FLUORIDE ION REACTIONS OF FLUOROCARBON DERIVATIVES

Final Report

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ABSTRACT

The relative reactivity of various unsaturated fluorocarbon derivatives toward cesium fluoride at temperatures up to $200°$ is described by the series $CF_3N=CF_2$ > $CF_2=CF_2$ > $CF_3CF=CF_2$ > CF_2CFCl, $CF_2=CCl_2$ > $CFCl=CFCl$ > $CF_2=CHF$, $(CF_3)_2C=CF_2$, $CF_3CF=CFCF_3$, $\overline{CF_2CF=CFCF_2}$. Of these, only $CF_3N=CF_2$ and $CF_3CF=CF_2$ gave products which could logically be ascribed to an ionic mechanism.

With mixtures of two compounds, the pairs $CF_2=CCl_2/CF_3CF=CF_2$, $CFCl=CFCl/CF_3CF=CF_2$, $CFCl=CFCl/CF_3N=CF_2$, and $CF_2=CF_2/(CF_3)_2C=CF_2$ gave independent reaction of one compound. In the presence of a solvent, some interaction between the two components was observed in the pairs $CF_2=CF_2/(CF_3)_2C=CF_2$ and $CF_2=CF_2/CF_3N=CF_2$, but the reactions were low-yield and quite complex. Highly specific 1:1 interaction occurred in the pairs $CF_3CF=CF_2/CF_3N=CF_2$, $(CF_3)_2C=CF_2/CF_3N=CF_2$, and $(CF_3)_2C=CF_2/CF_3CF=CF_2$; excellent yields were obtained of products which all had structures just the reverse of those expected. Thermodynamic rather than kinetic control of such reactions is indicated.

Reaction of fluoroanions with inorganic fluorides such as SF_4 and SOF_2 was successfully achieved and good yields of the 1:1 and 2:1 adducts were obtained. The 2:1 adduct with SOF_2 was a sulfide rather than a sulfoxide because of a complicating reaction involving loss of an oxygen atom. The structures of the adducts indicate that fluoride ion adds preferentially to carbon rather than to sulfur, in cases where competing reactions are possible. No reaction occurred between $CF_3N=CF_2$ and SF_4, but the azomethine reacted very well with cyanuric fluoride to form the 1:1, 2:1, and 3:1 adducts.
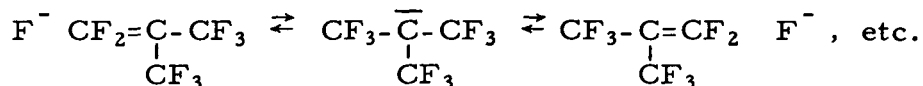
INTRODUCTION

Alkali metal fluorides are known to catalyze a surprising variety of reactions of fluorocarbons and their derivatives. These reactions have been used rather empirically and information concerning steric and electronic effects is very scanty.

A generalized equation which describes the reactions of interest to this program is as follows:
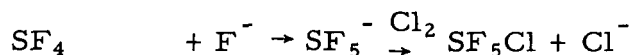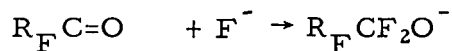
$$R_F-\overset{\overset{X}{|}\overset{Y}{|}}{M=N}-Z + F^- \rightarrow R_F-\overset{Y}{\underset{X}{\overline{M}}}-\overset{Y}{\underset{Z}{N}}-F$$
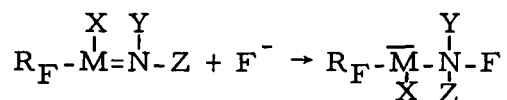
A fluoride ion adds to the positive end of a polarized multiple bond, creating a fluoroanion which can then undergo various reactions such as (1) β-elimination of fluoride ion, resulting in double bond migration, (2) attack of the anion on another molecule of the original compound, resulting in dimerization and (by repetition) polymerization, and (3) attack of the anion on a different molecule, resulting in net perfluoroalkylation of the second molecule. Fluoride ion or some other negatively charged species is eliminated at some subsequent step in the last two reactions.

No systematic study has been made of structural effects in this generalized reaction, * although it has long been known that some fluorocarbon olefins are more reactive than others in related nucleophilic additions; the proclivity of olefins with large numbers of β-fluorine atoms for nucleophilic attack has been ascribed in such compounds to negative hyperconjugation and resultant stabilization of the carbanion formed.

$$F^- \quad CF_2=\underset{CF_3}{\overset{|}{C}}-CF_3 \ \rightleftarrows \ CF_3-\underset{CF_3}{\overset{|}{\overline{C}}}-CF_3 \ \rightleftarrows \ CF_3-\underset{CF_3}{\overset{|}{C}}=CF_2 \quad F^- \ , \ etc.$$

---

* During the course of this work, a Ph.D. thesis at Cornell (M. Fraticelli, author) has described some structural effects in fluoride-olefin reactions in solution.

