

AROMATIC 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 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.

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PREFACE

Although the field of aliphatic fluorine chemistry has shown the most spectacular growth in recent years, there has been a steady increase of interest in aromatic molecules containing fluorine. Because of this and the desire to assess the progress in this field, this volume has been prepared. The bibliography and tables of compounds are believed to be complete up to the 1958 indexes of *Chemical Abstracts* and many of the articles appearing after this date in major chemical journals have been included. It is hoped that no important development reported up to the time of printing has been omitted.

This volume differs in one important respect from most monographs. This is in the inclusion of theoretical discussions of the preparation and physical properties of the compounds of interest. The inclusion of these topics was felt to be justified not only because of the extended usefulness that they give to the book but also to stimulate imaginative thinking by chemists to solve some of the unanswered problems that are discussed.

Although this monograph is entitled "Aromatic Fluorine Compounds," it is not limited to only carbocyclic systems. The term "aromatic" is taken to include conjugated cyclic systems containing hetero atoms. However, in order to keep the volume to a reasonable size certain restrictions have been adopted. Only compounds containing fluorine atoms directly attached to the aromatic nucleus or through a carbon-carbon chain are included. If the carbon chain contains a hetero atom only compounds where fluorine atoms are attached to the chain on the ring side of the chain are included. Other compounds were considered to be simple functional derivatives of aliphatic compounds. For example, ethyl-*p*-fluorobenzoate is of interest, while 2-fluoroethyl benzoate is an aliphatic fluorine derivative and was omitted. Only one exception to this rule was made. When a fluorine atom was attached to a hetero atom which in turn was attached to an aromatic system, the compound was included. These compounds are discussed in Chapter VII. In some cases compounds were discussed, but were not tabulated. These included acyl fluorides, sulfonyl fluorides, and salts of fluorine containing inorganic or aliphatic acids. These compounds in most reactions eliminate fluorine immediately and are therefore of little importance to this field.

Chapter IX summarizes the most important applications of aromatic fluorine compounds and attempts to indicate the theoret-

ical basis wherever possible for these applications. This chapter was written by three specialists in their fields. The portion on agricultural chemicals was prepared by Steven Dorman of the Stauffer Chemical Company Agricultural Laboratory; that on dyes by Don Gray of the Denver Research Institute; and that on pharmaceuticals by Ferenc Herr of Ayerst, McKenna & Harrison Laboratories. We cannot adequately express our gratitude for the efforts that went into this chapter.

The total preparation of this volume has been aided immeasurably by many people. First, we want to express our sincere thanks to Arthur Roe of the National Science Foundation, who not only encouraged the writing of this monograph, but was kind enough to offer editorial help and sacrificed his time to read and discuss the manuscript. Similarly, we want to thank William Foley and Eugene Teach of the Stauffer Chemical Company for their careful reading and helpful suggestions for improvement of the manuscript. The literature search was aided by Barna Toekes and especially by Harry Pacini, whose help in the final arrangement of the tables was invaluable. It is a pleasure to thank the typists, especially Lois Schoenberger, who worked so diligently to bring some order out of the handwritten manuscript. We are grateful to the Stauffer Chemical Company for their help and understanding offered during the preparation of this monograph, and we also thank Arthur D. Little, Inc. for the use of its facilities in the final preparation of the manuscript.

Finally, we can only indicate in print, but not truly express our thanks to those "silent contributors" without whom this book never would have been completed. In the preface of an earlier American Chemical Society Monograph, "The Furans," written by A. P. Dunlop and F. N. Peters, this contribution is expressed so well that we can do no more than repeat it.

"This is the spiritual aid, the comforting words, the sacrifice of social contacts, the job of keeping the children quiet—all uncomplainingly given over a number of years by our wives. No one who is not simultaneously a husband, father, and author can appreciate how deeply grateful we are for this help, the more so since there can be no adequate recompense."

If we add to this their work as secretaries, and even as technical assistants in our task to prepare this monograph, it is only as a poor compensation for their sacrifices that we dedicate this book to them.

