antimony and hydrogen fluoride. The last is used whenever possible because of its low cost, ease of handling, and high fluorine content. The fluorides of thallium, zinc, and potassium have been used in isolated instances. The choice of the reagent is based on the reactivity of the halogen to be replaced. Iodine is most easily and chlorine least easily replaced; however, side reactions are most prevalent with iodides, which in consequence have not been used extensively. Bromides occupy an intermediate place both with respect to ease of replacement and extent of side reactions; they have been used most often in replacement reactions carried out in open equipment. With the increased availability of pressure equipment, particularly in commercial practice, the use of chlorides has now become general.

"All replacement reactions of this type must be carried out under completely anhydrous conditions. The difficulty in removing the last traces of water from oxygen compounds, and the possibility of producing water by decomposition, account for the fact that it is often difficult to utilize halogen compounds which contain oxygen in the molecule." (26)

Swarts in 1890 discovered a procedure which has proved to be a very important means of synthesizing organic fluorides. He discovered that saturated polyhalides of the types $RCX_2R$ and $RCX_3$ can be transformed to the corresponding polyfluorides $RCF_2R$ and $RCF_3$ by long refluxing with antimony trifluoride or hydrogen fluoride. The reaction is so slow, however, that it

would be of little practical importance if it could not be accelerated by the addition of small amounts (2 to 5%) of a pentavalent antimony salt. The pentavalent antimony is usually produced by adding free halogen to the antimony trifluoride. Swarts recommended the addition of about 5% of bromine or antimony pentachloride. The current practice involves the addition of chlorine in amounts commensurate with the difficulty encountered in the halogen exchange. With the types just mentioned, in which all the halogen atoms are attached to one carbon atom, not more than 1% of chlorine should be added to the antimony trifluoride. The interchange then gives nearly quantitative yields. In more difficult preparations enough chlorine is added to transform the trifluoride to antimony trifluorodichloride, SbF$_3$Cl$_2$. When more halogen atoms are present in the molecule, or when halogen and hydrogen are present on the same carbon atom, the exchange becomes more difficult and side reactions increase in significance. The reagent must frequently contain a high percentage of pentavalent antimony salt. (26)

The foregoing remarks indicate the place of antimony fluorides in fluorinations. Henne and co-workers, starting in 1937, published many papers which deal with this type of reaction. The work of Henne has been mainly in the aliphatic field. Of course, the Swarts reaction has also been applied to aromatic compounds which have alkyl chains attached.

---

Silver and mercury fluorides are capable of effecting all the replacements which can be accomplished by the other inorganic fluorides and in addition some replacements which are not effected by the others. Silver fluoride has a disadvantage in that only half of its fluorine is available because the exchange reaction stops with the formation of the compound AgF. AgCl. The mercury fluorides are better, although they, like silver fluoride, are difficult to prepare in anhydrous form. It is recommended that a cheaper reagent be used for relatively easy stages of fluorination, and a mercury fluoride to complete the more difficult stages.

Mercuric fluoride is a very effective reagent, but very expensive. The only good method for its preparation consists in the treatment of mercuric chloride with fluorine.

"Several procedures have been devised to circumvent the necessity of synthesizing mercuric fluoride. The nascent salt, prepared by passing hydrogen fluoride into a mixture of mercuric oxide and the organic reagent, may be employed. The oxide is instantly converted to the fluoride, which reacts at once with the organic halide. The mercury halide produced can be recovered and used for the preparation of mercuric oxide for another run. Another procedure consists in adding a halogen to mercurous fluoride in order to generate a mercuric fluoro halide; such a salt acts substantially as a mixture of mercuric fluoride and mercuric halide." (26)

Henne applied the nascent fluoride reagent to another type of synthesis involving chlorinated olefins. (29)

--

Lead dioxide and hydrogen fluoride are combined with the organic material. The oxide and fluoride react to yield nascent lead tetrafluoride, $\text{PbF}_4$, which immediately decomposes into the di-fluoride and 2 free fluorine atoms. The fluorine adds to the double bond to yield a di-fluoro derivative.

Very active halogen atoms, such as those of an acyl or sulfonyl halide, can be replaced with fluorine by the action of almost any inorganic fluoride. The most convenient method consists in heating gently a mixture of an acyl or sulfonyl chloride with zinc or antimony fluoride in an apparatus which permits the acyl fluoride to distill as it is formed.

Potassium fluoride can be used in synthesizing formyl or acetyl fluorides from mixtures of formic or acetic acid and benzoyl chloride in boiling acetic anhydride. Gottlieb also used potassium fluoride to prepare 1-fluoro, 2,4-dinitrobenzene from the corresponding chloro-compound by double decomposition. (17)

The latest metallic fluorides to be used in organic fluorinations are the cobalt and manganese compounds, CoF$_3$ and MnF$_4$. Fowler and his associates describe the use of cobalt trifluoride for making completely fluorinated hydrocarbons. (10)

"The reaction between solid CoF$_3$ and liquid hydrocarbons is violent and could not be controlled. No diluent inert to CoF$_3$ was available at the time. The diluents used, CCl$_4$ and Freon 113, gave mixed chlorofluorocarbons, such as C$_6$H$_{10}$F$_2$Cl from hexane in carbon tetrachloride. Later, with fluorocarbons as diluents, several groups developed successful liquid-phase syntheses."