It has also been known that the multiple bond need not be a carbon-carbon bond and that, in fact, a multiple bond need not be present; a strong Lewis acid can accept fluoride ion and can subsequently form a stable molecule if it is capable of valence shell expansion. Typical reactions of these types are shown below:

$$CF_3N{=}CF_2 + F^- \rightarrow (CF_3)_2N^-$$

$$R_FC{=}O \quad + F^- \rightarrow R_FCF_2O^-$$

$$SF_4 \quad\quad + F^- \rightarrow SF_5^- \xrightarrow{Cl_2} SF_5Cl + Cl^-$$
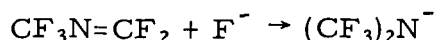
It can be seen that the availability of heteratomic nucleophiles such as those above might make possible the synthesis of a great many different types of fluorocarbon derivatives.

The objectives of this program were twofold: the first was to vary in stepwise fashion the atoms or groups surrounding the multiple bond and to observe the effects of such variation on extent, rate, and type of reaction; the second was to utilize reactions employing fluoride ion catalysis to prepare new types of fluorocarbon derivatives with unusual interatomic bonding.

Both these objectives were successfully achieved. This field of study has been, however, an extremely active one in fluorine chemistry and unfortunately many of the results obtained here have been duplicated or approximated by other workers and have appeared in print since the submission of this proposal in July 1965.

DISCUSSION

A.   Structural Effects

In order to establish a comparative series of relative reactivities, each of the olefins given in Table I was heated under autogenous pressure in a small Monel bomb with cesium fluoride under the conditions shown. After the heating, the gas was returned to the same volume and the drop in total pressure was regarded as a measure of reaction. A polar solvent was purposely omitted since it was feared that its presence would so increase the ease of reaction that a comparative scale of reactivity could not be easily developed. This apprehension was well founded since, during the course of this work, Miller[1] reported an account of similar work using a polar solvent in which even branched chain, internally unsaturated, and cyclic olefins were condensed by cesium fluoride.

TABLE I

Relative Reactivity of Fluoroolefins Toward Cesium Fluoride[a]

Olefin	% Unrecovered after 12 hrs at			% Cl$^-$ (12 hrs/200°)	Product
	100°	150°	200°		
$CF_2=CF_2$	78				High polymer
$CF_3CF=CF_2$			20		Linear dimer
$CF_2=CFCl$		7	50-60	10	Polymers, cyclic dimer
$CF_2=CCl_2$		8	50-60	23	Tar, cyclic dimer
$CFCl=CFCl$		0	5	2	Tar
$CF_3N=CF_2$	95[b]				Linear dimer

[a] The following showed <5% reaction after 12 hr/200°: $CF_2=CHF$, $(CF_3)_2C=CF_2$, $CF_3CF=CFCF_3$, $\underline{c}\text{-}C_4F_6$.

[b] After 12 hr/50°.

On the basis of the results shown in Table I, three general classes of reactivity can be distinguished. The first group, which produced acyclic dimers, included $CF_3N=CF_2$ and $CF_3CF=CF_2$, the former being overwhelmingly the most reactive compound tested. Only these two gave products which could clearly be ascribed to an anionic mechanism. The second group, which gave tars and polymers, was composed of those olefins commonly regarded as highly reactive in free radical reactions — $CF_2=CF_2$, $CF_2=CFCl$, and $CF_2=CCl_2$ — and as might be expected C_2F_4 was by far the most reactive of these. High polymers were obtained from C_2F_4 and from $CF_2=CFCl$, but these may have been formed by a free radical rather than by an ionic mechanism. In addition, very small amounts of cyclodimerization products were formed by $CF_2=CFCl$ and $CF_2=CCl_2$, and these two olefins exhibited considerable halogen exchange with the cesium fluoride. The third group, which all showed less than 5% reaction after twelve hours at 200°, included $CF_2=CHF$, $(CF_3)_2C=CF_2$, $CF_3CF=CFCF_3$, $CFCl=CFCl$, and $\underline{c}\text{-}C_4F_6$.

It is apparent that under the test conditions three requirements must be fulfilled for the occurrence of a facile reaction involving a carbanion intermediate. These are (1) a terminal CF_2 group, (2) absence of appreciable steric hindrance, and (3) capability for carbanion stabilization. Lack of any one of these qualifications will prevent anionic self-condensation. A case in point is perfluoroisobutylene, $(CF_3)_2C=CF_2$, which was recovered unchanged after extended reaction periods at 100° and 200°. Both theoretical considerations and studies where a solvent was present[2,3] indicate that the $(CF_3)_3C^-$ anion is formed very readily. The absence of reaction under the present conditions, where a substrate amenable to attack is lacking, must be ascribed to steric hindrance which prevents attack of the carbanion on a second molecule of the olefin.

B.   Codimerization of Olefins

When a mixture of two olefins is heated with cesium fluoride, several possibilities for reaction exist. One or both of the olefins may react independently, the two may interact in a random fashion, or one may react preferentially with the other. The actual results should depend not only on the reactivity of each olefin toward fluoride ion, but also on its reactivity toward the carbanions derived from itself and from the other olefin. These factors may differ considerably; $(CF_3)_2C=CF_2$ is known to be very reactive toward nucleophiles and easily forms a carbanion with fluoride ion, yet Table I shows that it does not self-condense by reaction with its own carbanion, probably because of steric hindrance. Consequently, the rate limiting factor is apt to be its reaction with substrate, rather than carbanion formation. The tetrafluoroethylene anion, $C_2F_5^-$, cannot be stabilized to nearly as large a degree by hyperconjugation and Graham[4] has found that the rate of self-condensation of C_2F_4 in diglyme increases with increasing amounts of cesium fluoride; carbanion formation may therefore be the rate limiting factor in this case.