Attila E. Pavlath

September, 1962

Amos J. Leffler

USE OF THE TABLES

At the end of Chapters III to VIII are tables containing all of the fluorinated aromatic compounds reported in the literature up to the 1958 Formula Index of *Chemical Abstracts*. These are arranged according to the following system:

Chapter III. Compounds Containing Carbon, Hydrogen, and Fluorine.

- A-1 Benzene substituted
- A-2 Biphenyl derivatives
- A-3 Condensed ring systems
- A-4 Unsaturated side chains
- B-1 Side-chain fluorinated
- B-2 Unsaturated side-chain fluorinated
- C Mixed nuclear and side-chain fluorinated

Chapter IV. Compounds Containing Other Halogens in Addition to the Foregoing Elements.

Chapter V. Compounds Containing Oxygen in Addition to the Previous Elements.

- A- Phenols (Derivatives: ethers, peroxides, and esters including phosphate esters)
- B- Alcohols (Derivatives: ethers, esters, and urethanes)
- C- Aldehydes (Derivatives: oximes, hydrazones, and semi-carbazones)
- D- Ketones (Derivatives as for aldehydes)
- E- Quinones
- F- Acids (Derivatives: esters, nitriles, amides, azides, acyl halides, peracids, and hydrazides)

Some nitrogen derivatives are listed here because they are derivatives of the groups discussed in this chapter and are not repeated in Chapter VI.

Chapter VI. Compounds Containing Nitrogen in Addition to the Previous Elements.

- A- Nitro
- B- Amino (Derivatives: N-alkyl, aryl and acyl), A diphenyl-

amine is listed according to the fluorine containing amine from which it can be derived. If both rings contain fluorine it is listed in both possible ways.

- C- Nitroamino (Derivatives as in B)
- D- Azo
- E- Hydrazines, nitroso, isocyanates

Chapter VII. Compounds Containing Sulfur, Metal or Metalloid Atoms in Addition to the Previous Elements.

- A- Compounds containing sulfur. The disulfides are listed under the corresponding mercaptans while sulfoxides and sulfones are separately listed. Under sulfonic acids are listed amides, halides and esters.
- B- Compounds containing silicon
- C- Compounds containing other metals and metalloids

Chapter VIII. Compounds Containing Fluorine Attached to Heterocyclic Rings.

- A- Rings containing oxygen
- B- Rings containing sulfur
- C- Rings containing nitrogen
- D- Rings containing more than one nitrogen atom
- E- Rings containing oxygen and nitrogen
- F- Rings containing sulfur and nitrogen

The derivative rules apply here also to the individual functional groups.

The compounds are tabulated according to major functional groups with each table listing compounds containing all previously listed groups as well as that of the group being listed. For instance in Table VI-A are listed nitro compounds containing carboxyl groups. If a list of all of the aromatic fluorinated carboxylic acids was desired it would be necessary to search all of the later tables to find the substituted acids. In order to avoid this effort a list of acids containing other groups discussed in later chapters has been placed at the end of the chapter. This has been done for all groups including those in the same chapter but in succeeding tables.

The formula listing system has been modified from that used by *Chemical Abstracts* in order to make it more useful for fluorine chemistry. The following element order is used: increasing carbon, increasing fluorine, decreasing hydrogen, other elements in alphabetical order in increasing number. This system causes

the simplest fluorine containing compounds to appear first rather than the perfluorinated materials. It also causes all compounds that are monofluoro, difluoro, and so on to appear in order, rather than this being controlled by the number of hydrogen atoms present. In order to permit rapid comparison with the Formula Index of *Chemical Abstracts* a separate table has been prepared which uses the C. A. system and the number of the compound in the property tables. This allows the user to have the advantages of both systems.

In the tabulation of the compounds, derivatives are listed indented below the parent compound in order of increasing complexity. This system was chosen because the main difficulty encountered in preparative chemistry is making a specific structure, while functional groups can be modified with relative ease. Thus a phenol can be readily converted into a methoxy or ethoxy group, and the latter are listed as derived from the phenol.

