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Organic Fluorine Chemistry

Expanding rapidly, the science of these compounds has assumed both theoretical and practical importance.

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Fluorinated organic compounds attract attention mainly because of dramatic differences between their properties and those of ordinary hydrocarbon compounds. Ultimates in chemical resistance and thermal stability, extraordinary behavior in such different areas as outdoor durability and surface activity, and extremes of biological activity are often associated with fluorocarbons. Another fascinating aspect of organic fluorine chemistry is the fact that it is not a chemistry of compounds occurring in nature and so is not really "organic." Apart from minerals, only a few derivatives of fluorine occur naturally at levels above trace amounts (*1*). Those working in the field, therefore, have an awareness of having built a whole chemistry, almost all of it within the last 25 years.

The inception of organic fluorine chemistry can be traced to Henri Moissan's preparation and identification of the elusive and violently reactive element fluorine in 1886. His subsequent chemical studies (*2*) and those of Ruff (*3*), another pioneer, gave the first clues to the formation of fluorocarbons.

This small beginning was broadened into a foundation for organic fluorine chemistry by the Belgian chemist Swarts (*4*) and later by Henne in the United States (*5*). They developed the first general methods for formation of the carbon-fluorine bond, especially by exchange of the chlorine in organic chlorides for fluorine. This reaction, when accomplished by the use of hydrogen fluoride and catalytic amounts of antimony chlorides or fluorides, made many fluorochemicals accessible in quantity. Soon the unexpected stability, low toxicity, and volatility of the lower chlorofluorocarbons was recognized, and their commercialization as refrigerants followed. Synthesis of the important refrigerant dichlorodifluoromethane is illustrated in Fig. 1 as an example.

Increasing numbers of chemists entered the field during the 1930's. All were still hampered by the conviction that fluorocarbons, like chlorocarbons, would be inherently unstable if a chain of carbon atoms longer than three or four were present. Then Simons and Block reported the reaction of fluorine with carbon to give small amounts of completely fluorinated liquids containing seven and more carbon atoms per molecule (*6*). These remarkable materials, members of the class now termed fluorocarbons, were found to be both thermally and chemically very stable. Recognition of organic fluorine chemistry as a large and important area of chemistry was now possible.

The properties of these fluorocarbons coincided with those required for materials used in handling uranium hexafluoride. Manipulation of this corrosive uranium compound was one of the keys to the atomic energy program, so the search for better ways of synthesizing fluorocarbons was intensively pursued in this country during World War II (*7*). Eventually two methods for the complete but controlled fluorination of organic compounds by potent fluorinating agents were developed.

Hydrocarbons are easily fluorinated by fluorine gas, but the vigor of this reaction causes extensive decomposition. Fluorinations with elemental fluorine, moderated by various mixing techniques in the presence of copper screening or silver-plated copper, were studied by many workers, among them Bigelow (*8*) and Cady (*9*). With the use of such modifications, hydrocarbons such as benzene are easily saturated and all the hydrogen replaced by fluorine, as shown in Fig. 2. Success with this method was followed by development of the more adaptable metal fluoride route by Fowler (see *7*) and others. Metal fluorides with higher valences, notably cobalt trifluoride, were found to give relatively clean syntheses of fluorocarbons from hydrocarbons and halogenated hydrocarbons. With these techniques the gulf between partially fluorinated and completely fluorinated, or perfluorinated, organic materials had been spanned.

Free-Radical Chemistry

Characterization of the new fluorocarbons showed that even members with high molecular weights were stable up to nearly 400°C and decomposed very slowly at 400°C. Both caustic soda and sulfuric acid have no effect at 300°C. Resistance to strong oxidizing and reducing agents is excellent. These unusual properties are also shown, but to a lesser degree, by the chlorofluorocarbons prepared for the war effort by polymerization of

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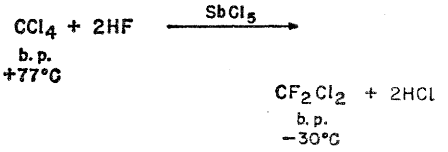
chlorotrifluoroethylene (*10*). These polymeric oils and solids can be converted by reaction with such agents as cobalt trifluoride to very stable materials containing little residual chlorine. An example of this route is given in Fig. 3. Relative ease of preparation and low requirements for elemental fluorine (or a metal fluoride derived from it) are real advantages of the fluoropolymer route. Polymers from tetrafluoroethylene were developed independently (*11*), making fluorocarbons with high molecular weights available for the first time. Since the molecular weight of this completely fluorinated polymer chain is easily controlled by the proper choice of reaction conditions, a practical alternative to fluorination of short-chain hydrocarbons was provided as well.