At the start of the present work it was hoped that a general perfluorovinylation process could be developed. This would be a valuable synthetic adjunct, since perfluorovinylation with trifluorovinyl lithium has many disadvantages. Conceivably, this result could be accomplished in two ways. In one, a vinyl fluorine atom of C_2F_4 would be replaced by a perfluoroalkyl group.

$$CF_3N=CF_2 + F^- \rightarrow (CF_3)_2N^- \xrightarrow{CF_2=CF_2} (CF_3)_2NCF=CF_2 + F^-$$
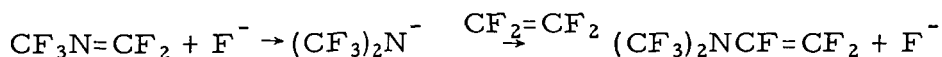
In the second, a $CF_2ClCFCl^-$ group would be introduced which could then be dehalogenated to give a terminal olefin.

$$CFCl=CFCl \xrightarrow{F^-} CF_2ClCFCl^- \xrightarrow{RF} CF_2ClCFClR \rightarrow CF_2=CFR$$
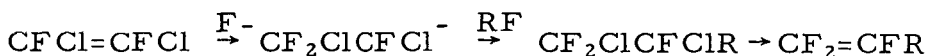
The first of these would require that the terminal olefin formed not be subject to rearrangement; the carbanion $(CF_3)_2CF^-$, for instance, would hypothetically give $(CF_3)_2CFCF=CF_2$, which would be certain to rearrange to $(CF_3)_2C=CFCF_3$. For this purpose, therefore, $(CF_3)_2C=CF_2$ and $CF_3N=CF_2$ were chosen since their products would be incapable of rearrangement. In the second method, success would depend on effective carbanion formation from $CFCl=CFCl$, which is known to be a fairly un-reactive electrophile.
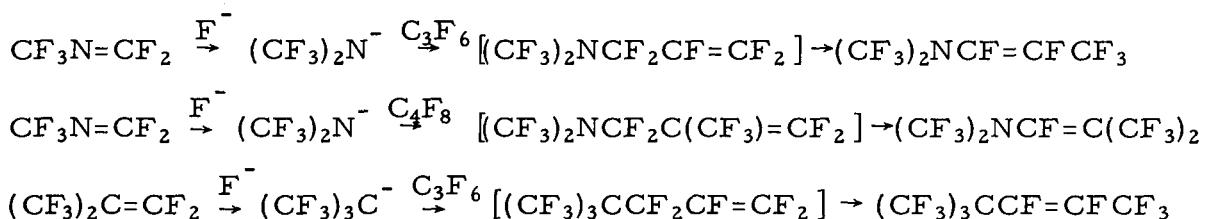
Experimental results showed that mixtures of a two-carbon olefin with a three- or four-carbon olefin known to be reactive toward cesium fluoride led to independent reaction of the two components, with only small amounts of crossed products. Thus, the pair $CF_2=CCl_2/$ $CF_3CF=CF_2$ gave $\underline{c}-(CF_2CCl_2)_2$ and the three reported dimers of C_3F_6, the pair $CFCl=CFCl/C_3F_6$ gave 63% unreacted $CFCl=CFCl$, some $(C_3F_6)_2$, and a very complex mixture containing 5-10 components, and the pair $CFCl=CFCl/CF_3N=CF_2$ gave a similarly complex mixture. Reaction of C_2F_4 with $(CF_3)_2C=CF_2$ resulted in almost complete recovery of the latter, although some was evidently incorporated in the high polymer formed from the C_2F_4 as this polymer showed a definite melt-ing point at 310-315°. Reaction of C_2F_4 with $CF_3N=CF_2$ at room tempera-ture or at 100° in the absence of a solvent gave only $CF_3N=CF_2$ dimer and unreacted C_2F_4.