Because of limited space in the main tables it was not possible to include much available data. However, available spectral data is especially important and this has been added at the end of each chapter using the code number of the compounds and references. The following abbreviations are used:

UV, IR, R, MW, NMR	= ultraviolet, infrared, Raman, microwave and nuclear magnetic resonance spectra in total or part
p	= vapor pressure equation
V	= molar volume
ΔH	= heat of oxidation or formation
α	= coefficient of expansion
Therm.	= other thermodynamic properties
D	= density as a function of temperature
n	= refractive index at other wavelengths than NaD
Flash	= flash point
Eut.	= eutectics, freezing point diagrams, heat of fusion cryoscopic properties
Az.	= azeotropes, boiling point diagrams,
Cryst.	= crystalline structure
Struct.	= bond distance, electronic structure, electron diffraction
Rad.	= radiation, ionization potential, X-ray spectrum
$[\alpha], \gamma, \epsilon, \eta, \mu$	= optical rotation, surface tension, dielectric constant (including Kerr constant), viscosity, dipole moment
P	= parachor
K	= dissociation constant, acidity, basicity constants
Phos.	= phosphorescence, fluorescence, scintillation
Chrom.	= chromatography, absorption
Misc.	= miscellaneous physical properties: ultrasonic velocity, photovoltaic properties, polarography, etc.
rk.	= kinetics of formation or reaction
Nucl.	= nucleophilic reactivity
Pol.	= polymerization

Sol.	= solvolysis, solvent effect, solubility
Compl.	= complex and chelate formation
σ	= Hammett constant
React.	= other reactions: isomerization, racemization, hydrolysis, quaternization, etc.
Cat.	= catalytic effects: antioxidant, antiknock agent, stabilizer, inhibitor
Deh.	= dehydrogenating agent
Anal.	= analysis and analytical application
Bio.	= biological and biochemical effects, antimetabolite, bacteriostatic effect (see Pharm. also)
Pharm.	= pharmacological application and effects (see Bio. also)
Carc.	= carcinogenic and anticarcinogenic effect
Tox.	= toxicity, LD ₅₀ , LC ₅₀
Pept.	= peptide reagent
Plant.	= herbicide, growth regulator, phytotoxicity, action on plant cells
Pres.	= fungicide, wood preservative, fumigant, mildew prevention agent
Ins.	= insecticide, miticide, ascaricide
Dye	= dyestuff, diazo component, coupling component
Flame.	= flameproofing agent
Vulc.	= effect in vulcanization
Lubr.	= lubricant

The code number of a compound indicates the chapter, table in the chapter, and number in the table. For example, V-A-231 indicates a compound in Chapter V, the first table, and the 231st compound of the table. The naming of the compounds is according to the usual practice. In cases where it is obvious, the derivative is indicated without repeating the entire name of the parent compound or referring to it by the abbreviation "C." However, where there is some question or the derivative has a different name, the entire new name is indicated. For example, p-fluoroanisole is so listed and not as the methoxy derivative of p-fluorophenol. Yields are given whenever reported and in some cases, where amounts are given, were calculated from these figures. Boiling and melting points are given in centigrade. If several references are given for a particular value the most probable figure has been chosen. Boiling points are first listed at atmospheric pressure and if more space is available at other pressures.

All references in which the same method of preparation was used are listed together unless the product was reported to have very different physical properties. (To facilitate pagination of the book, these references are placed at the end of the tables of data for each chapter). In some cases only applications or spectral data are listed for compounds for which the methods of preparation and physical properties are either not well determined or are to be published at a later date. Correspondence with the author is the only way to obtain this information prior to publication.

In order to indicate the method of preparation of each compound without writing a detailed reaction, a table of methods has been drawn up and listed below. This will enable the user to obtain an idea of the various methods used without consulting the original literature. In some cases the methods are rather general since they cover a wide number of reactions. It is strongly recommended that the reader consult the original literature or at least *Chemical Abstracts* for details of preparation before going to the laboratory.