Polymerization of fluorinated olefins can now be recognized as a major advance in organic fluorine chemistry. Contrary to some early expectations, the spatial requirements for three or four fluorine atoms attached to an olefinic double bond are not great enough to inhibit polymerization. The realization in the 1930's that such tetrasubstituted olefins as chlorotrifluoroethylene and tetrafluoroethylene are easily polymerized with free radicals as catalysts opened the doors to a tremendous number of completely and partially fluorinated polymers. Many olefins with substituents such as hydrogen, chlorine, or a fluoroalkyl group in addition to fluorine atoms were synthesized, polymerized, and copolymerized to both high- and low-molecular-weight materials. After this work, the versatility of fluoroolefins in the polymerization reaction was established, and methods for the synthesis of fluoroolefins were available.

Fluoropolymers offer a spectrum of special properties that led to commercialization in the 1940's and 1950's of both resins and elastomers based on the monomers shown in Fig. 4. Homopolymers and various copolymers of these monomers provide inert, insoluble materials into which can be tailored such properties as low coefficient of friction, low power loss, or flexibility at low temperature.

The effect of discoveries in the free-radical polymerization of fluoroolefins was soon felt in the fluorochemical field. Conditions for the formation of low-molecular-weight waxes and oils were translated into systems designed to give polymers of very low molecular weight. Such materials, containing from one to ten or more units of monomer per molecule, have chemical and physical properties which depend heavily on the end groups as well as on the internal polymer chain. These fluorochemicals, or telomers, are available in nearly endless variety. Their preparation is illustrated in Fig. 5 by a reaction of tetrafluoroethylene with an alcohol. The fluorinated alcohols, esters, halocarbons, ethers, sulfides, and other functional group types emanating from studies of the free-radical chemistry of fluoroolefins helped provide a broad base for fluorochemicals as well as fluoropolymers (*12*). These studies also provided important information on factors involved in free-radical addition to a double bond: steric effects, electronic influences, and, especially, stability of radical intermediates.



$$\underset{\text{b. p. } +77^\circ\text{C}}{CCl_4} + 2HF \xrightarrow{SbCl_5} \underset{\text{b. p. } -30^\circ\text{C}}{CF_2Cl_2} + 2HCl$$

Fig. 1. Synthesis of dichlorodifluoromethane by halogen exchange.

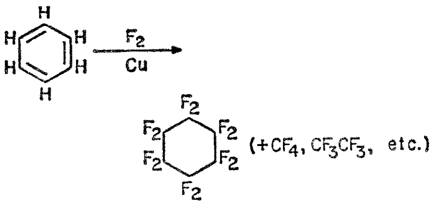
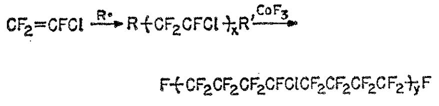


Fig. 2. Direct fluorination of benzene.



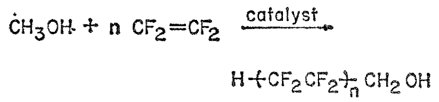
$$CF_2{=}CFCl \xrightarrow{R\cdot} R\text{-}(CF_2CFCl)_x\text{-}R' \xrightarrow{CoF_3} F\text{-}(CF_2CF_2CF_2CFClCF_2CF_2CF_2CF_2)_y\text{-}F$$

Fig. 3. Preparation of chlorofluorocarbons.