"An alternative method of dilution was to convert the hydrocarbon to a gas and mix it with an inert gas such as nitrogen. In the first successful vapor-phase experiment, a mixture of hexane vapor and nitrogen was passed over a bed of solid $\text{CoF}_3$ in a heated copper tube, and the products were condensed in a trap at $-78^\circ\text{C}$." (10)

In the fluorination, the cobalt trifluoride is reduced to the difluoride; elementary fluorine is used to regenerate the trifluoride. Cobalt trifluoride is said to be a good fluorinating agent for hydrocarbons of moderate molecular weight, such as C6, C7, and C8.

Research is now being done on other metallic fluorides. Fowler found that manganese trifluoride and ceric fluoride had about the same fluorinating power as the cobalt fluoride. (11) An investigation of other fluorides showed that some "might have been fluorinating agents but were experimentally difficult to apply," and "others gave no evidence of causing substitution upon contact with hydrocarbons." It can be seen from this statement that this type of fluorination needs much study. Many compounds yet remain to be fluorinated by this process, and, doubtless, improved operating condition may yet permit the use of the obstreperous fluorides mentioned above.

Aromatic fluorides are nearly always prepared from the diazotized amines. It was shown in 1886 that fluorobenzene can be prepared from aniline in a yield of 20% of theory. A copper catalyst is used in this reaction, but the use of a copper catalyst in analogous reactions has been harmful. The yield of fluorobenzene may be increased by the use of concentrated (50 to 70%) hydrofluoric acid. This method has been displaced by two other methods; namely, diazotization and decomposition of the diazonium fluoride in anhydrous hydrogen fluoride, and the preparation of the insoluble diazonium fluoborate and subsequent decomposition of the dried salt...

The fluoborate method for preparing aromatic fluorides was developed by Balz and Schiemann.... The diazonium fluoborates, in contrast to most diazonium salts, are relatively insoluble. They are precipitated by the addition of fluoboric acid or sodium fluoborate to an aqueous solution of the diazonium chloride.

"Aromatic amino acids and aminophenols, because of the high solubilities of their diazonium fluoborates, are converted first to esters or methoxy derivatives. Then the resulting fluoro-derivative can be hydrolyzed or demethyalted by standard methods. An important property of diazonium fluoborates is their stability to shock and percussion. They do not explode when heated, but are decomposed smoothly. However, the decomposition of nitrobenzene diazonium fluoborate can become violent, and is best carried out by admixture with an inert material such as sand, soda, or alkali fluoborate. The decomposition can also be carried out under diminished pressure.

The yields from this method depends on two factors: first, on the solubility of the diazonium fluoborate; and second, on the course of the thermal decomposition of the fluoborate....

"Schiemann also applied this procedure with success to tetrazotized diamines, thereby introducing 2 atoms of fluorine into the molecule in one step....
"The Schiemann fluoborate process is excellent for laboratory use not only because of its wide range or application, but also because no special apparatus is necessary. The preparation of diazonium fluoborates can be carried out in a paraffin-lined flask, and the thermal decomposition can be conducted in ordinary glass apparatus. Also, the costs of the inorganic materials, aqueous hydrofluoric acid and boric acid, are small."(5)

The original investigators, Balz and Schiemann, prepared some 75 mono- and di-fluoro-derivatives of benzene by this process. It is a good process to use for the reasons outlined above. Since sodium fluoborate is now available commercially, it is not necessary to generate fluoboric acid in the laboratory. The use of the sodium salt thus precludes the handling of hydrofluoric acid; no paraffin lined vessels are needed, either.

This process can be extended further by starting with compounds which can be nitrated. The steps are: nitration; reduction to the amine; and replacement of the amino group by a fluorine atom. Fluorination of amino acids has been accomplished through this series of reactions.

Fluosulfonic acid is perhaps the newest chemical to be used in research on organic fluorides. According to Ruff and Braun, \(^\text{39}\) fuming H\(_2\)SO\(_4\) reacts according to CaF\(_2\) + H\(_2\)SO\(_4\) + 2 SO\(_3\) \rightarrow CaSO\(_4\) + 2 HSO\(_3\)F. Acid containing about 60% SO\(_3\) gives a nearly theoretical yield. \(^\text{39}\) Directions are given for preparing both aqueous and 95% HSO\(_3\)F in quantity.

