ALIPHATIC FLUORINE COMPOUNDS
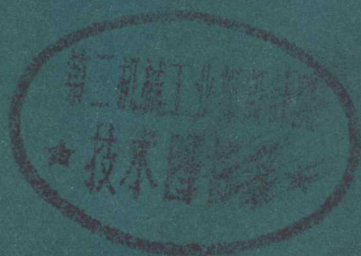
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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe

iii

rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

Preface

This book is concerned with a comprehensive treatment of the preparation and properties of all classes of aliphatic fluorine compounds. The subject is approached from the point of view of preparative organic chemistry and is arranged in a general order similar to the arrangement of treatises on classical organic chemistry. Each chapter is devoted to a specific class or classes of fluoroorganic compounds such as alkanes, alkenes, alcohols, etc. The first chapter describes various fluorination processes which may be employed for the introduction of fluorine into an organic compound. Wherever possible, the influence of fluorine on the chemical and physical properties of various classes of compounds is noted. Likewise, similarities and differences in reactivities and properties between fluorine-containing organic compounds and their hydrocarbon analogs are pointed out. Special attention is given to recent advances in the field, and where applicable, industrial or commercial importance of organic fluorine compounds is indicated.

Each chapter is complete with a bibliography and tables which describe physical properties of the compounds listed. An explanation of the tables is given on page vi. The literature has been extensively reviewed from Moissan's time up to and including the year 1955. In some cases, papers published in 1956 and early 1957 have been utilized. However, every published paper on the subject is not included in the bibliographies, nor has every organic fluorine compound prepared been included in the tables. But quite a representative number of the contributions to the subject have been incorporated in the book.

From the time of Moissan until the advent of World War II, the activity in the field of fluorocarbon chemistry has been relatively modest. However, during this period, research was stimulated by the discovery that certain fluorocarbons (Freons, Genetrons) possessed physical, chemical and physiological properties which made their application for refrigerants very desirable. During World War II the requirements for materials with the unusual properties of chemical inertness and thermal stability generated a crash program on fluorocarbon research. These properties which are characteristic of organic fluorine compounds are responsible for the continuing emphasis being placed upon research in this field. During the last decade numerous fluorocarbon products have gained wide-spread recognition for applications such as: propellants, wetting agents, textile

treating agents, pharmaceutical intermediates, lubricants, elastomers, adhesives, sealants, plastics, films, protective coatings and fire extinguishing agents.

Some fluorine-containing starting materials and intermediates are commercially available to the research chemist. Representative chlorofluoro- and bromofluoromethanes and -ethanes are available under the trade names of Freons (E. I. duPont de Nemours, Inc.) and Genetrons (General Chemical Division of Allied Chemical and Dye Company). In addition, materials of this type may be available from Pennsalt Chemicals Corp. and the Chemical Division of Union Carbide Company. A few fluorine-containing olefins such as chlorotrifluoroethylene may also be available. The Minnesota Mining and Manufacturing Company markets certain perfluorocarboxylic acids. Additional fluoroorganic compounds may be obtained from certain specialty chemical companies.

The chemist undertaking a research program in organic fluorine chemistry for the first time should acquaint himself with the hazards associated with the handling of fluorocarbons as well as hydrogen fluoride. Generally such information necessary for the safe handling of these materials can be made available by the supplier.

The satisfactory analysis of fluorocarbon compounds requires, in many cases, that special techniques be employed. A comprehensive review of this subject by P. J. Elving, C. A. Horton and H. H. Willard is contained in Simons' "Fluorine Chemistry."*

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*Simons, J. H., "Fluorine Chemistry," Vol. II, New York, Academic Press, Inc., 1954.

Explanation of Tables

Each chapter is accompanied by tables which are separated for convenience by functional groups. In most cases, only compounds whose structure has been proven are included. The nomenclature used, is in most cases, that which is generally accepted or that which is used in the original literature. The methods refer to the appropriate subdivision of the text in which the general reaction is discussed. The methods are numbered serially for each chapter. The first number or numbers refer to the chapter, the last two numbers designate the method in that chapter.

All compounds are arranged by empirical formula in each table according to the accepted Chemical Abstract order. Where several structures apply to a given empirical formula they are arbitrarily listed under that empirical formula.

The yields reported are the actual yields from the original literature and where applicable, a range is indicated. The references are those for the paper or papers describing the preparation of the compound and refer only to the bibliography of that chapter.

