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NEWSLETTER

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Chairman's Column

Bill Miller came to Cornell in 1936 from Stanford, Duke, and his native North Carolina. His span of service to Cornell and our Department thus intersects most of our professional lives — all of us have some occasion to recall him as a teacher, research advisor, colleague or just as a perceptive, congenial and valued friend.

Bill has been actively engaged in fluorine chemistry for nearly 50 years. His contributions were honored in 1974 by the American Chemical Society's Award for Creative Work in Fluorine Chemistry. On the occasion of his seventieth birthday many of his friends and colleagues contributed to a special issue of the Journal of Fluorine Chemistry, dedicated to him. Bill himself wrote a characteristically modest retrospective article about his work for that issue. It gives me great pleasure to reproduce this article for you in this Newsletter.

MY EARLY DAYS IN FLUORINE CHEMISTRY

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INTRODUCTION

First, I wish to express my deep appreciation to those who have made this issue of the Journal of Fluorine Chemistry possible. I am pleased to respond to their invitation to record some of my experiences in fluorine chemistry. It has been an important part of my life. In the following account I have tried to indicate the path that we followed in the earlier years.

My first contact with fluorine chemistry was at Duke University where I worked as a graduate student with Professor L.A. Bigelow. Professor Bigelow was interested in fluorinating aromatic compounds with elemental fluorine. However, at the time I began work unsatisfactory results were being obtained. I undertook the analysis of the fluorine being used and was able to show that considerable and variable amounts of oxygen and oxygen fluoride were present. The trouble was that the fused electrolyte which was open to the atmosphere at the cathode was hygroscopic. We constructed a closed cell which gave fluorine of high purity and obtained much improved results, in my case, first with hexachlorobenzene in the vapor phase [1,2]. I found that it was possible to show from the literature that much of the early work with fluorine was carried out with fluorine containing considerable amounts of oxygen [3] and presumably oxygen fluoride [4], a very different reagent from pure fluorine.

In 1935 when I received my Ph.D. degree there were very few positions available for chemists. I applied for a National Research Council fellowship and proposed a problem on the fluorination of chlorinated aliphatic compounds. I did not receive the fellowship. However, I considered myself fortunate to have a choice between a job with the Thomas and Hochwalt Laboratory of Dayton, Ohio and a postdoctoral appointment at Stanford University. Thomas and Hochwalt, which subsequently became the research department for the Monsanto Chemical Company, offered \$1,800. Stanford offered \$1,200 for the academic year from a grant made by the Eli Lilly Company. I chose Stanford and spent a year working on bismuth compounds which were of interest for the treatment of human syphilis. For the following year, 1936-37, I secured an instructorship at Cornell and felt that I was on my way to an academic career, salary \$1,600. Another job opportunity was to become a forensic chemist with the F.B.I.

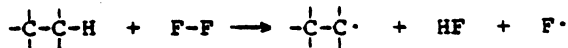
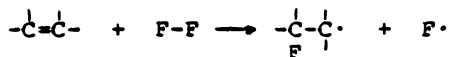
In applying to Cornell I had stated that I wished to do research on the mechanisms of organic fluorination reactions. Physical organic chemistry was developing rapidly and I was attracted to this field. At Cornell, in addition to the heavy load of elementary teaching that was customary at the time, I was encouraged to offer a graduate course entitled, 'Physical Aspects of Organic Chemistry'. This was in 1938 and was the first such course given at Cornell. I had not had any instruction in the subject and I learned a great deal. I mention this course specifically because my experience with it had a considerable influence on my own research. My first doctorate student's research, which was completed in 1941, consisted of synthesizing and studying the reactivities of a series of substituted benzyl fluorides [5,6]. Probably our most significant result was the discovery that their alcoholysis reactions were catalysed by acid. We concluded that the catalytic effect, which was proportional to acid strength and fluoride basicity, was due to hydrogen bonding between the fluoride and hydronium ion so that the leaving group was

effectively HF. In beginning work at Cornell I was especially appreciative of the excellent chemical library. For the first time I had access to the Belgian chemical publications which contained the pioneering work of Frédéric Swarts on aliphatic halofluoro compounds.