In organic syntheses, the free acid or its alkali salts can be used. Acyl fluorides may be prepared by distilling a mixture of fluosulfonic acid and concentrated organic acids; e.g., acetyl, chloroacetyl-, and propionyl fluorides have been prepared from their respective acids. Similar reactions occur when the alkali metal salts of the two acids are distilled, e.g., phenyl acetyl fluoride and phenyl propionyl fluoride have been prepared by this method. \(^\text{48}\)

Both mono- and disulfonyl fluorides can be readily synthesized by direct reaction of fluosulfonic acid with a wide variety of aromatic hydrocarbons.

\[ C_6H_6 + 2 \text{HSO}_3\text{F} \xrightarrow{160-200^\circ C} C_6H_5\text{SO}_2\text{F} + \text{HF} + \text{H}_2\text{SO}_4 \]

They may also be prepared by reacting fluosulfonic acid with aromatic sulfonyl chlorides.

\[ C_6H_5\text{SO}_2\text{Cl} + \text{HSO}_3\text{F} \rightarrow C_6H_5\text{SO}_2\text{F} + \text{HSO}_3\text{Cl} \]

Steinkopf and co-workers prepared a great number of these compounds, including those of the benzene and anthracene series. \(^\text{47}\) Ruff, O., and Braun, J., Ber., 47, 646 (1919). \(^\text{48}\) Traube, A., and Krahmer, A., Ber., 52B, 1293 (1919).
compounds, including those of the benzene and naphthalene series. (47) Renoll (37) prepared two new biphenyl sulfonyl fluorides in 1942 by using this procedure.

These are the main fluorinations which can be accomplished with fluosulfonic acid. In addition, this reagent acts as a catalyst, as a source of boron trifluoride, as an alkylator, and as a reagent for preparing alkyl and aryl fluosulfonates. The aryl fluosulfonates are said to be good insecticides.

EXPERIMENTAL WORK

**FLUORO BENZENE**

\[
\text{N}_2H_4 + HCl \rightarrow N^+F_2^-
\]

\[
NaNO_2 + HCl \xrightarrow{\text{0°C}} H_2O + NaCl
\]

\[
N=N - Cl + NaBF_4 \rightarrow N=N - BF_4 + NaCl
\]

\[
N=N - BF_4 \xrightarrow{122°C} F + N_2 \uparrow + BF_3 \uparrow
\]

**EXPERIMENTAL WORK**

The reaction apparatus is that shown in Figure 1. One mole (91.2g) of aniline was added to three moles (249.6g) of concentrated hydrochloric acid in a two-liter beaker. Crushed ice was used to keep the temperature of the well-stirred mixture at 0°C to 5°C. A 60°C, 30% sodium nitrite solution was slowly added to the aniline hydrochloride through a dropping funnel; additional crushed ice kept the temperature from 0°C to 5°C. After the last addition of sodium nitrite, the 0°C mixture was stirred for one-half hour and then tested with starch-potassium iodide-paper for complete diazotization.

A chilled 50% sodium fluoroborate solution was added to the diazotized solution with constant stirring. The resulting slurry was stirred for one hour and was then filtered in the cold with suction on a large Büchner funnel. The light-
The reaction apparatus is that shown in Figure 1. One mole (91.2 cc) of aniline was added to three moles (249 cc) of concentrated hydrochloric acid in a two-liter beaker. Crushed ice was used to keep the temperature of the well stirred mixture at 0° C to 5° C. A 0° C, 30% sodium nitrite solution was slowly added to the aniline hydrochloride through a dropping funnel; additional crushed ice kept the temperature from 0° C to 5° C. After the last addition of sodium nitrite, the 0° C mixture was stirred for one-half hour and then tested with starch-potassium iodide-paper for complete diazotization.

A chilled 50% sodium fluoborate solution was added to the diazotized solution with constant stirring. The resulting slurry was stirred for one hour and was then filtered in the cold with suction on a large Büchner funnel. The light-
APPARATUS USED FOR MAKING

FLUOBORATE PRECIPITATES
yellow precipitate was sucked dry and then removed from the filter paper in the form of large cakes. These were finely divided and dried by spreading on several thicknesses of filter paper (or paper towels). The aniline diazonium fluoborate was dried in the fume chamber for 2-3 days with good ventilation and away from direct sunlight.

The thoroughly dried product was collected and prepared by further subdivision for decomposition by yeast. The decomposition apparatus is shown in Figure 2.

1. Part A is a 1-3 liter 3-necked flask equipped with a thermometer. The size depends on the amount of material to be decomposed at one time.

2. Parts B, C, and D are large, wide-mouth bottles surrounded by cooling baths of cracked ice.

3. Part E is a Liebig condenser.

The product was placed in the 3-necked flask, which was then slowly heated. The substance began to melt and suddenly decomposed with the evolution of dense, white fumes of BF$_3$. When the reaction subsided, the flask was heated strongly for ten minutes to insure complete decomposition. The receivers were disconnected, a little ice water was poured into each, and they were aerated in the fume chamber for 30-45 minutes.
The crude yield of fluorobenzene was collected and placed in the decomposition flask to be steam distilled. The product was separated from the distillate, washed with alkali, then with water, and dried over calcium chloride. The dried product was distilled, collecting the fraction which boils at 83°C to 85°C or the pure substance. Yield: 55% of the theoretical.