METHODS OF PREPARATION

- I- The introduction of fluorine by the use of a complex diazonium fluoride such as a diazonium fluoroborate, diazonium fluorophosphate, or a diazonium silicofluoride.
- II- Introduction of fluorine by diazotization in anhydrous hydrogen fluoride or by treatment of diazonium derivatives with hydrogen fluoride.
- III- Introduction of fluorine by replacement of another halogen or other group except hydrogen or amino by metal fluorides or hydrogen fluoride. Both nuclear and side-chain atoms are included.
- IV- The introduction of fluorine by substitution or addition using elementary fluorine, halogen fluorides or metal fluorides of higher valence. The addition of hydrogen fluoride is also included.
 - 1- The introduction of halogens either by addition of the elementary halogen or hydrogen halide or by replacement of hydrogen with a halogen. The replacement of hydroxyls or amino groups by halogen is not included.
 - 2- The introduction of nitro or nitroso groups by replacement of hydrogen or addition to an unsaturated system. The replacement of halogen or amino groups is excluded.
 - 3- The introduction of a tetra- or hexavalent sulfur-containing group as in 2.
 - 4- Alkylation of an aromatic ring. The acylation of a carbon atom or alkylation of hetero-atoms is excluded.
 - 5- The acylation of an aromatic ring only where the keto group enters alpha to the ring. Acylation of the side chain or heteroatoms is excluded.
 - 5a- Substitution of an aromatic hydrogen by a metal or metalloid.
 - 6- Oxidation and intermolecular disproportionation reactions.

- 7- Hydrogenation of unsaturated linkages and reduction of nitro, carbonyl, and sulfonyl groups. The replacement of halogens by hydrogen is included but deamination is excluded.
- 8- The replacement of amino groups by diazotization except hydrogen; halogen exchange, and introduction of nitro or cyano groups by the appropriate metal salts. The introduction of alkoxy, acyloxy, and corresponding nitrogen and sulfur-containing groups is excluded.
- 9- The addition or condensation involving a carbonyl linkage without formation of a new carbon-carbon linkage. Hydrolysis of nitriles is not included.
- 10- Ring formation, coupling, and CO or CO₂ additions as well as any addition or condensation reaction not included in 4 and 5.
- 11- Alkylation and acylation of oxygen, nitrogen, and sulfur atoms excluded in 8. The replacement of hydroxyls or amino groups by halogen also is included.
- 12- Hydrolysis of esters, ethers, amides, nitriles, and carbon-carbon bonds.
- 13- The intramolecular elimination of all groups as well as deamination and decarboxylation.
- 14- Rearrangement and degradation reactions.

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I. PREPARATION OF AROMATIC FLUORINE COMPOUNDS

It is only recently that fluorine chemistry has begun to receive the careful attention its unique reactions deserve. This is due to the slow development of preparative methods and of a technology that allows handling of these compounds. The field of aromatic fluorine chemistry is actually older than aliphatic fluorine chemistry, but its growth has been slower because of the difficulty of introducing fluorine into an aromatic molecule. Fluorine is the most electronegative of the elements and its reactions differ greatly from the other halogens not only in degree, but in type, making fluorine chemistry a special field similar to organic chemistry, but with somewhat different "ground rules."

Fluorine differs from other halogens in that it cannot be introduced into an aromatic ring by direct reaction because of its great reactivity. This has necessitated the development of special methods and has been both difficult and slow. Less difficulty has been encountered in the preparation of side chain-fluorinated materials which resemble aliphatic fluorine compounds in reactivity and properties and more is known of them.

Aromatic fluorine compounds have been prepared by substituting fluorine for other atoms in aromatic starting materials and by synthesis from fluorinated aliphatic compounds. More complex molecules are usually prepared by general synthetic methods from simple fluorinated aromatic compounds. This will be discussed in later chapters.

The choice of methods is usually determined by the degree of fluorination of the desired compound. Molecules with small numbers of fluorine atoms are prepared by substituting fluorine for other groups. These groups may include hydrogen, amino, and other halogens, depending on the starting material. The high reactivity of elementary fluorine and its derivatives such as halogen fluorides has been an obstacle to direct fluorination, and it is only recently that progress has been made in this method. Amines are converted to fluorinated compounds through a diazotization procedure, and a number of different variations have been worked out and will be discussed in detail. The method suffers from unavailability of some amines, unreactivity, or in some cases in-

stability of the starting material, as well as complex side reactions of the intermediate diazonium compounds during decomposition. Recently the nucleophilic substitution of activated halogen atoms by inorganic fluorides has been studied and found to be applicable in aromatic molecules. The method is limited because of the need for activating groups such as nitro and trifluoromethyl, but is useful in many cases, where the diazotization methods fail.