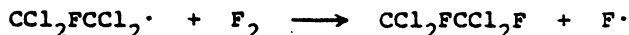
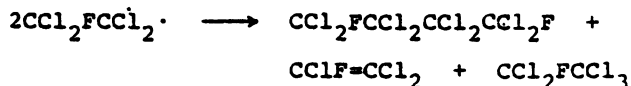
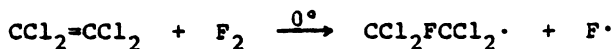
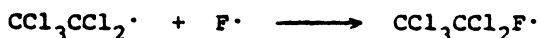
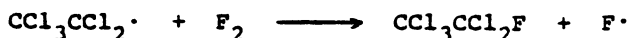
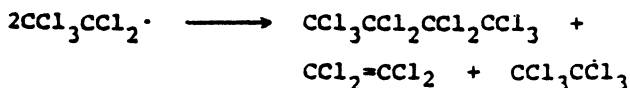
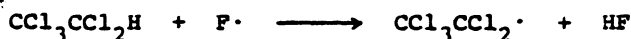
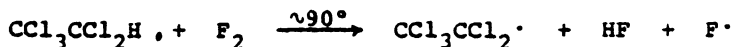
During my first year at Cornell I rebuilt an old fluorine cell which had been used by L.M. Dennis in attempting to prepare inorganic hypofluorites. There was no money for a new cell. Before the end of the first term using 'pure' fluorine I was able to prepare pentachlorofluoroethane from pentachloroethane as a lecture table demonstration. This fluorination was easy to observe because the liquid reactant (mp -29°) was converted into a crystalline product (mp 101°). I remember the occasion clearly, perhaps because W.H. Mills, a well known stereochemist from Cambridge University, who was the Baker Lecturer at Cornell that year, warmly complimented me on my accomplishment.

By the summer of 1940 I had concluded that the fluorine reactions we were studying with simple aliphatic chlorinated compounds [7] proceeded by free-radical mechanisms. Most important, our results seemed best interpreted as involving molecular fluorine free-radical initiation reactions in which "even molecules" produced free radicals by one-electron transfers, a completely new idea.

Fluorine free-radical initiation reactions



The relatively high yield of fluorine dimer-addition product obtained from tetrachloroethylene and the coupling and disproportionation products formed from pentachloroethane were especially persuasive.

Fluorination of tetrachloroethyleneFluorination of pentachloroethane

My problem with the molecular free-radical initiation reactions was that the then accepted bond dissociation energy for fluorine was 63.5 kcal [8]. This value seemed to rule out such processes. However, before and after World War II we carried out additional experiments which supported our first conclusions. These experiments included the use of fluorine to initiate known free-radical chain oxidation and chlorination reactions with tetrachloroethylene [9,10] and pentachloroethane [10], and the reaction of fluorine with mixtures of other highly halogenated reactants to yield predicted products [11,12]. By 1951 Doescher had demonstrated experimentally

that the bond dissociation energy of fluorine was, in fact, about 37 kcal [13], a value consistent with our results. I was pleased to find that Doescher had utilized the chlorotrifluoroethylene polymer oil which we developed during World War II as his fluorine-stable manometer fluid.

The summer of 1941 was a stirring time. Hitler had invaded Czechoslovakia on September 1, 1939 and by 1941 many people thought that we would soon join Great Britain in the war. Our direct involvement, of course, came very suddenly in December with the attack on Pearl Harbor. Government sponsored research programs directed toward war needs were already under way or were being started. These programs resulted in a tremendous acceleration in the development of fluorine chemistry. After the importance of constructing an atomic bomb was accepted by the U.S. Government, it was realized that if the diffusive separation of the fissionable uranium isotope, U-235, was to be undertaken, fluorine chemistry would play an essential role. Uranium hexafluoride appeared to be the only practical process gas. However, this highly reactive material could not be allowed to come into contact with ordinary organic materials such as oil, rubber, plastic, etc., which would otherwise have been utilized. In addition to destruction of the materials involved, non-volatile solid uranium tetrafluoride would be produced which would plug the diffusive membranes. Resistant materials were required not only to contain UF_6 and fluorine but also as lubricants and coolants. As is now well known, saturated fluorocarbons were found to be sufficiently stable. Small liquid samples which had been prepared by J.H. Simons' procedure for fluorinating carbon were utilized for testing. It was my understanding that the use of fluorocarbons in the gaseous diffusion plant was first suggested by A.V. Grosse. However, no practical methods were available for the production of fluorocarbons in appreciable quantities and no methods were available for the production of materials with the necessary physical properties.

