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THE ADDITION OF FLUORINE TO PERHALOGENATED COMPOUNDS CONTAINING CARBON-NITROGEN DOUBLE BONDS

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SUMMARY

The reaction of elementary fluorine with ten perhalogenated compounds containing carbon-nitrogen double bonds is reported. The reactions were carried out without added catalysts in a static system. With $CF_3N{=}CF_2$, $(CF_3)_2NCF{=}NCF_3$, $SF_5N{=}CF_2$, $CF_2{=}NCl$, $CF_3CF{=}NCl$ and $CF_2{=}NF$ a simple addition of fluorine to the carbon-nitrogen double bond was observed forming the respective N-fluoroamines in high yield. Two imines, $CF_3CF{=}NF$ and $(CF{=}NF)_2$, were unreactive under the same conditions and reactions of $CF_3CF_2CF{=}NF$ and $(CF_3)_2C{=}NF$ were explosive.

INTRODUCTION

The addition of fluorine to carbon-nitrogen multiple bonds is a basic reaction important to the development of organonitrogen fluorine chemistry. Using elementary fluorine, electrochemical fluorination and high valency metal fluorides, a wide variety of unsaturated organonitrogen compounds have been partially or completely fluorinated in reactions involving the net addition of fluorine across the carbon-nitrogen multiple bond [2]. In spite of these extensive studies, there have been very few reports of reactions involving only the simple addition of elementary fluorine across a carbon-nitrogen double bond.

Recently, a general method for the synthesis of R_fNClF derivatives was reported, in which the addition of fluorine across the carbon-nitrogen double bond in $R_fCF{=}NCl$ was potentially involved [3].

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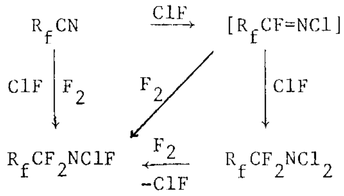
*See ref. 1.



Further investigation showed that this reaction played only a minor role in the high yield synthesis of R_fNClF shown.[4] However, the independent confirmation of the reaction using isolated $R_fCF=NCl$ suggested that other perhalogenated compounds containing carbon-nitrogen double bonds should be investigated. This was undertaken with ten perhalogenated $>C=N-$ derivatives which were readily available by virtue of other ongoing synthetic work.

EXPERIMENTAL

General. All compounds were manipulated in a glass or stainless steel vacuum system equipped with glass-Teflon and Teflon packed stainless steel valves, respectively. Pressures in the glass system were measured with a Wallace and Tiernan differential pressure gauge (series 1500) and a precision Heise Bourdon tube gauge in the metal system. Amounts of volatile products were determined by PVT measurements. Molecular weights of gases were determined by vapor density measurements. Temperatures were measured with a digital-indicating copper-constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer using a 10 cm glass cell filled with AgCl windows. NMR spectra were taken at 29°C on Varian XL-100-15 spectrometer using ∿15 mole % $CFCl_3$ as an internal standard and solvent. Chemical shifts are given as ϕ^* values (δ relative to internal $CFCl_3$ not at infinite dilution).

Reagents. Fluorine (Air Products and Chemical Co.) was used after passing through a NaF scrubber. The perhalo $>C=N-$ derivatives $CF_3N=CF_2$[5], $CF_3N=CFN(CF_3)_2$[6], $SF_5N=CF_2$[7], $CF_2=NCl$[8], $CF_3CF=NCl$[9], $CF_2=NF$[9], $CF_3CF=NF$[9], $CF_3CF_2CF=NF$[9], $(CF_3)_2C=NF$[10], and $(CF=NF)_2$[10] were prepared by literature methods.

General Procedure for the Reaction of $>C=N-$ Derivaties with F_2. A clean 75 ml 304 stainless steel reactor, which was briefly passivated with ∿1 atm of fluorine, was used in all reactions. The vessel was cooled to -195° and the $>C=N-$ compound (3.0 mmol) was condensed in by vacuum transfer. Fluorine (3.0 mmol) was then added by partial condensation and the reactor was warmed to 25° over 1 hour and maintained at this temperature for an appropriate time. The reactor was then cooled to -195° and any materials volatile at this temperature were pumped out. The remaining volatile products were then separated by glc using a 10'x3/8"stainless steel column packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P. The results are summarized in Table 1.

TABLE 1.

Reaction of Fluorine with Perhaloimines[a]

Imine	Time at 25°C[b]	Products (%)[c]
$CF_3N=CF_2$	3 hr	$(CF_3)_2NF$ (87)
$(CF_3)_2NCF=NCF_3$	7 d	$(CF_3)_2NCF_2NFCF_3$ (98)
$SF_5N=CF_2$	23 hr	SF_5NFCF_3 (57)
$CF_2=NCl$	3 hr	CF_3NClF (89)
$CF_3CF=NCl$	3 hr	CF_3CF_2NClF (80)
$CF_2=NF$	4 hr	CF_3NF_2 (97)
$CF_3CF=NF$	10 hr	recovered $CF_3CF=NF$ (93)
$CF_3CF_2CF=NF$	4 hr	explosion C, CF_4, other
$(CF_3)_2C=NF$	5 hr	explosion C, CF_4, other
$(CF=NF)_2$[d]	1 d	recovered $(CF=NF)_2$ (91)

a. 3 mmol of F_2 and imine in a 304 stainless steel reactor

b. After warming from -195°C to 25°C over 1 hr.

c. Yield based on starting imine, not all products were identified.

d. 6 mmol of F_2 were used.