In a polar solvent, somewhat different results were obtained. Reaction of C_2F_4 with an equimolar amount of $CsC(CF_3)_3$, preformed in dioxane, gave principally a liquid of extended boiling range, 50-150°, accompanied by CF_3CF_2H and C_2F_6. The most volatile part of this liquid showed infrared absorption at 1770 cm^{-1}, and the least volatile part at 1630-1670 cm^{-1}. Reaction of C_2F_4 with $CF_3N=CF_2$ in diglyme at 50° gave a liquid, part of which decomposed when treated with water and which showed infrared absorption at 1500 and 1750 cm^{-1}. These results certainly seem to indicate some sort of interaction between the com-ponents rather than mere independent condensation. A boiling point near 50° is in the range to be expected of a C_6 compound, while the infrared absorption at 1750-1770 cm^{-1} is clear evidence of a terminal double bond, probably of the type $R_FCF=CF_2$ rather than $(R_F)_2C=CF_2$. It is likely that $(CF_3)_3CCF=CF_2$ and either $(CF_3)_2NCF=CF_2$ or
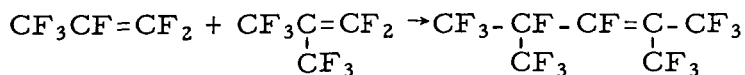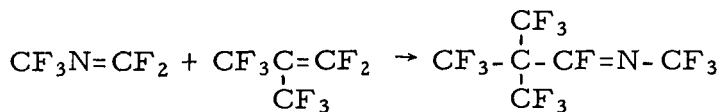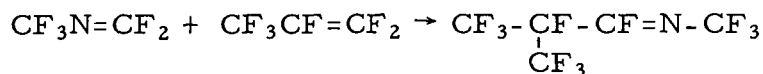
$CF_3CF_2CF_2N=CF_2$ were produced in low yield; however, the reactions were far from clean, as the presence of C_2F_6 and C_2F_5H as well as the absence of narrow distillation fractions would indicate, and low polymers of C_2F_4 similar to those reported by Graham[4] were also produced in substantial amounts. For practical purposes, neither of the proposed reactions for perfluorovinylation was satisfactory.

Crossed reaction of a mixture of two olefins, each of which was itself reactive toward cesium fluoride, led to dramatically different results. The pairs $CF_3CF=CF_2/CF_3N=CF_2$, $(CF_3)_2C=CF_2/CF_3N=CF_2$, and $(CF_3)_2C=CF_2/CF_3CF=CF_2$ all gave high yields of single products, 1:1 adducts of the two reactants, with only negligible amounts of the self-condensation product of either reactant.

In advance, the structures of such products seemed easy to predict; the more reactive olefin should preferentially form a carbanion, which would then add to the other olefin by an S_N2' mechanism, followed by double bond migration and conversion of terminal to internal unsaturation. This route would give the following series of reactions and products:

$$CF_3N=CF_2 \xrightarrow{F^-} (CF_3)_2N^- \xrightarrow{C_3F_6} [(CF_3)_2NCF_2CF=CF_2] \rightarrow (CF_3)_2NCF=CFCF_3$$

$$CF_3N=CF_2 \xrightarrow{F^-} (CF_3)_2N^- \xrightarrow{C_4F_8} [(CF_3)_2NCF_2C(CF_3)=CF_2] \rightarrow (CF_3)_2NCF=C(CF_3)_2$$

$$(CF_3)_2C=CF_2 \xrightarrow{F^-} (CF_3)_3C^- \xrightarrow{C_3F_6} [(CF_3)_3CCF_2CF=CF_2] \rightarrow (CF_3)_3CCF=CFCF_3$$

In actuality, all three compounds proved to have structures just the reverse of those predicted. The correct structures, as shown unequivocally by NMR spectra, are given below:

$$CF_3N=CF_2 + CF_3CF=CF_2 \rightarrow CF_3-\underset{\underset{CF_3}{|}}{CF}-CF=N-CF_3$$

$$CF_3N=CF_2 + CF_3\underset{\underset{CF_3}{|}}{C}=CF_2 \rightarrow CF_3-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-CF=N-CF_3$$

$$CF_3CF=CF_2 + CF_3\underset{\underset{CF_3}{|}}{C}=CF_2 \rightarrow CF_3-\underset{\underset{CF_3}{|}}{CF}-CF=\underset{\underset{CF_3}{|}}{C}-CF_3$$

These remarkable results indicate that the reactions are completely under thermodynamic rather than kinetic control and therefore yield ultimately those structures whose carbanions can be stabilized to the greatest degree. Such control demonstrably favors internal, highly branched olefins; in dimerization of C_3F_6, for instance, the hypothetical initial product $(CF_3)_2CFCF_2CF=CF_2$ has never been detected and the concentration of its successor, $(CF_3)_2CFCF=CFCF_3$, decreases with time as it is converted to the final product $(CF_3)_2C=CFCF_2CF_3$.[5] Thermodynamic control would also favor $C=N$ rather than $C=C$ unsaturation since the former, being more polar, could be better stabilized by the ionic crystal lattice.

Thermodynamic control implies an equilibrium involving all possible reactants and products. Corroborative evidence for such an equilibrium was obtained by reaction of C_3F_6 with the dimer of $CF_3N=CF_2$, $(CF_3)_2NCF=NCF_3$, which gave an 80% yield of $(CF_3)_2CFCF=NCF_3$ and only 5% recovery of the original dimer. There are two reasonable explanations of this result. Either a monomer-dimer equilibrium of the azomethine permitted attack of $(CF_3)_2CF^-$ on monomeric $CF_3N=CF_2$ as it formed, or the $(CF_3)_2CF^-$ carbanion attacked the $CF_3N=CF_2$ dimer directly, causing elimination of $(CF_3)_2N^-$ either as such or as fluoride ion and molecular $CF_3N=CF_2$. These two possibilities are illustrated below:

1) $(CF_3)_2NCF=NCF_3 \; \underset{\leftarrow}{\rightarrow} \; 2 \; CF_3N=CF_2$

  $(CF_3)_2CF^- + CF_3N=CF_2 \; \rightarrow \; (CF_3)_2CFCF=NCF_3 + F^-$

2) $(CF_3)_2CF^- + (CF_3)_2NCF=NCF_3 \rightarrow (CF_3)_2NCF\overline{N}CF_3$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\displaystyle CF(CF_3)_2}{|}$$