$CF_2{=}CF_2$ $CF_2{=}CFCl$

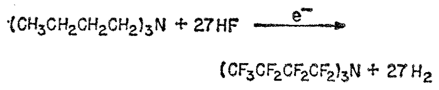
$CF_2{=}CH_2$ $CF_2{=}CFCF_3$

Fig. 4. Important fluorinated monomers.



$$CH_3OH + n\ CF_2{=}CF_2 \xrightarrow{\text{catalyst}} H\text{-}(CF_2CF_2)_n\text{-}CH_2OH$$

Fig. 5. Telomerization of tetrafluoroethylene with methanol.



$$(CH_3CH_2CH_2CH_2)_3N + 27HF \xrightarrow{e^-} (CF_3CF_2CF_2CF_2)_3N + 27H_2$$

Fig. 6. Electrochemical fluorination of tributylamine.

Organic fluorine chemistry benefited similarly from Simons's work on electrochemical fluorination (*13*). Many classes of organic compounds can be completely fluorinated by electrolysis in liquid hydrogen fluoride at potentials less than that required to liberate fluorine. The reaction involves saturation of double bonds and replacement of hydrogen atoms with fluorine atoms all in a single step, without the use of prohibitively expensive reagents and under conditions where degradation is minimized. The fluorocarbons and perfluorinated acids, ethers, and amines made electrochemically have become an important source of highly fluorinated materials. Fig. 6 shows one example out of many.

By 1950, the tremendous scope of organic fluorine chemistry was apparent. Development of some of the more accessible fluorinated compounds as aerosol propellants, surface-active agents, lubricating oils and greases, and dielectric fluids was pursued in an attempt to capitalize on some inherent properties other than sheer stability. Successful commercialization of fluorochemicals by several companies aroused further interest in the area. Research in organic fluorine chemistry by industry continued to grow, particularly in the United States. Academic interest in fluorine chemistry also increased, but was tempered by the expense and special equipment often required in such research. Another deterrent may once have been a feeling that organic fluorine chemistry was an isolated segment of chemistry, but now it clearly overlaps extensively with classical organic chemistry and fits logically into the framework of organic chemistry.

Anionic Reactions

A striking example of the extremes possible between conventional organic and organic fluorine chemistry—that is, between hydrocarbons and fluorocarbons—lies in the responses to acids and bases. Olefins are generally indifferent to bases and reactive to acids. In the special case of the proton as the acidic reagent, addition of a proton and elimination of a different proton from the intermediate carbonium ion can result in a series of equilibria between isomeric olefins. If one ignores geometric isomers and possibilities for migration of alkyl groups, the group of *n*-hexenes in Fig. 7 might be obtained starting from any member.

Fluoroolefins, on the other hand, are generally unreactive to acids and sensitive to attack by bases. The presence of extremely electronegative fluorine atoms and fluoroalkyl groups on a double bond changes that unsaturated center from one that is electron-rich and easily attacked by electrophiles to an electron-deficient center which is resistant to such attack. Understandably enough, the double bond is instead attacked by nucleophiles. As Miller *et al.* have pointed out (*14*), the fluoride ion is uniquely related to fluoroolefin chemistry in the same way the proton is related to chemistry of hydrocarbon olefins. Migration of double bonds can be accomplished by addition and elimination of fluoride ions as shown in Fig. 8.

The intermediate carbanions are stabilized by branching with fluoroalkyl groups, just as carbonium ions are stabilized by alkyl groups. A resonance effect similar to the hyperconjugation of alkyl groups may be in operation, allowing distribution of the negative charge as indicated in Fig. 9. Such a carbanion, prepared either from the fluoroolefin and an anion or by removal of a cation (usually a proton) from the corresponding fluoroalkane, has sufficient longevity and reactivity in many environments to serve as an intermediate.

Recently discovered anion chemistry of fluoroolefins is indicative of the breadth available for both substitution and addition chemistry (*15*). Often either type of reaction can be made to occur, depending on the presence of a suitable trapping agent for the fluorocarbanion, as illustrated by Fig. 10.

Moreover, fluoride ion can catalyze these condensation reactions of a fluoroolefin, either with another substrate or with itself. Two examples from many are presented in Fig. 11.