NOTES

1. The acid-amino ratio should be about 3:1 to prevent to a large extent the undesired coupling and formation of diazo-amino compounds.

2. The ice added to the amine hydrochloride serves two functions; first, it cools the hydrochloride salt solution faster; second, it makes stirring of the salt solution easier. Excess ice must not be added at any stage in the entire procedure. The diazonium fluoborate is quite soluble and losses in yield due to its solubility may result.

3. The nitrite must be added slowly and with efficient stirring to prevent undue accumulation of nitrous acid, evidence by the formation and escape of dense fumes of nitrogen dioxide.

4. The temperature must not be allowed to use above 2º or 3ºC during the actual diazotization or auto-decomposition occurs with the resultant formation
of considerable amounts of phenol and a consequent lowering of yield.

5. The stem of the separatory funnel is extended below the surface of the reaction mixture to prevent the escape of any nitrous acid decomposition products which would otherwise not further the reaction.

6. 105% of the theoretical amount of sodium nitrite is used. The excess thus introduced insures complete diazotization, but the stirred solution must still be tested with potassium iodide-starch paper.

7. 150% of the required amount of sodium fluoborate is used for the precipitation. The diazotized solution should be cooled as much as possible before adding the fluoborate solution.

8. Complete and thorough drying of the precipitate is essential, for autodecomposition is greatly encouraged by an unduly moist product. Sunlight also produces decomposition of the drying product at ordinary temperatures.

9. This particular salt can be decomposed safely in one portion. However, in working on salts prepared from other amines, caution should be observed. Dilution with gravel or sodium fluoborate may be required, and it may be necessary to decompose the salt in small portions. In trying new products a small portion may be decomposed in a test tube first; this trial will show whether or not the decomposition of the whole
will proceed safely and smoothly.

10. The decomposition temperature is not the point at which dense white fumes are observed in the flask. Rather, it is the temperature at which the first drops of fluorobenzene fall into the first receiver.

11. The residue in the decomposition flask contains a small amount of fluorobenzene. The yield of fluorobenzene is increased by steam distilling from this flask.

2.79 moles of concentrated sulfuric acid (155.5 cc) and 2.79 moles of fuming sulfuric acid (115 cc) were placed in a 1000 ml. round bottom flask provided with a water-jacketed condenser. With constant shaking, 2 moles of fluorobenzene (192 cc) was gradually added. The sulfonation required about 15 minutes. After the fluorobenzene was added, the mixture was heated on the water-bath, with occasional shaking, for about 2½ hours.

The mixture was poured into six liters of cold water, heated to boiling, and neutralized with 5.5 moles of calcium
2.79 moles of concentrated sulfuric acid (155.5 cc) and 2.79 moles of fuming sulfuric acid (115 cc) were placed in a 1000 ml. round bottom flask provided with a water-jacketed condenser. With constant shaking, 2 moles of fluorobenzene (192 cc) was gradually added. The sulfonation required about 15 minutes. After the fluorobenzene was added, the mixture was heated on the water-bath, with occasional shaking, for about 2 1/2 hours.

The mixture was poured into six liters of cold water, heated to boiling, and neutralized with 5.5 moles of calcium carbonate (549.6 g). The solution should then not react acid to methyl orange. The hot mixture was worked up by suspending it in hot water and then filtering. The filtrate contains the potassium P-fluoro-benzene sulfonate. One half of the calculated quantity of potassium carbonate was added to the reaction mixture as long as a precipitate was formed. The end point was determined by the opalescence of a small portion of the reaction mixture. The remainder of the potassium carbonate must be evaporated. The solution of potassium P-fluoro-benzene sulfonate was concentrated in a water bath and then evaporated.
carbonate (549.6 g). The solution should then not react acid to methyl orange. The hot mixture was filtered through a Büchner funnel. The precipitate was washed twice by suspending it in hot water and then filtering. The filtrate contains the soluble calcium sulfonate.

One-half of the calculated quantity of potassium carbonate was added to the filtrate in solid form. A solution of the remainder of the carbonate was then added in small portions as long as a precipitate of calcium carbonate was formed. The end point was determined by filtering off a small portion and treating the clear solution with additional potassium carbonate. An excess of potassium carbonate must be avoided. The solution now contained potassium p-fluoro-benzene sulfonate.

The calcium carbonate was filtered off; the filtrate was concentrated by boiling. The solution had to be evaporated to a small volume before the product separated out. The solution was cooled and the crystals were filtered by suction. The product was recrystallized from hot water and dried on filter paper. The yield was 70% of the theoretical.

NOTES

1. In the sulfonation, the addition of each new portion of fluorobenzene should not take place until the last portion (which at first floats upon the top) has been dissolved by shaking. This insures complete sulfonation. Incomplete sulfonation may cause a fire when
the diluted mixture is heated later.