  $(CF_3)_2NCFNCF_3 \; \rightarrow \; (CF_3)_2CFCF=NCF_3 + (CF_3)_2N^-$
$$\quad\; \underset{\displaystyle CF(CF_3)_2}{|}$$

  $(CF_3)_2N^- \; \rightarrow \; CF_3N=CF_2 + F^-$

Formation of the most thermodynamically favored olefin seems to be the only explanation for the formation of $(CF_3)_2CFCF=C(CF_3)_2$ rather than $(CF_3)_3CCF=CFCF_3$, since the carbanion $(CF_3)_2CF^-$, which would lead to the former, is much less stablized that $(CF_3)_3C^-$, which
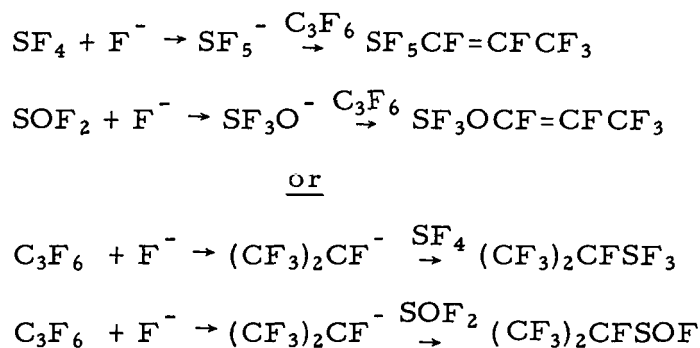
would lead to the latter;* neverthelss, exclusive formation of the first olefin is surprising.

C. Displacement Reactions of Fluoroanions with Inorganic Fluorides and Cyanuric Fluoride

For this work, $CF_3CF=CF_2$ and $CF_3N=CF_2$ were chosen as olefins and thionyl fluoride and sulfur tetrafluoride as electrophiles. These choices were made for the following reasons: the cited olefins were among the most reactive toward cesium fluoride, were available, and were relatively inexpensive; the sulfur compounds were also available and inexpensive. In addition, SF_4 was known to undergo reaction with cesium fluoride to form $Cs^+SF_5^-$; this fact did not guarantee its reactivity toward $(CF_3)_2CF^-$ and $(CF_3)_2N^-$ but pointed in that direction. These reasons must apparently have seemed equally cogent to other investigators since the same compounds were among those chosen in at least two other studies.

Two entirely different types of reaction are possible with olefins and SF_4 or SOF_2. Since both the olefins and the sulfur compounds contain positive centers, fluoride ion could hypothetically add to either and the anion so formed could then attack the other, as shown below:

$$SF_4 + F^- \rightarrow SF_5^- \xrightarrow{C_3F_6} SF_5CF=CFCF_3$$

$$SOF_2 + F^- \rightarrow SF_3O^- \xrightarrow{C_3F_6} SF_3OCF=CFCF_3$$

or

$$C_3F_6 + F^- \rightarrow (CF_3)_2CF^- \xrightarrow{SF_4} (CF_3)_2CFSF_3$$

$$C_3F_6 + F^- \rightarrow (CF_3)_2CF^- \xrightarrow{SOF_2} (CF_3)_2CFSOF$$

The salts $CsSF_5$ and $CsOSF_5$ are known;[6,7] the existence of $CsOSF_3$ is unreported although it has been postulated as an intermediate.[7] It has been found[8] in fluoride-catalyzed reactions between olefins and carbonyl fluorides, where dual possibilities also exist, that only the second type of reaction shown above occurs; ketones are formed but not ethers. With the sulfur compounds the second pair of reactions was

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* The relative acidities of the respective conjugate acids $(CF_3)_2CFH$ and $(CF_3)_3CH$ differ by a factor of 10^7. (D. J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, 1965, p. 70.)

therefore probable but not certain. These were, in fact, the ones that did occur.

A preliminary small scale experiment with SOF_2 and C_3F_6 at 150° indicated successful reaction and the formation of two products, one boiling near 40° and one near 78°, presumably the 1:1 and 2:1 adducts, respectively. Larger scale runs gave the following results:
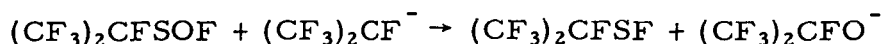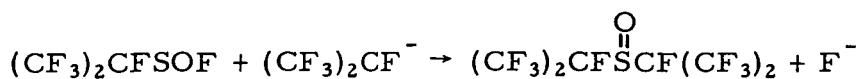
TABLE II

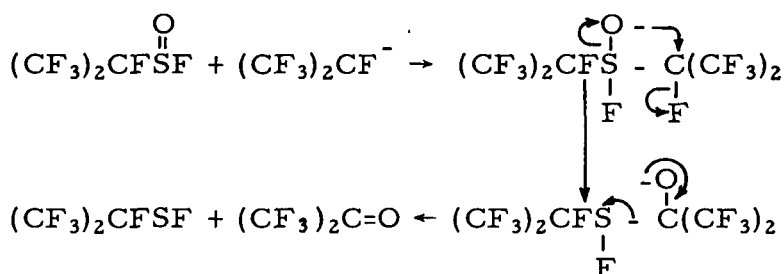Reaction of Perfluoropropene with Thionyl Fluoride