Advances in our knowledge of anion chemistry of fluoroolefins are continuing, and vigorous expansion of anion chemistry into other areas has also begun. Fluoroaromatic compounds, by which is meant aromatic rings bearing a multiplicity of fluorine atoms, have been synthesized in large numbers. Hexafluorobenzene, obtainable by a number of routes, is a principal intermediate to other fluoroaromatics through substitution reactions with bases. Attack on a ring carbon atom with displacement of fluoride occurs readily, even when the base is an uncharged nucleophile such as ammonia (Fig. 12). Pursuit of this chemistry, largely in England up to this point, is spreading.

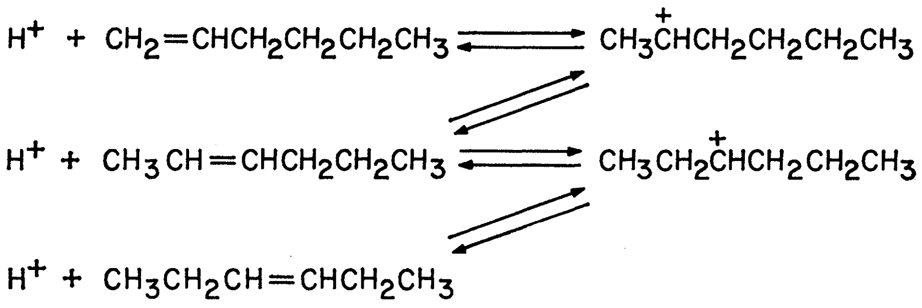


Fig. 7. Double bond migration in hexenes.

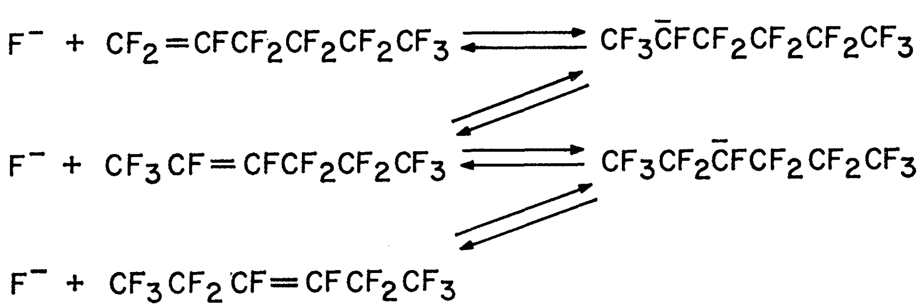


Fig. 8. Double bond migration in perfluorohexenes.

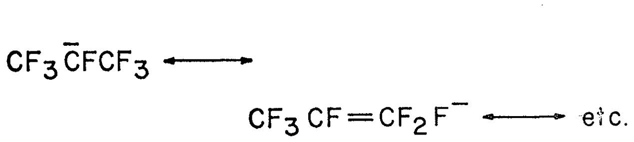


Fig. 9. Possible stabilization mechanism for fluorocarbanions.

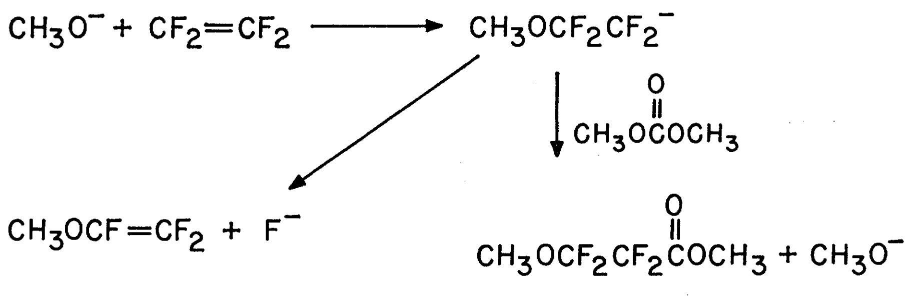


Fig. 10. Reactions of fluorocarbanions.