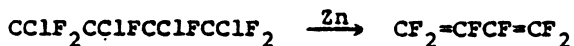
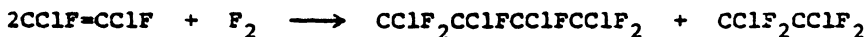
Fluorine chemists throughout the country were asked to propose ways to produce the desired type materials. However, they were not informed as to the real reason that such materials

were needed. I was told among other things that highly stable lubricants for machine gun bullets and anti-aircraft shells were an important war need. I proposed the preparation of a wide range of materials by the polymerization of fluoroolefins. I planned to obtain the fluoroolefins from Freon-type materials, hopefully from those already commercially available. It seems to me now that I was rather brash since I had not done any polymer chemistry, but of course I was just thirty years old. In any case, we had no competition from other war research groups in our chosen area of fluoroolefin polymerization [14]. The high degree of reactivity of fluoroolefins was not generally appreciated at that time. In this connection, I should point out also that the DuPont Company's work on tetrafluoroethylene was not a part of the war research program nor were we informed about it. My graduate students and I began experimental work at Cornell under a National Defense Research Committee contract in late 1941. We continued work until the spring of 1943 when we were moved to the S.A.M. Laboratories of the Manhattan Project at Columbia University in New York City. I then learned the real purpose of our research. Our work on fluoroolefins was continued at S.A.M. with expanded facilities and personnel and with the very considerable advantage of close contact with other workers who were familiar with the diffusion plant requirements. We were the only group of organic chemists inside the project and I became a consultant on organic and fluorine chemical problems in addition to my other duties. As time went on the emphasis of our work was shifted toward the practical application of our fluorocarbon products to project needs. Processes and materials were followed through to plant utilization.

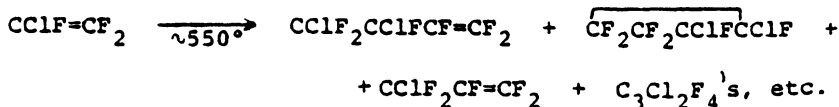
Our move from Cornell to the S.A.M. Laboratories illustrates the nature of the times. I was asked to visit H.C. Urey at Columbia. Dr. Urey was then head of the S.A.M. Laboratories. We discussed what I was doing and what I thought could be done with fluorocarbons. Dr. Urey then asked me whether or not Cornell would release me to come to New York. I replied that I did not think so since I was carrying a heavy teaching load in addition to my war research. In fact, I felt that I was an

essential person at Cornell and that I was doing about all I could to help the war effort. However, while I sat in his office Dr. Urey called J.B. Conant in Washington and asked him to call E.E. Day, who was President of Cornell, and explain "the situation regarding Miller". Within a few minutes the phone rang and I was informed that Dr. Day had agreed that Cornell could release Miller. I do not recall that Dr. Urey asked me whether or not I would like to come to Columbia. Certainly, at that time, he did not tell me the real purpose of the S.A.M. research. There was a high degree of motivation and support for the war on the part of most people. We worked about as hard as we could.

Our fluorocarbon products were prepared largely by free-radical polymerizations of hexafluoro-1,3-butadiene and of chlorotrifluoroethylene. At the start of the war research program we were told that only completely fluorinated products were desired and we concentrated our work on hexafluorobutadiene. We first prepared the diene by the fluorine free-radical dimerization of syn-dichlorodifluoroethylene to form 1,2,3,4-tetrachloroperfluorobutane which was dehalogenated with zinc, a synthesis based upon our previous fluorination studies with haloolefins [14,15].