Approx. Mole Ratio		Conversions (%)	
C_3F_6	: SOF_2	1:1 adduct	2:1 adduct
1	1	8[a]	26[a]
1	1	34	44
2	1	12	24
3	1	0[a]	42[a]

[a] Small scale runs, conversions approximate

The figures indicate decreasing proportions of the 1:1 adduct as the $C_3F_6 : SOF_2$ ratio increased. The products were identified by their molecular weight, infrared and NMR spectra. The 1:1 adduct, $(CF_3)_2CFSOF$, b.p. 38°, was also converted into the sulfinate ester $(CF_3)_2CFSOOC_2H_5$ by reaction with ethanol. The properties of both compounds agreed with those reported by Muetterties,[9] who obtained them in low yield by fluoride catalyzed reaction of C_3F_6 and SF_4; apparently the SF_4 contained some SOF_2. The 2:1 adduct, b.p. 78°, was initially thought to be the sulfoxide $(CF_3)_2CFS(O)CF(CF_3)_2$, but failure of oxidation to a sulfone and identity of infrared spectra revealed that it was in fact the sulfide $(CF_3)_2CFSCF(CF_3)_2$. (Fluorocarbon sulfides cannot normally be oxidized to sulfones.) It was subsequently learned that Madison and Miller, in unpublished work,[10] had also studied the C_3F_6/SOF_2 reaction and had identified the 2:1 product as the sulfide, although they had not succeeded in obtaining the sulfinyl fluoride. Apparently reaction of the initially formed sulfinyl fluoride with additional olefin occurs as shown below:

$$(CF_3)_2CFSOF + (CF_3)_2CF^- \rightarrow (CF_3)_2CF\overset{\overset{O}{\|}}{S}CF(CF_3)_2 + F^-$$

$$(CF_3)_2CFSOF + (CF_3)_2CF^- \rightarrow (CF_3)_2CFSF + (CF_3)_2CFO^-$$

The sulfenyl fluoride then reacts with more C_3F_6 to form the observed sulfide, and the perfluoroisopropoxide ion decomposes to hexafluoroacetone and fluoride ion. In the Dow experiments[10] only a catalytic amount of cesium fluoride was used and consequently the acetone was isolated as such; in the Denver Research Institute work an excess of fluoride was used which retained the acetone as its cesium fluoride adduct. This is a fairly reasonable explanation of the overall results, even though no sulfenyl fluoride was detected by either group; however, the mechanism proposed by the Dow workers advocates attack of $(CF_3)_2CF^-$ at the oxygen atom of the sulfinyl fluoride, which seems unlikely. Other mechanisms such as the one below can also be postulated which involve a more probable attack at sulfur.

$$(CF_3)_2CF\overset{\overset{O}{\|}}{S}F + (CF_3)_2CF^- \rightarrow (CF_3)_2CF\overset{\overset{O^-}{|}}{\underset{F}{S}} - C(CF_3)_2$$

$$(CF_3)_2CFSF + (CF_3)_2C=O \leftarrow (CF_3)_2CF\overset{}{\underset{F}{S}} - C(CF_3)_2$$

The 2:1 adduct, $[(CF_3)_2CF]_2S$, was also obtained by reaction of $(CF_3)_2CFSOF$ with $CF_3CF=CF_2$, in 41% conversion.

The reaction of perfluoropropene and thionyl fluoride was not particularly clean. As shown in Table II, conversions were generally only about 40%, appreciable amounts of C_3F_6 dimer and higher-boiling products were formed, and chromatograms indicated the presence of many other components in trace amounts. Reaction with sulfur tetrafluoride, on the other hand, was very clean; conversions were high and the two adducts were easily isolated in > 95% purity. No high boilers or C_3F_6 dimers were found. Conversion to the 2:1 adduct, $[(CF_3)_2CF]_2SF_2$, was favored, almost 70% being obtained at a 2:1 C_3F_6:SF_4 ratio, but the 1:1 adduct, $(CF_3)_2CFSF_3$, was obtained in 29% conversion at a 1:3 ratio. The 1:1 adduct was very reactive toward moisture, but the 2:1 adduct was strangely resistant to hydrolysis and could even be steam-distilled.

NMR spectra agreed with those reported by Muetterties[9] and supported the assigned structures for the two compounds.

No addition occurred when $CF_3N=CF_2$ was substituted for perfluoropropene in reaction with either sulfur tetrafluoride or thionyl fluoride. It is almost certain that the azomethine was completely dimerized before temperatures high enough for reaction with the sulfur compounds were reached, but small amounts of monomeric azomethine should have become available through the equilibrium previously discussed. Evidently the $(CF_3)_2N^-$ anion is not a strong enough nucleophile to attack the S=O bond in thionyl fluoride or the sulfur atom in sulfur tetrafluoride. Reaction of SF_4 with $CF_2=CF_2$ gave only Teflon (again, some of a second component must have been incorporated since the polymer melted near 310°) and unreacted starting materials.