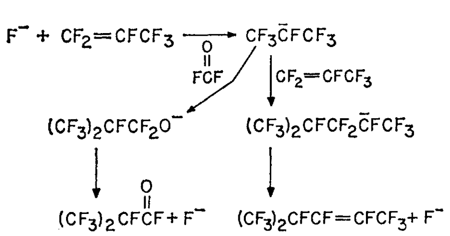


Fig. 11. Catalysis by fluoride ion.

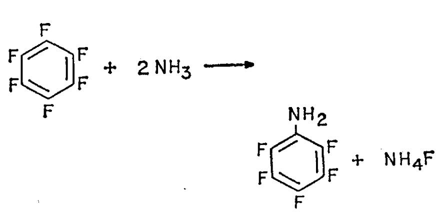


Fig. 12. Substitution reaction of hexafluorobenzene.

Recent Developments

Simultaneously with these studies of the electrophilic character of unsaturated fluorocarbons, free-radical chemistry received further attention. Some of the newer fluorocarbon products with unusual properties came out of this work. For example, copolymerization of tetrafluoroethylene with hexafluoropropylene provided a completely fluorinated thermoplastic which can be formed into clear tough sheets or coatings by conventional methods. In contrast, polytetrafluoroethylene must be fabricated by special techniques because of its insolubility and high melting point. Polymer from vinyl fluoride contains little fluorine, but happens to be extremely resistant to outdoor exposure and is now used as a protective coating to impart weatherability to many substrates. Poly(vinylidene fluoride) has properties which make it an effective and readily extruded electrical insulating material. Polymers containing highly fluorinated branches only six to eight carbons in length are amazing in their ability to prevent soiling. Waxes prepared from tetrafluoroethylene are effective dry lubricants and mold release agents. No doubt many other fluoropolymers and fluorochemicals will appear in the next few years.

Research on which the rising comercial significance of organic fluorine chemistry is based has continued to provide results of scientific interest. This is true of physical studies, for instance, of surface phenomena underlying the property of oil and water repellency, and is particularly true of chemical studies. An important example is the synthesis of tetrafluoroethylene, shown in Fig. 13.

This pyrolysis and the attendant side reactions involve difluorocarbene, a relatively stable species which can be observed spectroscopically under synthesis conditions. As indicated by the second equation in Fig. 13, tetrafluoroethylene can dissociate to difluorocarbene at elevated temperatures. At high enough pressures and long reaction times, addition of the carbene to another molecule of tetrafluoroethylene proceeds to form hexafluoropropylene and, further, isomeric octafluorobutenes (Fig. 14).

Other methods of generating and studying difluorocarbene have been devised. This carbene is apparently one of few in which the ground state is singlet (paired electrons) rather than triplet (unpaired electrons). More recently, carbenes bearing fluoroalkyl branches have also been formed and reacted as true chemical intermediates. Such findings take fluorine chemistry beyond the bounds of hydrocarbon chemistry.

Cycloaddition reactions are of great importance in fluoroolefin chemistry, since the reactions will proceed readily to give cyclobutane rings. Formation of these four-membered rings is difficult with hydrocarbon olefins, but strongly favored for fluoroolefins, even when formation of the usual six-membered rings is a possibility. Tetrafluoroethylene, for instance, will cyclodimerize to octafluorocyclobutane at 200°C under moderate pressure. Cycloaddition of tetrafluoroethylene to butadiene occurs so rapidly, however, that good yields of mixed cycloadduct can be formed, and it is the four- rather than six-membered ring product that is obtained as shown in Fig. 15. Fluoroketones such as hexafluoroacetone do form six-membered ring adducts when heated with butadiene (Fig. 15). This is in contrast to other ketones, which give no thermal adducts at all with butadiene.

$$CF_2HCl \rightleftharpoons HCl + CF_2:$$

$$2CF_2: \rightleftharpoons CF_2{=}CF_2$$

Fig. 13. Synthesis of tetrafluoroethylene.

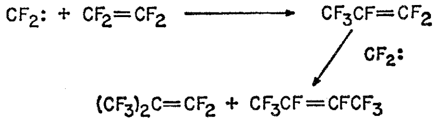


Fig. 14. Insertion of reactions of difluorocarbene.