2. The calcium carbonate should be added under a hood; the carbon dioxide vapor carries along choking carbonate dust. Powdered marble is suitable for this neutralization. The carbonate should be added in small portions. Too rapid addition will cause great ebullition of carbon dioxide and the mixture will foam over.

3. A 20% excess of calcium carbonate is used. This excess has been included in the figure above, 5.5 moles. To find the amount of calcium carbonate necessary, the following must be considered: Ordinary concentrated sulfuric acid contains 96% H₂SO₄; 262 g. of 20% fuming sulfuric acid is equivalent to 273 g. of 100% sulfuric acid; the neutralizing capacity of the sulfonic acid is reduced to one-half of the original acid.

4. The slurry must not be heated except when it is being stirred.

5. One mole, 138.2 g., of potassium carbonate is needed. Avoid adding an excess, otherwise the product will be contaminated with carbonate.
1.4 moles of concentrated sulfuric acid (78 cc) and 1.4 moles of fuming sulfuric acid (58 cc) were placed in a 500 ml. round-bottom flask fitted with a water-jacketed condenser. With constant shaking, one mole of fluorobenzene (96 cc) was gradually added. After the fluorobenzene had been added, the mixture was heated on the water bath, with occasional shaking, for about 2½ hours. The mixture was poured into three liters of cold water,
heated to boiling and neutralized with 2.76 moles of lead carbonate (736.2 g). The solution should then not react acid to methyl orange. The hot mixture was filtered through a Bucher funnel. The precipitate was washed twice by suspending it in hot water and then filtering. The filtrate contains the soluble lead sulfonate.

The cooled filtrate was placed in two large Erlenmeyer flasks. Hydrogen sulfide gas was bubbled in until no more black lead sulfide was formed. The contents of the flasks were allowed to settle and the clear supernatant liquid was decanted through a filter. The precipitate was washed twice with hot water and filtered off. The filtrate is now concentrated to a small volume by boiling.

The free sulfonic acids are hygroscopic materials and this preparation was no exception. The yield could not be crystallized out so it was converted to the sodium salt. The concentrated solution of free sulfonic acid was diluted with 200 cc of water and neutralized with sodium hydroxide solution. The neutral solution was concentrated again to a small volume, and the crystals were filtered out. The yield was about 66% of the theoretical for the sodium salt.

**NOTES**

1. In the sulfonation, the addition of each new portion of fluorobenzene should not take place until the last portion (which at first floats upon the top) has been dissolved by shaking. This insured complete sulfonation.
Incomplete sulfonation may cause a fire when the diluted mixture is heated later.

2. The lead carbonate should be added under a hood; carbon dioxide vapor carries along choking carbonate dust. The carbonate should be added in small portions. Too rapid addition will cause great ebullition of carbon dioxide and the mixture may foam over.

3. A 20% excess of lead carbonate is used. The excess has been included in the figure above, 2.76 moles. To find the amount of lead carbonate necessary, the following must be considered: Ordinary concentrated sulfuric acid contains 96% H₂SO₄; 131.0 g. of 20% fuming sulfuric acid is equivalent to 136.6 g. of 100% sulfurous acid; the neutralizing capacity of the sulfonic acid is reduced to one-half of the original acid.

4. The end-point of the precipitation with hydrogen sulfide was determined thus: A small portion was filtered and the filtrate treated with hydrogen sulfide. If no black precipitate of lead sulfide was formed, precipitation was complete.
BENZENE-SULFONYL-FLUORIDE  METHOD A

\[
\ce{\text{\(O\)}} + \ce{2HS03F} \xrightarrow{16^\circ-20^\circ C} \ce{\text{\(O\)}} + \ce{HF} \uparrow + \ce{H2SO4}
\]

D = S = 0

The reaction apparatus is that shown in Figure 3. Part A is a 1000 ml. 3-necked flask. Part B is a small electric motor connected to a mercury-sealed stirrer. Part C is a separatory funnel. Part D is a gas-exit tube, about 4 feet long. Part E is a water-bath containing water at 16\(^\circ\)-20\(^\circ\)C.

2.25 moles of fluosulfonic acid (129.3 cc) were placed in the flask. 0.705 moles (62.5 cc) of benzene was added to the acid through the dropping funnel over a period of six hours, while stirring constantly. The mixture was then stirred for nine hours more at a temperature of 16\(^\circ\)-20\(^\circ\)C.

The reaction mixture was poured on cracked ice and the product extracted with ether. The ether extract was washed with water and the acid eliminated with calcium carbonate. The ether was distilled off and the residue distilled with steam. The product was separated from the distillate and was distilled again using an air condenser. The vapors which come over at 209\(^\circ\)-210\(^\circ\)C were collected. The yield was 40% of the theoretical.
APPARATUS FOR PREPARATION OF SULFONYL FLUORIDES
NOTES

1. The benzene must be added to the acid very slowly or too many fumes will be produced. The mixture should not be stirred too fast for the same reason.

