

Some Anomalous Properties of Organic Fluorine Compounds

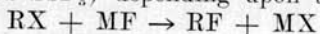
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The abundance of fluorine is three times that of copper and fifteen times that of lead in the earth's crust. In spite of this abundance, the chemistry of fluorine compounds is the least understood of the common elements because of the extreme reactivity of the element and the extremely toxic and corrosive properties of many of its inorganic compounds. A number of inorganic fluorides are very well known but practically nothing is mentioned in the average college textbook on the organic compounds.

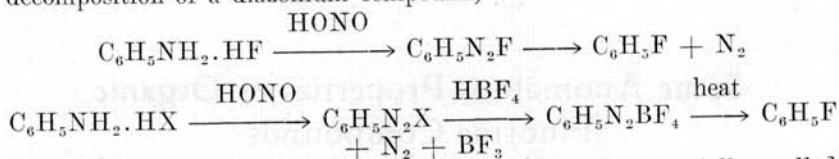
The advent of Freon (dichlorodifluoromethane) as a new refrigerant in 1930 signalized a new epoch in synthetic organic fluorine chemistry, especially in the commercial world as it refuted the traditional concept that all fluorine compounds are either corrosive or toxic or difficult to prepare. Other refrigerants, new non-fading dyes, solvents, electrical condenser insulators, etc., containing fluorine have made their appearance and for certain purposes are superior to anything else that is available. Unfortunately the chemistry of these compounds is scattered throughout the scientific and patent literature and has never been correlated or compiled in any single publication.

Very few of the general methods of synthesizing organic halides are applicable to fluorine compounds. Direct fluorination takes place with explosive violence and with the disruption of the molecule due to the high heat of reaction which is much greater than that of the "Thermite" process. The usual products of direct fluorination are a mixture of organic fluorides, carbon, and hydrogen fluoride although an excess of fluorine gives carbon tetrafluoride. The treatment of an alcohol with hydrogen fluoride gives an equilibrium mixture of the alkyl fluoride and ether. The reaction of PF_3 with an alcohol gives phosphorous esters. The addition of HF to an olefine has not been reported in the research literature, however, a patent has been issued using propylene as an example to give a propyl fluoride. This leaves two general methods of synthesis, (1) the replacement of a halogen atom by fluorine through reaction with certain anhydrous metallic fluorides (AgF , Hg_2F_2 or HgF_2 , TlF , ZnF_2 , and SbF_3) depending upon the compound desired,



and (2) the introduction of fluorine into an aromatic nucleus by the

decomposition of a diazonium compound,



The new refrigerant dichlorodifluoromethane (commercially called Freon) and some of the new solvents and dyes are made by the first reaction with SbF_3 under heat and pressure with SbCl_5 as a catalyst. In the laboratory some of these reactions can be carried out in glass with considerable etching or in platinum but commercially monel metal, copper, and iron serve very well if certain precautions are taken.

The physical properties of the fluorine compounds are very unusual in comparison to the chlorine analogs. Their boiling points are much lower than the chlorine compounds and in a large number of cases lower than the parent hydrocarbons as illustrated in Table I; the melting points are also much lower. The odor of many of them is much milder and the compounds less toxic. Organic solvents readily dissolve them and they themselves possess unique solvent properties. Hydrogen fluoride is highly associated but in general the organic fluorine compounds are not. Many of them exhibit low inflammability and low corrosive properties making it possible to work in ordinary equipment without unusual hazardous conditions. The fluorinated acetic acids, especially trifluoroacetic acid, are as highly ionized as our strong mineral acids, and the fluoroalcohols also show definite acidic properties.

TABLE I.—THE EFFECT OF FLUORINE SUBSTITUTION UPON THE BOILING POINTS OF ORGANIC COMPOUNDS

Compounds	B. P. °C.	Compounds	B. P. °C.	Compound	B. P. °C.	Compound	B. P. °C.
CH_4	-164.7	CH_3F	-78	CHF_3	-2/20 atm.	CF_4	-128
CCl_4	76	CCl_3F	24.1	CCl_2F_2	-28	CClF_3	-80
CH_3COCH_3	56.5	$\text{CH}_2\text{FCOCH}_3$	72	$\text{CHF}_2\text{COCH}_3$	46.2	CF_3COCH_3	21.9
CH_3COOH	118.1	CF_3COOH	72.4	CCl_3COOH	195	CBr_3COOH	245
$\text{CH}_3\text{CH}_2\text{OH}$	78.4	$\text{CH}_2\text{FCH}_2\text{OH}$	103.3	$\text{CHF}_2\text{CH}_2\text{OH}$	96	$\text{CF}_3\text{CH}_2\text{OH}$	74
C_6H_6	80.4	$\text{C}_6\text{H}_5\text{F}$	85	$\text{C}_6\text{H}_5\text{Cl}$	132	$\text{C}_6\text{H}_5\text{Br}$	156
$\text{C}_6\text{H}_5\text{CH}_3$	111	$\text{C}_6\text{H}_5\text{CF}_3$	103.5	$\text{C}_6\text{H}_5\text{CCl}_3$	214	$\text{C}_6\text{H}_5\text{CBr}_3$

The chemical properties of these compounds are as unusual as their physical characteristics. In general they are more stable than their chlorine analogs, reaching a maximum when the carbon atom carrying the fluorine contains no hydrogen as in the case of the $-\text{CF}_3$ group. This group will resist hydrolysis by water, alkalies, and acids almost indefinitely even under the most severe conditions. The aliphatic monofluorides are quite sensitive to fuming nitric and concentrated

sulfuric acids. The acid fluorides are very much like the aromatic sulphonyl chlorides in stability. The organic fluorine compounds resist reduction to an almost unbelievable degree. For all practical purposes they do not corrode such metals as copper, monel, nickel, iron, and they will not form the Grignard reagent, and with sodium in liquid ammonia they form sodium fluoride which is used as a basis for analysis. In some cases the fluorine atoms may be activated by other substituents such as in the case of chloroacetyl fluoride which hydrolyzes very rapidly due to the chlorine substitution. Benzotrifluoride ($C_6H_5CF_3$) can be nitrated almost quantitatively to the meta nitro benzotrifluoride, which in turn will not hydrolyze even under strenuous treatment. Since the $-CF_3$ group in an aromatic compound has a similar effect as a nitro group on color this type of compound is commercially used in a few non-fading dyes. Some of the highly substituted chlorofluorine liquid compounds are excellent electrical insulators due to their extreme stability, high dielectric constants, and low viscosity changes with ordinary temperatures.

The analysis of organic fluorine compounds is very difficult and the best known methods still leave much to be desired as far as accuracy, applicability, and ease of manipulation is concerned. There are about as many modifications on analysis as there are original papers on new fluorine compounds. The determination of carbon and hydrogen in a compound necessitates packing the combustion tube with special materials for complete oxidation and also for the retention of the fluorine. Fluorine is usually analyzed by two methods, (1) the Na_2O_2 bomb fusion method, and (2) the sodium-liquid ammonia method of Nieuwland. Both methods require highly refined technique for accuracy although the latter is rapidly gaining favor because of its simplicity and non-hazardous manipulation. After the organic fluorine has been converted to an inorganic fluoride, the problem evolves into choosing a method with the smallest correction factor.