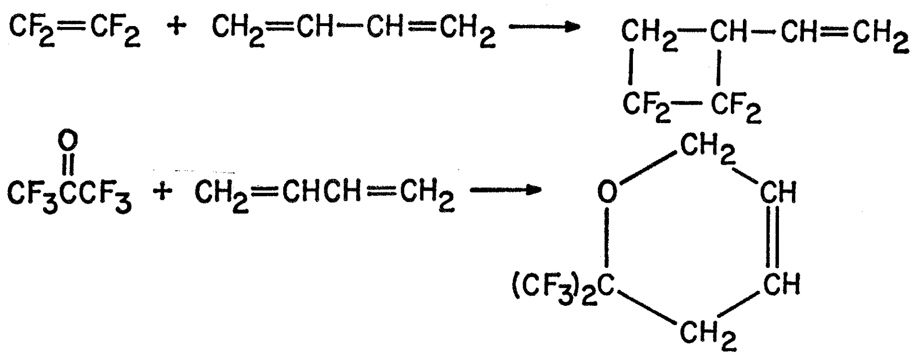


Fig. 15. Cycloaddition reactions.

$$CF_3I \longrightarrow I\cdot + CF_3\cdot \xrightarrow{S_x}$$

$$CF_3S_xCF_3 \longrightarrow CF_3SSCF_3$$

Fig. 16. Reaction of trifluoromethyl radical with sulfur.

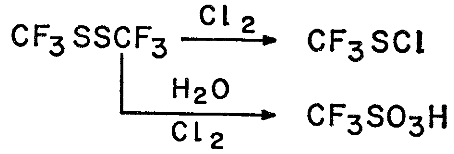


Fig. 17. Oxidation of fluorinated disulfides.

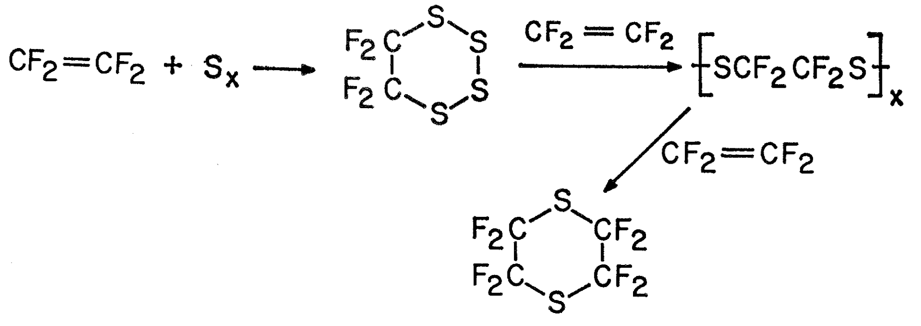


Fig. 18. Reaction of sulfur radicals with a fluoroolefin.

Derivatives of Nonmetals

Free radical intermediates have been effective in forming perfluoroalkyl derivatives of such elements as sulfur, phosphorus, and arsenic. The initial problem of finding a suitable source of perfluoroalkyl radicals was solved by the use of perfluoroalkyl iodides. This class of compounds undergoes homolysis of the carbon-iodine bond cleanly and easily when heated to 200°C or when irradiated with ultraviolet light. With this convenient source of radicals, the susceptibility of many substrates to attack has been probed. Reactions with many nonmetals are particularly successful, yielding a variety of unusual structures. Fig. 16 sets forth an appropriate example, the interaction of trifluoromethyl iodide with sulfur at high temperatures. Polysulfide chains of various lengths and capped with trifluoromethyl groups are formed initially, but sulfur is slowly eliminated at reaction temperature to give bis(trifluoromethyl) disulfide as the main product. The disulfide can be converted by chlorine to a reactive sulfenyl chloride or oxidized to a stable and very strong sulfonic acid by chlorine and water (Fig. 17). The extensive studies of fluoroalkyl groups attached to sulfur and other heteroatoms have provided information on bonding and reactivity at the heteroatom as well as for the fluoroalkyl group.