Later in attempting to dehalogenate chlorotrifluoroethylene intermolecularly with molten tin as an alternate synthesis for the diene, we discovered that 3,4-dichloroperfluorobutene was formed by pyrolysis. This compound was converted into the butadiene [14].



The pyrolysis synthesis had the advantage that no elemental fluorine was required. It yielded by-products which, while undesired at the time, subsequently were utilized in our investigation of fluoroolefin S_N-2' substitution reactions. This work led to the discovery of the facile reactions of fluoride ion with fluoroolefins.

Hexafluorobutadiene was found to be highly reactive, as predicted and in striking contrast to hexachlorobutadiene. It polymerized readily with peroxide initiation to form low polymers which were fluorinated to form saturated fluorocarbon oils, greases and solid waxes. Under extremely high pressures it was converted into a somewhat rubbery solid polymer. The very high pressure experiments, $\sim 16,000 \text{ kg/cm}^2$, were carried out personally by P.W. Bridgman at Harvard with J.B. Conant's encouragement. As the first perfluorodiene, the thermal and chemical behavior of hexafluorobutadiene were of great interest to us. We were able to establish some of its addition reactions and its thermal cyclization and oligomerization. The formation of hexafluorocyclobutene provided the first example of this type cyclization of a 1,3-diene. Reaction of hexafluorobutadiene and of its oligomers with fluorine yielded fluorocarbon oil fractions by stepwise dimerization.

However, there were a number of reasons for questioning the practicality of producing the materials needed for the diffusion plant from hexafluorobutadiene. The monomer was too difficult to obtain and too many steps were required to produce the final products. It was decided to discontinue work on this monomer in favor of chlorotrifluoroethylene. The shift to chlorotrifluoroethylene was supported both by favorable polymerization results and by the completion of tests which showed that chlorofluorocarbons were stable in contact with UF_6 provided that the proportion of chlorine was not too great. The production of chlorotrifluoroethylene could be carried out in one step by dehalogenation of the commercially available Freon 113, CCl_2F_2 , a process which we had already investigated.

Chlorotrifluoroethylene had been shown to polymerize to a hard wax prior to our work [16]. However, neither low polymers in the oil and grease range of molecular weight nor high

polymers with useful mechanical properties had been prepared. After considerable experimentation, we obtained the desired low polymers by utilizing chloroform as a chain transfer reagent with peroxide promoters [14,17]. Free-radical chain transfer reactions were a new idea at the time [18] and were just beginning to be applied experimentally [19]. The crude polymer was treated with cobalt trifluoride to stabilize reactive end-groupings by fluorination. Additional crude oil fraction was obtained by thermally cracking by-product polymers having a molecular weight exceeding that desired. The code designation MFL for 'Miller's Fluorolube' was assigned to the chlorotrifluoroethylene polymer oil by the Manhattan District, U.S. Engineers. Its physical properties were superior to those of the fluorocarbon oils which had been prepared by fluorinating petroleum fractions and it could be more easily manufactured. Only a relatively small amount of elemental fluorine was required and a range of products from light oils to greases and waxes could be obtained from the same starting material.

High polymers of chlorotrifluoroethylene which were designated similarly as MFP were prepared by slow bulk polymerization at $\sim 15^\circ$ using bis-trichloroacetyl peroxide as the promoter, usually with a reaction time of about one week. We had prepared the new perhalo peroxide while specifically seeking a low temperature promoter. The bulk polymerization of pure monomer avoided contamination. The low temperature process gave a very high molecular weight material which, however, could be processed with conventional equipment, an important consideration. Its physical properties were judged excellent for our purposes and could be varied over a considerable range by the control of crystallinity [14]. Transparent sheets could be produced. The S.A.M. fluorocarbon group announced that MFP stood for 'Mighty-Fine-Product'.