Highly fluorinated aromatic compounds are more easily prepared from aliphatic fluoro compounds either by aromatization of highly fluorinated cycloaliphatic compounds or by forming aromatic rings from small aliphatic units. This is a new approach and only a small number of compounds have been prepared in this way, but it can be expected to grow rapidly in the future.

A. Direct Fluorination

In an aromatic compound there are two possible types of hydrogen atoms: those attached to the nucleus and those on side chains when the latter are present. The substitution of the second type is difficult, but can be accomplished successfully in aliphatic compounds, while very little success has been obtained until recently in the replacement of aromatic hydrogens. The basic difficulty is the great reactivity of the fluorine molecule that destroys the aromatic system and forms cyclic or straight-chain aliphatic fluorine compounds. This is the reverse of the situation that is found in the other halogens in which substitution is the normal reaction and special conditions are necessary for addition.

It was initially assumed that the failure to obtain aromatic fluorine compounds was due to the large heat of reaction which caused extensive destruction of the starting material. In Table 1.1 are shown the energies involved in substitution of one hydrogen by a halogen and in the addition of a halogen molecule to an aromatic double bond. Also shown are the energies of halogenation of an olefinic double bond, the complete saturation of the benzene ring, and the breakage of a carbon-carbon single bond by halogen.

An examination of the table shows that the heats of reaction of fluorine with organic molecules are much larger than those of the other halogens. Reaction of fluorine in any way will yield more energy than is required to rupture any bond in an aromatic hydrocarbon. This can be seen by comparing the 104.6 Kcal evolved in substitution of a fluorine for a hydrogen or 100.3 Kcal evolved in the addition of a fluorine molecule to an olefin with the energy of 98.8 Kcal of a carbon-hydrogen bond and 147.0 Kcal of a carbon-carbon double bond. In order to have either substitution or addition instead of destruction, some means must be found to dissipate

TABLE 1.1

HEATS OF REACTION OF HALOGENATION OF VARIOUS BONDS IN KCAL/MOL*

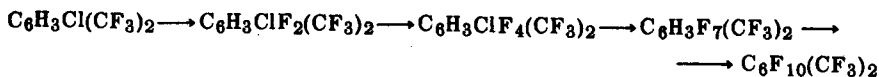
Type of Reaction	Fluorine	Chlorine	Bromine	Iodine
Substitution of one C—H in benzene	104.6	24.9	8.5	-6.1
Addition of X ₂ to an aromatic double bond**	68.8	3.1	-10.2	-17.2
Addition of X ₂ to an olefinic double bond	100.3	35.1	21.8	14.8
Complete saturation of benzene ring/3	88.0	22.8	9.5	2.5
C—C + X ₂ → 2C—X	91.1	15.9	2.6	-4.4

*Values are calculated on the basis of bond and resonance energies given in Pauling, L., "The Nature of the Chemical Bond," 3rd edition, Cornell University Press, 1960.

**The product is a dihalo-cyclohexadiene.

the energy of the reaction. This situation does not occur with the other halogens where the energies of substitution and addition are less than the bond energies.

The most obvious method of controlling an extremely exothermic reaction such as fluorination is by dilution with an inert material such as nitrogen. In the case of benzene only saturated compounds such as perfluorocyclohexane and fluorinated ring fragments were obtained from the reaction (828). A small amount of undecafluorocyclohexane was also found. Starting with a deactivated ring system such as 2,4-bis(trifluoromethyl)chlorobenzene a number of intermediates have been obtained, all of which were either saturated or partially saturated fluorocycloaliphatic compounds, as shown below(216,2236).



It can be seen that there was no hydrogen substitution of the intermediate compounds until all unsaturation was removed.

In other cases the use of anhydrous hydrogen fluoride as solvent for the fluorination of aromatic compounds was not successful since no aromatic fluorine compounds were obtained (399/a,-837/a,1736).

Another method that has been tried for fluorine substitution is