Formation of fluoroalkyl derivatives of elements such as sulfur can also be accomplished by the opposite scheme, which involves attack of sulfur free-radicals on a fluorocarbon. For example, sulfur and tetrafluoroethylene can be directed to any one product in the series shown in Fig. 18 by proper control of reaction conditions. Sulfur, or thiiyl, radicals are involved in each step.

Metals as well as metalloids can form stable bonds to fluoroalkyl groups. Strongly electropositive metals, including lithium, magnesium, and sodium, form unstable derivatives which have nevertheless found some use in fluoroalkylation reactions. These fluoroorganometallics tend to decompose at 0°C by *β*-elimination (process *a* of Fig. 19), or, if *a* is not possible, by *α*-elimination (process *b* of Fig. 19). Less positive metals such as tetravalent silicon and tin form more covalent bonds with fluoroalkyl groups, so that these derivatives are more stable with respect to elimination of metal fluoride. Decomposition usually requires heating and can be by *α*- or *β*-elimination. The *α*-elimination reaction is frequently used as a source of fluorinated carbenes. At least one metal, mercury, forms very stable fluorinated derivatives which undergo homolytic scission on heating (process *c* of Fig. 19). Illustrative examples appear in Fig. 20.

The electronegative fluoroalkyl group attached to a metal atom accepts a major share of the electron pair constituting the bond. The ionic character thus introduced stabilizes the bond further. A clear demonstration of this effect is the formation of very stable fluoroalkyl derivatives of transition metals. For instance, CF_3- can be attached to iron by a stable sigma bond in a compound, $CF_3Fe(CO)_4I$, where the corresponding CH_3- derivative would probably be unstable. Unsaturated fluorocarbons can form stable structures having probable pi-bonding with transition metals. In cases such as $[(C_6H_5)_3P]Ir(CF_2{=}CF_2)(CO)Cl$ and $(C_5H_5)Co(CF_3C{\equiv}CCF_3)_2$ the structures containing fluoroolefin and fluoroacetylene seem more thermally stable than their hydrocarbon counterparts. Derivatives in which such unsaturated fluorinated groups as trifluorovinyl or pentafluorophenyl are sigma-bonded to the metal decompose much less readily than saturated derivatives. Loss of metal fluoride is difficult in these cases because very energetic triple bonds are formed. These organometallic derivatives can therefore be used rather freely as reagents for effecting substitutions on fluoroolefins and fluoroaromatics, as well as to generate fluoroacetylenes and fluorobenzynes.

New Fluorinating Agents

The developments referred to above and many additional important results indicate that organic fluorine chemistry has come of age. It now encompasses most of the chemical elements and is parallel to and interwoven with classical organic chemistry. Increasingly sophisticated methods and concepts are used for investigations in this area, and many of the old obstacles have been toppled. Even the early problem of effective, but not drastic, fluorinating agents has been given a new, improved solution by the use of sulfur tetrafluoride. The value of this reagent lies in its specificity in converting hydroxyl and carbonyl groups to the corresponding perfluorinated groups, for example $-CO_2H$ to $-CF_3$, under mild conditions. Such transformations were not feasible previously and have made whole new groups of compounds available. For example, alkanes with trifluoromethyl groups at the ends have been prepared with the aid of sulfur tetrafluoride (Fig. 21). Medicinals bearing trifluoromethyl groups are often proving to be particularly efficacious. A number of new drugs have appeared, for example a tranquilizer of the phenothiazine class, in which im-

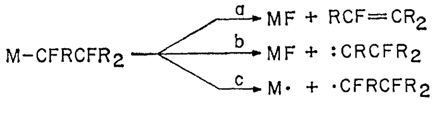
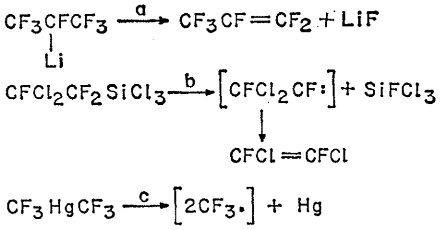


Fig. 19. Modes of decomposition of fluoroorganometallic compounds.