Copolymers of chlorotrifluoroethylene and tetrafluoroethylene were also prepared by the low temperature method but the addition of TFE was found to reduce the required resistance to cold flow and to increase the difficulty of fabrication, roughly in proportion to the TFE content. On the other hand,

a low temperature polymer of tetrafluoroethylene with hexafluoropropene had much more interesting properties. Unfortunately, this observation came too late to be followed up before the close of the war program.

Although I feel that we were very fortunate to obtain materials with the desired properties in time for their effective use, there were also many periods of discouragement. For example, our first relatively large scale polymerization tests, designed to demonstrate the practicality of the low temperature process, failed completely. Some of the alcohol which had been used for 'thorough' cleaning had remained in the equipment. We were tired and it was hard to endure the time required to show that we did not have a major equipment problem. Everyone was under pressure.

MFP, produced at S.A.M., was first utilized to solve laboratory apparatus problems. These applications which usually involved exposure to fluorine or UF_6 provided valuable information on use properties to supplement our test data. Plant applications followed which required industrial production [14]. The most important use of MFP in the diffusion plant was to solve a critical problem, which arose late in the plant construction schedule, with essential equipment which failed to function as planned.

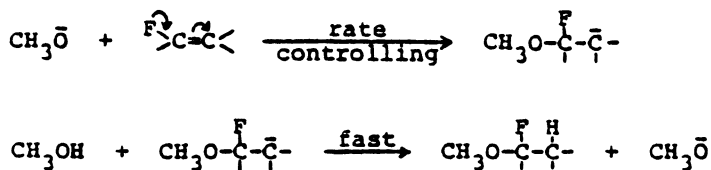
Both MFL- and MFP-type products have been produced commercially in the United States and in other countries under various trade names (Halocarbon, Kel-F, Fluoroethene, Poly-fluoron, Hostafion, Teflex, Ekafluvin, etc.). To the best of my knowledge they are the only fluorocarbon products developed by the war research program which are now commercially available.

At the close of the war research program in the Spring of 1946 I returned to Cornell with some of the graduate students who had accompanied me to the S.A.M. Laboratories in 1943. We continued research on the thermal reactions of hexafluorobutadiene [20] and on the free-radical reactions of elemental fluorine which I discussed above. General mechanisms were developed which accounted satisfactorily for all of the observed fluorination products. We did not explore the

reactions of fluorine with compounds of relatively high electron availability. However, a number of recent experimental results suggest that both one- and two-electron reactions [10] can occur with such compounds.

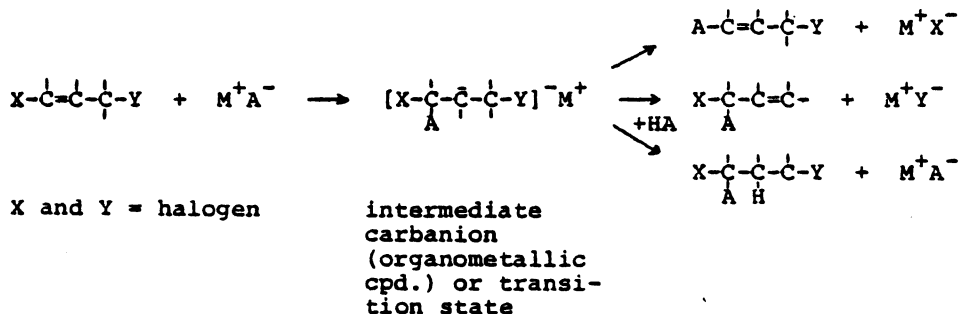
Ample evidence was available in 1946 to show that an unlimited number of highly fluorinated carbon compounds could exist and that such compounds exhibited a diverse and exciting chemistry. I wanted to continue to explore this chemistry, especially that of the carbon-fluorine and carbon-fluorine-halogen compounds. It seemed evident that the bimolecular reaction paths of general significance for such compounds involved initial reagent attack either on unsaturated carbon or on halogen. Reaction on saturated carbon was sterically inhibited. I began to classify reactions of CF- and CFX-compounds by the initial reaction site, and as oxidative or reductive for those involving one-electron transfers, and electrophilic or nucleophilic for those involving two-electron transfers or movement. This simple reaction classification on the basis of mechanism has served us well as a framework for much of our research until the present time.