The physical constants when available follow the appropriate compound. All boiling, melting and freezing points are in degrees centigrade and pressures are in millimeters of mercury. Indices of refraction (n_D^t) are for sodium light at the temperature t°C. Densities (d_4^t) are referenced to water at 4°C and recorded at temperature t°C. When the temperature (t) is the same for the refractive index and density it is listed in the right column (t°C). If the density was recorded at a different temperature this is added in parentheses following the density.

Table of Contents

List of Tables

CHAPTER I

Fluorination

TABLE OF CONTENTS

INTRODUCTION

This chapter is concerned with the methods and processes for the introduction of fluorine into organic compounds, more specifically the formation of the carbon-fluorine bond. Subsequent chapters deal mostly

1

with the reactions of organic fluorine compounds.   Three main processes have been used for the preparation of organic fluorine compounds; these are (A) the use of metallic fluorides, (B) the use of hydrogen fluoride, and (C) the use of fluorine.

The use of metallic fluorides can involve either substitution of organic halides or direct replacement of hydrogen.   The reactivity of the more important metal fluorides are summarized in the following table:

Group of Periodic Table	Metallic Fluoride	Substitution of Organic Halides	Direct Replacement of Hydrogen
IA	KF	+	γ
IB	CuF	+	
	AgF	+	
	AgF_2	+	+
IIA	CaF_2	+	
IIB	HgF	+	
	HgF_2	+	+
III	TlF	+	
IV	SnF_4	+	
	PbF_4	+	+
V	SbF_3	+	
	SbF_3Cl_2	+	
	SbF_5	+	
Transition Elements	TiF_4	+	
	CrF_3	+	
	MnF_3	+	+
	FeF_3	+	
	CoF_3	+	+

Although nickel is not included in this table it is of importance as a material for the construction of fluorination reactors and it is probable that the nickel fluoride formed plays some part in the fluorination reaction.

Hydrogen fluoride is probably the most important present-day reagent for the preparation of organic fluorine compounds.   Hydrogen fluoride is extensively used in the commercial preparation of fluorine-containing organic compounds.   It is used either in conjunction with a metal salt or metal oxide to generate an active metal fluoride, for fluorinating organic halides, for addition to unsaturated compounds, and in the electrochemical fluorination process.

Fluorine is used to directly fluorinate various organic compounds or to prepare various active metal fluorides such as cobaltic fluoride or manganic fluoride.

METHOD 101 Fluorides of Group IA Elements; Potassium

The substitution reaction between potassium fluoride and organic monochlorides and monobromides yields monofluoroorganic compounds. In addition, potassium fluoride reacts with alkyl tosylates or dimethyl sulfone to yield monofluoroalkanes (cf. Method 208). Various classes of haloorganic compounds have been fluorinated by means of substitution with potassium fluoride. Mono- and dichloro- and bromoalkanes were converted into the fluorides.[37,71,72,113,114,169] Halogen-containing alcohols,[112,114,129,170] esters,[16,70,71,169,187] ethers,[70,72,170] and amides[4] have also been similarly fluorinated. Ethyl- and methylchlorocarbonate have been converted into the respective fluorocarbonates.[70,169]

Various conditions have been employed in using potassium fluoride as a fluorinating agent. Heating the organic halide and anhydrous potassium fluoride in anhydrous glycerol or ethylene glycol generally results in reasonable yields of alkyl fluorides. Reaction temperatures employed range from $50°$ for the fluorination of $CH_2BrCO_2CH_3$[169] to $150°$ to $200°$ for the fluorination of n-$C_{11}H_{23}Cl$.[70] However, no studies of optimum reaction conditions have been reported. High pressure autoclaves have been used as reaction vessels as well as conventional laboratory glassware.

Attempted fluorination of 4-chlorobutanol and its esters by this method led to the formation of tetrahydrofuran when the reaction was carried out at $120°$. However, at lower temperatures, low yields of the fluorinated alcohol were obtained.[172]

The use of the fluorides of the other alkali metals as fluorinating agents is not readily apparent from a review of the literature.

METHOD 102 Fluorides of Group IB Elements; Copper, Silver, and Gold

Copper fluoride is very seldom used as a fluorinating agent and it is only of historical interest. Midgley and Henne[153] treated carbon tetrachloride with a mixture of cupric fluoride and antimony sulfate and obtained CF_2Cl_2. Gleave[64] fluorinated carbon disulfide with hydrogen fluoride and cupric chloride and isolated CF_3Cl, CF_2Cl_2, and CF_3Cl. Gleave also treated carbon under similar conditions and obtained $CFCl_3$, and CF_2Cl_2.