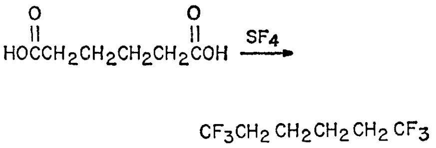


$$CF_3\underset{\displaystyle |\atop Li}{C}FCF_3 \xrightarrow{a} CF_3CF{=}CF_2 + LiF$$

$$CFCl_2CF_2SiCl_3 \xrightarrow{b} [CFCl_2CF\!:] + SiFCl_3 \quad [CFCl_2CF\!:] \rightarrow CFCl{=}CFCl$$

$$CF_3HgCF_3 \xrightarrow{c} [2CF_3\cdot] + Hg$$

Fig. 20. Variation of decomposition path with metal.



$$HO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OH \xrightarrow{SF_4} CF_3CH_2CH_2CH_2CH_2CF_3$$

Fig. 21. Fluorination with sulfur tetrafluoride.

$$XeF_4 + CH_2{=}CHCH_3 \longrightarrow XeF_2 + CH_2FCHFCH_3$$

Fig. 22. Fluorination with xenon tetrafluoride.

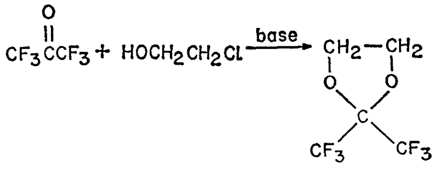


Fig. 23. Ketal formation from a fluoroketone.

proved activity is related to the presence of trifluoromethyl groups.

The recent discovery of fluorides of the rare gas xenon shattered a longstanding belief that the rare gases are incapable of bonding with another element. Not one, but three different fluorides have been isolated and characterized. These compounds (XeF_2, XeF_4, and XeF_6) vary markedly in strength of Xe—F bond. XeF_6 is an extremely active fluorinating agent, while XeF_2 is quite stable. XeF_4 is a convenient source of fluorine, combining moderate reactivity with ease of handling in reactions such as the addition of fluorine to the double bond of propylene, shown in Fig. 22.

Future Growth

Truly remarkable advances have been made during recent years in contrast to the rather slow and laborious beginning. Now the very size of organic fluorine chemistry makes it an impressive field. Judging by one of the best measures of its potential, namely numbers of academic and industrial groups around the world doing research and development, a continuing period of discovery and growth is at hand. Interest in organic fluorine chemistry as an area of science is high, and many directions for fruitful research are apparent. Much is yet to be learned about such general subjects as chemistry of fluorinated aromatic compounds, heterocycles, polymers, and organometallics. Even such a common functional group as the carbonyl group seems destined to yield novel chemistry when placed in a fluorocarbon environment. For instance, in complete contrast to reactions observed with nonfluorinated ketones, fluoroketones undergo a base-catalyzed formation of cyclic ketals (Fig. 23). Moreover, once formed, these ketals are insensitive to oxidation or to the action of acids and bases, quite unlike their hydrocarbon analogs. These and many other unusual findings provide indications that fluoroketones will prove to possess a chemistry very different from that of nonfluorinated ketones.

Many studies can be carried out with greater subtlety and precision than was possible before, so that our knowledge will become more profound as well as more extensive. Certainly studies in fluorine chemistry can contribute greatly to our understanding of free radicals and anions. Spectral techniques, particularly nuclear magnetic resonance and mass spectroscopy, should allow better definition of bonding situations of fluorine in various molecules. Explanations for many of the unusual properties of organofluorine compounds have been uncovered. Reactions that once seemed incongruous are now easily rationalized. The reasons behind the strange effects of fluorine atoms in an organic compound are thus yielding to scientific inquiry, but more discoveries and many surprises are to be expected in this chemistry of extremes.

Summary

Twenty-five years ago organic fluorine chemistry was a limited and difficult area of investigation. Research by both industrial and academic groups has transformed it into a broadly based, important segment of organic chemistry. General interest in organic fluorine chemistry has been sustained by translation of the unusual properties of fluorinated compounds into useful products. Further growth of this chemistry is occurring in many directions, and prospects are good for significant and unexpected scientific discoveries in the future.

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