Previous work in this laboratory has shown that $CF_3CF=CF_2$ reacts with cyanuric fluoride in the presence of cesium fluoride to form 1:1, 2:1, and 3:1 adducts in good yields.[11] The present program has extended this reaction to the use of $CF_3N=CF_2$, resulting in the compounds shown below:
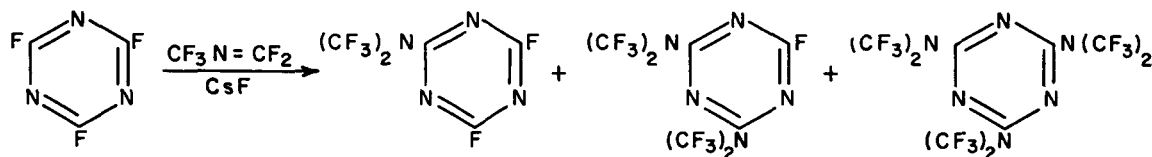
With a 5:1 mole ratio of $(CNF)_3$ to $CF_3N=CF_2$, conversions to the mono-, bis-, and tris(perfluorodimethylamino) compounds were respectively 19, 29, and 16%. This ratio could presumably be altered by varying the reactant mole ratios, as was the case with the $C_3F_6/(CNF)_3$ system, and the yields of the pure compounds could be raised by more efficient separation.

Attempts to extend this alkylation reaction to hexafluorobenzene, both with and without a solvent, were completely unsuccessful. The fluorine atoms in C_6F_6 are known to be much less reactive toward nucleophiles than are those in cyanuric fluoride. It has very recently been reported that the somewhat more reactive nitropentafluorobenzene and perfluoropyridine can be alkylated by perfluoropropene.[12]

EXPERIMENTAL

Cesium fluoride was purchased from the American Potash and Chemical Co. All olefins except $CF_3N=CF_2$ were used as obtained from Peninsular ChemResearch; the azomethine was made by pyrolysis of $(CF_3)_2NCOF^{13}$, which was synthesized by electrochemical fluorination at Denver Research Institute.

Relative reactivities of olefins. - Each olefin listed in Table I, 0.05 mole, measured in a calibrated vacuum system, was condensed into a small Monel bomb containing 10 g. (0.07 mole) of cesium fluoride previously dried for five hours at 400°. After heating under the conditions shown, the olefin was pumped off and returned to the same calibrated volume. The drop in pressure was regarded as a measure of reaction and, where the extent of reaction was large, the olefin was recovered by fractionation.

With the chloroolefins, reactions other than condensation were effected by the cesium fluoride, and an estimate of halogen exchange was obtained by titrating an aliquot of the residual catalyst mass for chloride ion. Compounds formed by processes involving halogen exchange were not identified.

Codimerizations. - Either the apparatus and quantities described above or about 0.2 mole of reactants in a larger bomb containing 50 g. (0.35 mole) of cesium fluoride were employed.

$(CF_3)_2CFCF=NCF_3$. - Perfluoropropene, 15 g. (0.1 mole), and $CF_3N=CF_2$, 13 g. (0.1 mole), were heated in the larger bomb for 6 days at 170-180°. After cooling, the bomb was continuously evacuated for several hours and the condensate so obtained was fractionated to give 22 g. of product, b.p. 28-31° (flat 29°), or 79% of theory. A chromatogram showed > 99.5% purity.

The product was identified as $(CF_3)CFCF=NCF_3$ on the basis of the following information. Neither the boiling point (29°) nor the infrared spectrum agreed well with those of the known dimers $(CF_3N=CF_2)_2$ (b.p. 34°) and $(C_3F_6)_2$ (b.p. 39°). Infrared absorption for the double bond appeared at 1765 cm^{-1}., compared to 1760 for $(CF_3)_2$ $NCF=NCF_3$ and 1750 for cis-$(CF_3)_2CFCF=CFCF_3$ (trans $(CF_3)_2CFCF=CFCF_3$, the more common form, shows no C=C absorption); this indicated an internal C=N bond.

NMR. The NMR spectrum showed four peaks, area ratios 6:3:1:1, at 74.5, 59.9, 17.3, and 191 ppm. respectively ($CFCl_3$ reference). These are reasonable chemical shifts for $C\underline{F}_3$-CF, CF_3-N, $-CF=N$, and $(CF_3)_2C\underline{F}CF-$, respectively. The alternative formula $(CF_3)_2NCF=CFCF_3$ would require transposition of the observed chemical shifts for the six-fluorine peak and the three-fluorine peak.

$(CF_3)_3CCF=NCF_3$. - Perfluoro-2-azapropene, 5.2 g. (0.04 mole), and perfluoroisobutene, 7.9 g. (0.04 mole), were heated in a smaller bomb for six days at 170-180°. Fractionation of the crude product gave 9.0 g. of product, b.p. 51-53° (mostly 52-53°). Since 3.6 g. of unreacted olefins were obtained, the yield was at least 95% and the conversion 69%. Chromatographic purity was > 99%.