Fluorides of silver are very effective fluorinating agents and have been widely employed. Silver fluoride (AgF) was used by early investigators to prepare alkyl fluorides. Moissan[160,164] prepared methyl, ethyl, and isopropyl fluorides from the respective iodides with this reagent. Meslans[152] treated $CH_2ICH=CH_2$ with AgF and isolated $CH_2FCH=CH_2$. Chabrie[34,35] used this reagent to fluorinate CCl_4 and obtained CF_4. Swarts[216] found that treatment of n-amyl chloride with AgF yielded the fluoride but also resulted in coupling and olefin formation.

The observation was made by Henne[92] that the relative ease of replacement of halogens by inorganic fluorides is $I > Br > Cl$ and that side reactions occur more readily with iodides and less readily with chlorides. The former part of this observation is especially true when considering polyhalogenated carbon atoms; for example, $CClBr_2CO_2C_2H_5$ was converted to $CFClBrCO_2C_2H_5$ using AgF.[207] More recently silver fluoride was used to replace iodine and chlorine on fluorocarbon haloarsines such as $(CF_3)_2AsI$, $(CF_3)_3AsCl_2$ (cf. Method 1227).

Henne[92] also points out that the disadvantages of using silver fluoride lie in the fact that it is difficult to prepare in anhydrous form and that only half the available fluorine is used due to the formation of the compound $AgF \cdot AgCl$, during the fluorination reaction.

Silver fluoride, besides being used to replace halogens in alkyl halides,[34,35,151,160,164,213,216] can be used to replace halogens in esters,[26,173,187,207,214] ethers[215] and nitriles.[74]

Silver difluoride (AgF_2) is a powerful fluorinating agent, comparable to cobaltic fluoride (cf. Method 108). It should be noted that while AgF replaces halogens, AgF_2 replaces hydrogen as well. It can be prepared by the action of fluorine on silver foil[51] or on silver halides.[162] Silver difluoride is believed to be the active agent when silver plated copper packing is used in the direct fluorination process (cf. Method 112). Important knowledge of its use was gained during World War II. McBee and Bechtol[136,137,138] prepared a series of perfluorinated fused ring compounds from aromatic hydrocarbons using AgF_2; temperatures employed were in the range of 160° to 400°. The reactor consisted of a bed of the silver salt over which fluorine gas was passed. The hydrocarbon vapor was swept through the reactor with nitrogen and the products were collected in traps at the end of the system. Such hydrocarbons as indene, napthalene, acenaphthene, phenanthrene and others were converted into the completely fluorinated saturated ring systems. Ethylbenzene and p-cymene were likewise fluorinated.[142] Kellogg and Cady[125] reacted methanol with AgF_2 and isolated CF_3OF (cf. Chapter IV).

Liquid phase fluorination of heptanes and lubricating oil fractions with AgF_2 was also extensively studied during World War II. The reaction was carried out in a fluorinated solvent at a reflux temperature of 240° for several hours.[202] Various halogenated polynuclear hydrocarbons and ketonic materials were fluorinated using AgF_2 in the liquid phase.[202]

Silver difluoride was also used in the intermediate or final fluorination stages after a chlorocarbon was partially fluorinated by use of the Swarts reaction. In the final step in the conversion of chlorofluoroheptanes to perfluoroheptane, silver difluoride was found to be more effective than cobaltic fluoride in the vapor-phase reaction at 300° to 325°.[202]

Sharpe[194] found that $AuBrF_6$ reacted violently with either carbon tetrachloride or benzene.

METHOD 103 Fluorides of Group IIA Elements; Calcium

Of this group of fluorides only calcium fluoride has been used as a fluorinating agent, and then only in conjunction with other inorganic fluorides. The use of calcium fluoride for this purpose is considered to be relatively unimportant. A French patent[50] describes the preparation of a mixture of chlorofluoromethanes from carbon tetrachloride using a mixture of calcium fluoride and antimony pentachloride. Bockemuller[20] employed a mixture of AgF and CaF_2 and Ruff used a mixture of HgF and CaF_2 for the fluorination of haloalkanes. Midgley and Henne[153] treated carbon tetrachloride with a mixture of calcium fluoride and antimony sulfate and obtained CF_2Cl_2.