We began experimental work on the reactions of ionic nucleophiles with fluoroolefins. The great ease of nucleophilic attack on unsaturated carbon in fluoroolefins had been observed qualitatively early in the war period, first with chlorotri-fluoroethylene and its thermal reaction products which contained allylic chlorine. Later, we concluded that carbanionic intermediates were formed during the base catalyzed addition of methyl alcohol to fluoroolefins [21] and began to believe that the



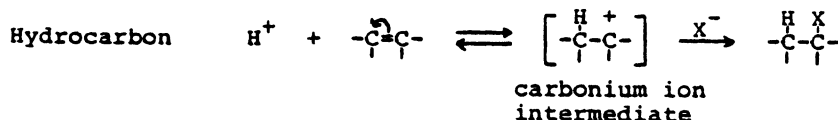
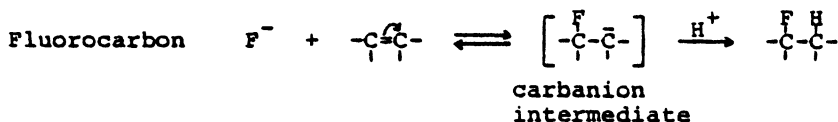
most important and characteristic chemical behavior of the highly fluorinated olefins would consist of their reactions with nucleophiles. In extending this work to perfluoroallylic systems we soon found that even such mild nucleophiles as the

halide ions were effective reagents. A general mechanism [22] in which addition of an anion yielded an intermediate carbanion (organometallic compound) or an S_N-2' transition state was proposed to account for the observed reaction products. These corresponded to the addition of HX, if a source of protons was available, or to substitution of vinyl or allyl halogen. The order of halide ion reactivity was found to be $F^- \gg Cl^- (Br^-) > I^-$, an unexpected result at the time.

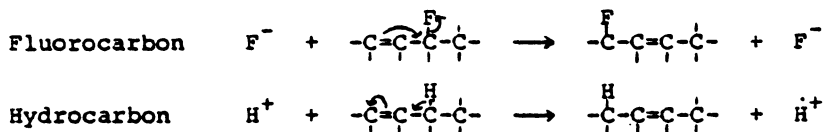


Our most important results have involved the reactions of fluoride ion. For unsaturated carbon-fluorine compounds fluoride ion is at once the common group and highly reactive reagent. It thus occupies a unique position as a nucleophile analogous to a proton as an electrophile for unsaturated hydrocarbons [23].

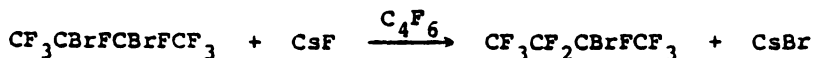
Addition



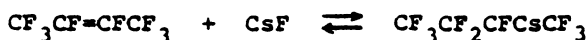
Rearrangement



Addition of fluoride ion to a fluoroolefin leads to the formation of a fluorocarbanion intermediate while S_N-2' substitution leads to rearrangement. A broad range of chemistry is inherent in these basic reactions. The fluorocarbanion, fluoroorgano-metallic compound, formed reversibly by the addition of a metal fluoride such as cesium fluoride to an unsaturated carbon-fluorine compound can add a cationic unit to form an addition product, or undergo a variety of other reactions as a nucleophile. Additions at unsaturated carbon and reactions on halogen which generate a new carbanionic center have been of especial interest to us. These processes are now finding application for planned syntheses of desired compounds. An interesting use of metal-halogen exchange is illustrated by the fluorination of $\text{CF}_3\text{CBrFCBrFCF}_3$ with cesium fluoride catalyzed by $\text{CF}_3\text{CF}=\text{CFCF}_3$.