The product was identified as $(CF_3)_3CCF=NCF_3$ on the basis of the following information. The mol. wt. was 326, calc. for $CF_3N=CF_2$: C_4F_8 333, $(CF_3N=CF_2)_2$ 266, $(C_4F_8)_2$ 400. Infrared absorption for the double bond appeared at 1760 cm^{-1}, compared to 1760 for $(CF_3)_2NCF=NCF_3$, 1765 for $(CF_3)_2CFCF=NCF_3$, and 1690 for $(CF_3)_2C=CFCF_2CF_3$; this indicated an internal C=N bond rather than a C=C bond.

NMR. The NMR spectrum showed three peaks, area ratios 9:3:1, at 62.1, 56.4, and 5.6 ppm. These are reasonable chemical shifts for $(CF_3)_3C-$, CF_3-N-, and $-CF=N-$, respectively. The alternative formula, $(CF_3)_2NCF=C(CF_3)_2$, would require a 6:3:3:1 distribution with the six-fluorine peak near 56 ppm. region.

$(CF_3)_2CFCF=C(CF_3)_2$. - Perfluoropropene, 7.5 g. (0.05 mole), and perfluoroisobutene, 10 g. (0.05 mole) were heated in the smaller bomb for six days at 170-180°. Fractionation of the crude product gave 2.5 g. of unreacted olefins, mostly iso-C_4F_8, and 14.5 g. of product, b.p. 58-64° (flat 63.5°), for a yield of at least 95% and a conversion of 83%.

The product was identified as $(CF_3)_2CFCF=C(CF_3)_2$ on the basis of the following information: Infrared double bond absorption appeared at 1680 cm^{-1} compared to 1690 for $(CF_3)_2=CFCF_2CF_3$ and 1750 for cis-$(CF_3)_2CFCF=CFCF_3$; this indicated an internal C-C double bond of the type $-CF=C(R_F)_2$ rather than $-CF=CF-$.

NMR. The NMR spectrum showed five peaks, area ratios 6:3:3:1:1, at 74.4, 59.4, 55.3, 95, and 183 ppm., respectively. These

values are consonant with those known for $(CF_3)_2CF-$, $(CF_3)_2C=$, $-CF-C-$, and $-CF=C-$. The alternative formula, $(CF_3)_3CCF=CFCF_3$, would require four peaks in a 9:3:1:1 ratio.

$(CF_3)_2CFSOF$ and $[(CF_3)_2CF]_2S$. - Perfluoropropene, 25 g. (0.17 mole) and thionyl fluoride, 19 g. (0.22 mole), were heated in the larger bomb for 17 hr. at 150°. The bomb was continuously evacuated for one hour and the condensate stripped through a short low-temperature column; 14.5 g. of unreacted material was recovered. Fractionation of the residue gave 15.0 g. of $(CF_3)_2CFSOF$, b.p. 38-39°, and 19.5 g. of $[(CF_3)_2CF]_2S$, b.p. 76-78°, for conversions of 34% and 44%, respectively. The sulfinyl fluoride so obtained always contained an appreciable amount of $CF_3CF=CF_2$ dimer which could be removed only by gas chromatography.

The sulfinyl fluoride was identified on the basis of its molecular weight (near 230 after correcting for $(C_3F_6)_2$ content, calc. value 236), infrared spectrum, NMR spectrum, and conversion to the known ethyl ester, b.p. 123°, n_D^{25} 1.3380. The spectra and physical constants of the sulfinyl fluoride and sulfinate ester agreed with those of Muetterties.[9] The ester decomposed slowly on standing at room temperature.

The sulfide was identified by its molecular weight and the correspondence of its infrared spectrum with that of the same compound given in the literature.[14]

$(CF_3)_2CFSF_3$ and $[(CF_3)_2CF]_2SF_2$. - Perfluoropropene, 11.6 g. (0.08 mole) and sulfur tetrafluoride, 25 g. (0.23 mole), were heated in the larger bomb for 9.5 hr. at 150°. After four hours of continuous evacuation, the condensate was stripped through a short low-temperature column. Only a small amount of material consisting of SOF_2 and SiF_4 was thus obtained, as excess SF_4 was retained by the cesium fluoride. Fractionation of the residue gave 7.0 g. of $(CF_3)_2CFSF_3$, b.p. 38-40°, and 20.0 g. of $[(CF_3)_2CF]_2SF_2$, b.p. 38-40°, for conversions of 29% and 61% respectively. Both compounds were > 95% pure chromatographically. Mol. wts. for the two compounds agreed with calculated values and NMR spectra duplicated those obtained by Muetterties.[9]

Perfluorodimethylamination of cyanuric fluoride. - Cyanuric fluoride, 10 g. (0.075 mole), and perfluoro-2-azapropene, 20 g. (0.15 mole), were heated at 110° for 26 hours in the larger bomb, then continuously evacuated for six hours. The residual material was

extracted with two 25 ml. portions of Freon 113, the solvent was re-
moved, and the liquid residue combined with the condensate from the
evacuation. Fractionation gave, in addition to intercuts, 3.8 g. of the
mon-substituted compound, 8.5 g. of the disubstituted compound, and
4.3 g. of the trisubstituted compound, all at least 88% pure, for con-
versions of 19, 29, and 16%, respectively.

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