2. Some etching of the glass parts which were in contact with the reaction mixture was observed.

0.204 moles (25.1 cc) of benzene-sulfonyl-chloride and 1.44 moles (83.3 cc) of fluosulfonic acid were allowed to stand together in a stoppered flask for 24 hours. The mixture was poured on cracked ice and the product extracted with ether. The ether extract was washed with water and the acid was eliminated with calcium carbonate. The ether was distilled off and the residue steam distilled. The product was separated from the distillate and then distilled again collecting the vapors which condensed at 209° - 210° C. The yield was 40% of the theoretical.
0.204 moles (26.1 cc) of benzene-sulfonyl-chloride and 1.44 moles (83.2 cc) of fluosulfonic acid were allowed to stand together in a stoppered flask for 24 hours. The mixture was poured on cracked ice and the product extracted with ether. The ether extract was washed with water and the acid was eliminated with calcium carbonate. The ether was distilled off and the residue steam distilled. The product was separated from the distillate and then distilled again collecting the vapors which condensed at 209° - 210°C. The yield was 40% of the theoretical.
The reaction apparatus is that shown in Figure 3.

4.0 moles (230 cc) of fluosulfonic acid were placed in the flask. 1.28 moles (125 cc) of fluorobenzene were added to the acid through a dropping funnel over a period of seven hours, while stirring constantly. The mixture was then stirred for eight hours more at a temperature of 16°-20°C.

The reaction mixture was poured on cracked ice and the product extracted with ether. The ether extract was washed with water and the acid was eliminated with calcium carbonate. The ether was distilled off and the residue distilled with steam. The product was separated from the distillate and distilled again, using an air-condenser. The vapors which condensed at 199°C-201°C were collected. The yield was 28% of the theoretical.

NOTES

1. The fluorobenzene must be added slowly to the acid and the reaction mixture must not be stirred too vigorously; otherwise, too many fumes will come off.

2. Some etching of the glass parts in contact with the reaction mixture was noticed.
### TABLE II

PHYSICAL CONSTANTS OF REACTING COMPOUNDS AS USED IN CALCULATIONS

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Moles WT</th>
<th>Density</th>
<th>MP</th>
<th>BP</th>
<th>Yield</th>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Calcium carbonate</td>
<td>CaCO₃</td>
<td>100.09</td>
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<tr>
<td>Fluosulfonic acid</td>
<td>HSO₂F</td>
<td>100.07</td>
<td>1.74</td>
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<td>Potassium carbonate</td>
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<tr>
<td>Sodium Fluoborate</td>
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</tr>
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<td>Sodium Nitrite</td>
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<td>1.8</td>
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<td>Fuming Sulfuric acid</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>ORGANIC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>C₆H₅NH₂</td>
<td>93.12</td>
<td>1.022</td>
<td>-6.2</td>
<td>184.4</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>78.11</td>
<td>0.879²⁰</td>
<td>5.5</td>
<td>80.09</td>
<td></td>
</tr>
<tr>
<td>Benzene-sulfonyl chloride</td>
<td>C₆H₅SO₂Cl</td>
<td>176.62</td>
<td>1.378²³</td>
<td>14.5</td>
<td>46.7d</td>
<td></td>
</tr>
<tr>
<td>Fluoro-benzene</td>
<td>C₆H₅F</td>
<td>96.10</td>
<td>1.024⁻⁴⁰</td>
<td>-41.9</td>
<td>84.85</td>
<td></td>
</tr>
</tbody>
</table>
EXPERIMENTAL DATA AND RESULTS

TABLE III

YIELDS AND CONSTANTS OF COMPOUNDS PREPARED

<table>
<thead>
<tr>
<th>NAME AND DESCRIPTION</th>
<th>FORMULA</th>
<th>M.P.</th>
<th>B.P.</th>
<th>R.I.</th>
<th>S.G.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorobenzene</td>
<td>C₆H₅F</td>
<td>-41.9°C</td>
<td>84-85°C</td>
<td>1.024</td>
<td>55%</td>
<td></td>
</tr>
<tr>
<td>(colorless liquid)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium p-fluorobenzene sulfonate</td>
<td>p-F₆H₄</td>
<td>unobt.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>70%</td>
</tr>
<tr>
<td>(colorless crystals)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium - p-fluorobenzene sulfonate</td>
<td>p-F₆H₄</td>
<td>unobt.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>65</td>
</tr>
<tr>
<td>(colorless crystals)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene-sulfonyl fluoride</td>
<td>C₆H₅SO₂F</td>
<td>209⁰-210⁰C</td>
<td>1.4932</td>
<td>1.329</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>(colorless liquid)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Fluoro-benzene-sulfonyl fluoride</td>
<td>p-F₆H₄-</td>
<td>199⁰-201⁰C</td>
<td>---</td>
<td>1.306</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>(colorless liquid)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

all temperatures uncorrected
The preparation of fluorobenzene has been undertaken many times in these laboratories. It is a good experiment to use as an introduction to the Balz-Schiemann reaction. No difficulties were encountered in the run made for this thesis. The various steps went off smoothly, and the same yield was obtained.