METHOD 104 Fluorides of Group IIB Elements; Mercury and Zinc

Mercurous fluoride has been prepared by the action of hydrofluoric acid on mercurous carbonate or by the reaction of sodium fluoride and mercurous nitrate. This fluorinating agent was used by Swarts to fluorinate $C_5H_{11}Cl$,[216] $C_2H_5OCH_2CHBrCH_2Br$,[215] $CH_2ICO_2CH_3$,[207] and $CH_2BrCH_2CO_2CH_3$.[214] The reaction was generally carried out at $160°$ for 24 hours. Swarts also found that the use of mercurous fluoride in fluorinating alkyl chlorides did not result in coupling or olefin formation as in the case of AgF. Henne and Renoll[102] studied this fluorination reaction and found that good yields of monoalkyl fluorides could be obtained from monoiodides and monobromides, but poor yields were obtained from monochlorides and polyiodides. Fluorination of polychlorides resulted in the loss of hydrogen chloride.

Mercuric fluoride is a more effective agent for halogen substitution and can be prepared by the action of fluorine on mercury salts. It is quite hygroscopic, a characteristic which limited its early application.

Henne and Midgley[98] prepared HgF_2 in a copper reaction vessel by the action of fluorine gas on mercuric chloride. Fluorination with this reagent resulted in good yields of products from polyiodides or polybromides; polychlorides were unreactive and were used as solvents for the reaction.

A great improvement in fluorination technique was introduced by Henne[91] when he demonstrated that the *in situ* preparation of HgF_2 could be accomplished by the reaction of HgO and anhydrous hydrogen fluoride. The water formed in this reaction combined with excess HF and floated on top of the layer of chloroform or methylene chloride which was used as a solvent. By this technique halogenated esters and alkanes were fluori-

nated in good yields at $-20°$. Further study showed that fluorination of $RCHCl_2$ could be readily accomplished by this procedure.[103] Side reactions occurred when the Swarts reaction was used on this type of compound and the difluoride was produced only with great difficulty.

Mercuric fluoride was tested as a fluorinating agent for hydrocarbons but the rapidity of the reaction of HgF_2 with air limited its use for this purpose.[48]

Huckel[118] treated both ICN and CH_3CN with mercuric fluoride at $160°$. From the first reaction, cyanuryl fluoride, $(FCN)_3$ was the product obtained and in the case of acetonitrile a mixture of $CH_3CF_2NF_2$, $CH_2=CFNF_2$, $CH_3CF=NF_2$ and $CH_2=C=NF$ was obtained. Similar results were observed by Nerdel[166] in the fluorination of acetonitrile.

Zinc fluoride can be used to produce acyl fluorides from acyl chlorides.[92]

METHOD 105 Fluorides of Group III Elements; Aluminum, Thallium, and Boron

Aluminum fluoride has been investigated as a fluorinating agent in both the liquid phase and the vapor phase reactions. It is believed that the reaction involves disproportionation (cf. Method 214) rather than substitution. Miller and Calfee[156] reacted CCl_3F with AlF_3 at $105°$ and isolated a mixture consisting of CCl_2F_2, $CClF_3$ and CCl_4. In the vapor phase at $300°$ to $400°$ the interaction of CH_3CClF_2 and AlF_3 resulted in the formation of CH_3CF_3.[155] At $375°$, both $CHClF_2$ and $CHCl_2F$ yielded CHF_3,[156] and at $650°$ to $700°$, treatment of CCl_3CClF_2 with AlF_3 resulted in the formation of a mixture of CCl_2F_2, CCl_4, CF_3Cl, $CF_2ClCFCl_2$, $CCl_2=CFCl$, and $CCl_2=CCl_2$.[33]

Thallous fluoride replaces chlorine in acyl chlorides, and alkyl chlorocarbonates at low temperatures.[67,70,174] Bromo- or iodoacetic esters are converted to the fluoro- derivative with TlF in refluxing ether or ethanol.[4,175,176,177]

Boron trifluoride has been used in conjunction with hydrogen fluoride and in this respect functions only as a catalyst (cf. Method 109).

METHOD 106 Fluorides of Group IV Elements; Silicon, Tin and Lead

References to the use of silicon and tin fluorides are few. Silver- and mercury fluorosilicate were employed by Paterno and Spallino[171] to fluorinate alkyl iodides to the corresponding fluorides. Whalley[230] treated 1,1-dichloroethane with hydrogen fluoride in the presence of 2.5 percent $SnCl_4$ and obtained a mixture of CH_3CHClF and CH_3CHF_2. Under similar conditions other chloroethanes yielded mixtures of fluorochloroethanes. This reaction was carried out at $50°$ to $100°$ and at 100 to 200 psi. The