Mechanism

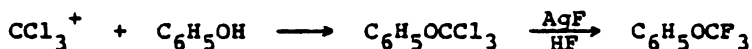
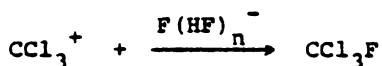
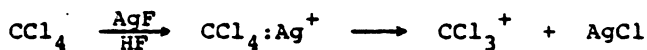


An elegant synthesis, which involves both carbanionic addition to unsaturated carbon and metal-halogen exchange, consists of the preparation of trans,trans-2-bromoperfluoro-3,4-dimethyl-2,4-hexadiene from perfluoro-2-butyne and 2-bromoperfluoro-2-butene in a single step [24].

The discovery of the high order of reactivity exhibited by fluoride ion with fluoroolefins, especially those containing the $\text{CF}_2=$ group, and the realization of its general significance to carbon-fluorine chemistry was a high point in our research. I believe that our results together with the large amount of excellent work carried out by others has fully justified our original conclusions regarding the general significance and utility of fluoride ion reactions to carbon-fluorine chemistry.

In recent years we have continued our work with fluoro-organometallic compounds, formed by fluoride ion additions and in other ways, and with the reactions of these reagents upon unsaturated carbon and halogen, most recently with copper compounds [25]. We have also made some progress in exploring the electrophilic reactions of CX- and CFX-compounds initiated on halogen or unsaturated carbon which complement those with nucleophilic reagents (p. 11). Our experiments in this area began before World War II with the use of aluminum chloride to replace fluorine in $\text{CCl}_2\text{FCClF}_2$ to form $\text{CCl}_3\text{CClF}_2$ [26]. This work led to the discovery that aluminum chloride also caused the rearrangement of $\text{CCl}_2\text{FCClF}_2$ to form CCl_3CF_3 [27], a new type reaction. Several years later we found that $[(\text{CF}_3)_2\text{CH}]_2\text{Hg}$ was formed by treating $\text{CF}_2=\text{CHCCl}_2\text{F}$ with HgO and HF . This observation caused us to undertake further investigations with silver and mercuric ions as electrophilic reagents in HF or TFA . We found that $\text{CF}_2=\text{CHCF}_3$ and $\text{CF}_2=\text{CFCF}_3$ readily added mercuric fluoride in HF with initial attack by mercury ion [28,29] while silver fluoride promoted the addition of HF . Fluoride ion is unreactive in HF due to strong hydrogen bonding with HF . On the other hand the weakly solvated metal ions are highly reactive. On treatment with silver trifluoroacetate in TFA trichlorobromomethane underwent trifluoroacetoxylation to form $\text{CCl}_3\text{OCOCF}_3$, a process analogous to polyhalide fluorination with mercuric fluoride in HF [30] and a new polyhalide substitution reaction. As would be expected, silver fluoride in HF was found to be an effective fluorination reagent for carbon tetrachloride and other polyhalides. We proposed the electro-

philic substitution mechanism shown below with carbon tetrachloride. Direct evidence for the formation of the relatively stable intermediate CCl_3^+ was obtained by trapping with phenol [31].



I believe that a more complete understanding of the reaction paths discussed above will result in the development of a variety of useful new preparative reactions. The large amount of work available on the fluorination of polyhalides should be of considerable help in developing new electrophilic substitution reactions.

In concluding, I would like to express my confidence in the future development of carbon-fluorine chemistry. As an unlimited system of carbon compounds potentially comparable in scope to the carbon hydrogen compounds and their derivatives, I believe that it is of unique importance. In addition to providing an area for developing a new chemistry and a rapidly expanding group of materials with practical uses, I believe that the continuing comparison of the properties of highly fluorinated compounds with those of the highly hydrogenated compounds on which present theories of carbon chemistry are almost wholly based will be productive of increased understanding not achievable by other routes. It is highly significant that such a comparison is possible over a uniquely wide range of carbon structures. I suggest that the greatest ultimate value of the study of carbon fluorine compounds and their derivatives will be in providing an expanded basis for the development of chemical theory, especially with regard to chemical bonding.

ACKNOWLEDGEMENT

It is a pleasure for me to acknowledge the contributions of the people who have worked with me. I shall always be grateful for their work and support and for the pleasure I have had in their company.

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