The alkali salts of the p-fluorobenzene sulfonic acids were prepared according to directions given in Adkins, McElvain, and Klein. The procedure is rather roundabout, but the solubility of the sulfonic acids and their salts necessitated this type of reaction. No melting points were obtainable up to 250°C. The presence of a metal in an organic compound usually has this effect.

The sulfonyl fluorides were prepared according to Steinkopf's directions. This author and his co-workers made benzene-sulfonyl-fluoride and other compounds by the use of fluorosulfonic acid in 1928. An identical run was made in these laboratories for the purpose of becoming acquainted with the technique involved. Some changes were made in the original procedure. A glass vessel was substituted for an ion vessel and the reaction was not dangerous. Steinkopf, however, reported a yield of 60%.

The next step was to try a similar reaction with fluorobenzene as the starting material. Since the presence of a halogen atom on the ring does not appreciably alter the chemical
properties, a procedure similar to that of Steinkopf was used. The directions in his paper showed that: (1) the hydrocarbon was added to the acid in very small portions, and (2) the mixture must be stirred for a long time. The molar reactant ratio was around 3 or 4 moles of acid to 1 mole of hydrocarbon. The run was made with these conditions in effect, and a moderate yield of product was obtained.

The sulfonyl fluorides prepared are in sharp contrast to the sulfonyl chlorides. The chlorides are lachrymators and corrosive materials; they also have some affinity for water. In contrast, the fluorides are pleasant-smelling materials and do not become cloudy due to the presence of water. Benzene-sulfonyl fluoride has a higher boiling point than the corresponding chloride; the ring-substituted sulfonyl fluoride boils higher than the unsubstituted sulfonyl fluoride. The differences in boiling points are not very great, however.

The Schie mann reaction. This reaction involves the replacement of an amino group with a fluorine atom by way of a diazotization process. The use of the new reagent fluosulfonic acid is discussed next. Uses for this acid are now being developed in the United States, based on directions given in various German papers.

Many of the aliphatic fluorides are low-boiling materials which require low temperature handling. The Swarts reaction was avoided for this reason. The dependability of the Bals
SUMMARY OF FLUORINATION METHODS AND CONCLUSIONS TO BE DRAWN FROM THE THESIS

In this thesis, an outline of important fluorination processes is given. First, direct fluorinations are taken up and ways and means to moderate their intensity are discussed. The next reaction of note is the use of metallic fluorides as synthesizing agents. The usefulness of the antimony compounds was discovered by Swarts. Extensions of this technique have been applied by Henne and lately by many others, as more metallic fluorides are investigated.

Hydrogen fluoride can be used as an inert solvent in the liquid state for direct fluorinations. It can be also caused to add to unsaturated materials. Lastly, it can be reacted with metallic oxides to yield nascent fluorides which serve as fluorinating agents.

Aromatic fluorides are best prepared by the Balz-Schiemann reaction. This reaction involves the replacement of an amino group with a fluorine atom by way of a diazotization process. The use of the new reagent fluosulfonic acid is discussed next. Uses for this acid are now being developed in the United States, based on directions given in various German papers.

Many of the aliphatic fluorides are low-boiling materials which require low temperature handling. The Swarts reaction was avoided for this reason. The dependability of the Balz-
Schiemann reaction was demonstrated in the preparation of fluorobenzene. Two sulfonation reactions were performed to obtain two alkali metal salts of fluorobenzene-sulfonic-acids. These sulfonic acid salts could be intermediate materials for the preparation of other fluorine compounds. The reagent fluosulfonic acid was then used to prepare some sulfonyl fluorides. This type of reaction can be used successfully on many compounds. Its uses are only now being exploited. The yields obtained were not high, but perhaps improvement or changes in operating conditions can increase the figures.

The search of the literature in connection with this thesis revealed that there are only a few comprehensive articles or books on fluorine in organic reactions. These are as follows:

1. The symposium on fluorine chemistry in the March, 1947 issue of Industrial and Engineering Chemistry.
2. Bigelow's review on Direct Fluorinations. (Reference 2.)
3. Henne's comprehensive articles on aliphatic fluorinations. (References 24 and 26.)
4. Bockemuller's book, Organische Fluorverbindungen; Alien Custodian License #A-656. (1936)
5. Two articles in Newer Methods of Preparative Organic Chemistry. (References 5 and 49.)

These articles and the references connected with them will help the reader to become acquainted with the state of organic fluorine chemistry today. Many new
developments have no doubt been discovered, but due to their connection with atomic research, they may not appear for some time. It is hoped that this information will be available soon, as it will save much repetition of research efforts.


4. Extension of the Baehr-Schleumann reaction to compounds other than aromatics.

5. Preparation and properties of various ring-substituted benzene-sulfonyl-fluorides.


7. Sulfonation of the benzene-sulfonyl-fluorides.

8. Effect of various factors (time, temperature, rate of addition, etc.) influencing the yield of the sulfonyl fluorides.
VI. Suggestions for Further Study

1. Application of the "nascent metallic fluoride" type of synthesis to other aliphatic compounds.

2. The use of benzene-sulfonyl-fluoride as a characterizing reagent.


4. Extension of the Balz-Schiemann reaction to compounds other than aromatics.

5. Preparation and properties of various ring-substituted benzene-sulfonyl-fluorides.


7. Sulfonation of the benzene-sulfonyl-fluorides.

8. Effect of various factors (time, temperature, rate of addition, etc.) influencing the yield of the sulfonyl fluorides.
VII. ANNOTATED BIBLIOGRAPHY


An advanced organic laboratory manual.


A description of the various researches dealing with the action of fluorine on organic compounds and free carbon; literature survey, 1945.


A comparison of the mechanism of chlorinations and fluorinations plus ways and means to moderate fluorinations.


A fluorination carried out at 0 C in CCl₄ solution; small yields of two compounds reported.


Fluorinations of methane with undiluted elementary fluorine over copper gauze catalyst.

An advanced organic laboratory manual.


A description of the various researches dealing with the action of fluorine on organic compounds and free carbon; literature is searched through December, 1945.


A comparison of the mechanism of chlorinations and fluorinations plus ways and means to moderate fluorinations.


A fluorination carried out at 0°C in CCl₄ solution; small yields of two compounds reported.


Fluorinations of ethane with undiluted elementary fluorine over copper gauze catalyst.

Fluorination of ethane with elementary fluorine, using progressively changing proportions of the two gases.


The vapor-phase fluorination of ethyl chloride with fluorine over copper gauze; an analytical procedure for determining chlorine and fluoride.


A standard organic chemistry reference work.


Completely fluorinated organic compounds are prepared by the use of cobalt trifluoride.

A comparison of the effectiveness of various metallic fluorides.


The direct fluorination of benzene, toluene, and other compounds by a new apparatus; no pure fluorine compounds were collected, however.


Vapor phase fluorination of hexachlorobenzene over a copper gauze to yield 12 products.


The direct fluorination of benzene, using a copper gauze catalyst.


The direct fluorination of acetone.


A description of the properties, uses, and salts of fluosulfonic acids; several reactions are suggested which employ this acid.

A fluoro-nitro-benzene is prepared by double decomposition of the chloro-compound and KF.


The addition of hydrogen fluoride to ethylene, propylene, cyclohexene, and cyclopropane.


The direct non-catalytic addition of HF to various mono-halo-

Physical and chemical properties of fluorocarbons in general and specifically.


The fluorination of methane with elementary fluorine.


2,2 dichloropropane is fluorinated with SbF$_3$ and Br$_2$; 85% yield of 2,2 difluoropropane.

Part of this work concerns the addition of HF to CH$_2$ = CClCH$_2$Cl.


A survey of the field of aliphatic fluorides as of January 1, 1941.


The addition of HF to various mono-halo- and di-halo'olefins.


Various methods of synthesizing aliphatic fluorides are discussed; an extensive table of compounds is included.


Part of this work concerns the addition of HF to CH$_3$CCl = CHCH$_3$.


Part of this work deals with the action of HF on CCl$_2$CHCH$_2$CH$_3$.

(29) Henne, A. L., and Waalkes, T. P., "The Addition of

Various chlorinated olefins are connected into fluorides by use of nascent PbF$_4$.


A statement on the nomenclature of fluorine compounds.


A standard college inorganic chemistry text.


Comments on fluorine reactions in general.


Direct fluorination of (1) hexachloroethane and (2) tetrachloroethylene over copper gauze.


The reaction of eight chlorinated compounds with undiluted fluorine.


A commercial fluorine-generating cell and its operation; also, a small cell for laboratory use.

The treatment of monochloroolefins with anhydrous HF.


Two sulfonyl fluorides of biphenyl and one fluorosulfonate were prepared by using fluorosulfonic acid.


An older inorganic textbook.


The preparation of fluorosulfonic acid.


The history, occurrence, uses, and properties of fluor spar, with the uses of the principal fluorine compounds.


Fluorination of carbon yields six perfluorocarbons.


Stable compounds were obtained by passing fluorine gas through carbon and a catalyst.


Some reactions between fluorine and (1) carbon tetrachloride (2) dichlorodifluoromethane.


Direct fluorination of acetophenone with elementary fluorine in liquid HF; other fluorinations.


A discussion of fluorine, its compounds and their properties, and some reactions.


A standard inorganic chemistry text.


The preparation and properties of aromatic sulfonyl fluorides by means of fluosulfonic acid.


The preparation of acyl fluorides by the use of fluosulfonic acid.

A variety of reactions involving hydrogen fluoride, including the preparation of fluorides.


The preparation and properties of fluorine and of some of its compounds.


The yield of partially fluorinated ethanes can be greatly increased by using nitrogen as a diluent for the elementary fluorine.
APPROVED

John R. Koch
Major Professor

Virgil Roach, S. J.
Dean

Date Jan 11, 1949