The products CF_3NFCF_3[11], SF_5NFCF_3[12], CF_3NClF[13], CF_3CF_2NClF[3,4] CF_3NF_2[10] were identified by mol wt and by comparison of their IR and ^{19}F NMR spectra with literature values. The unreacted imines, $CF_3CF=NF$ and $(CF=NF)_2$,were similarly identified by comparison with known pure samples. In these two cases, small amounts of other materials were collectively checked by ^{19}F NMR for $CF_3CF_2NF_2$[10] and $(CF_2NF_2)_2$[14] and found to be absent. In the reactions resulting in explosions, CF_4 was the main volatile product not pumped away at -195°. In the latter case, examination of the inside of the reactor showed a fine black deposit, assumed to be carbon. Characterization of the new compound $(CF_3)_2NCF_2NFCF_3$ follows.

$(CF_3^A)_2NCF_2^BNF^CCF_3^D$: b.p. 40.0°C; glass at -195°C; mol. wt. 304.0, calcd. 304.04; $\log P(torr) = 5.9919 - \frac{438.44}{T} - \frac{167740}{T^2}$; $\Delta H_{vap} = 6.9$ kcal/mol; $\Delta S_{vap} = 27.1$ eu; IR 1360-1320 (br,vs), 1270-1130 (br,vs), 1025 (m), 990 (vs), 881 (s), 858 (s), 747 (m), 731 (m), 698 (w), 652 (vw) cm^{-1}. NMR ϕ_A^* 83.9, br-m, ϕ_D^* 68.9, d-t; $J_{AB} = 12.0$, $J_{BC} = 29.0$; $J_{BD} = 12.0$; $J_{CD} = 12.0$ Hz; other coupling constants ≈ 0 Hz,

RESULTS AND DISCUSSION

The results of the reaction of fluorine with 10 imines are summarized in Table 1. Six of the imines add fluorine at various rates at 22° to give the expected perhaloamine in good to excellent yields. The variation in reactivity, however, is surprising. The latter cannot be due to differing experimental conditions, as all the reactions were carried out in an identical manner using a clean 304 stainless steel vessel that had been mildly passivated with fluorine before use. All the imines were identically purified by glc before use.

The uncontrolled reactions with $CF_3CF_2CF{=}NF$ and $(CF_3)_2C{=}NF$ must be due to a fast, radical chain reaction which results in the complete degradation of the starting material. In contrast, $CF_3CF{=}NF$ and $(CF{=}NF)_2$ essentially do not react under the stated conditions.

There are few, if any, reports in the literature on the reactions of isolated perhaloimines with fluorine alone. Bigelow and coworkers have carried out extensive studies on the fluorination of nitriles, using flow systems employing higher temperatures, excess fluorine and relatively high nitrogen dilutions.[15] They isolated a variety of perhalogenated N,N-difluoroamines in this work and in some cases they were able to observe N-fluoroimines. Their results were consistent with the following reaction scheme.

$$\begin{tikzcd}
R_fCF_2N{=}NCF_2R_f & R_fCN \arrow[d, "F_2"] & R_fCF_2NF_2 \\
{[(R_fCF{=}N)_2]} \arrow[u, "F_2"] & {[R_fCF{=}N\cdot]} \arrow[l] \arrow[r, "F2"] & R_fCF{=}NF \arrow[u, "F_2"]
\end{tikzcd}$$

This work probably involved the addition of fluorine to the intermediate N-fluoroimines but alternative routes to the observed N,N-difluoroamines may also have been possible under their conditions.

In subsequent work on the fluorination of perfluoronitriles, Ruff obtained high yields of N,N-difluoroamines at -78° using fluorine and a CsF catalyst.[10] In the absence of the catalyst, the nitriles were unreactive at -78°.

$$R_fCN \xrightarrow{F2/CsF} R_fCF_2NF_2$$
$$(R_f = CF_3,\ C_2F_5)$$

No N-fluoroimines were observed, even when a large excess of nitrile was employed. By reaction of $(CF_3)_2C{=}NH$ with F_2/CsF at -78°, $(CF_3)_2C{=}NF$ and $(CF_3)_2CFNF_2$ were obtained and subsequent fluorination of $(CF_3)_2C{=}NF$ under the same conditions produced $(CF_3)_2CFNF_2$ in high yield. This established the fact that N-fluoroimines could be converted to N,N-difluoroamines and further suggests that N-fluoroimines are probably intermediates in the fluorination of nitriles. This work also suggested that a catalyst was necessary for the low temperature addition of fluorine to a carbon-nitrogen double bond, although only one N-fluoroimine was tried.

Our results clearly show that a metal fluoride catalyst is not necessary for the addition of fluorine to perhaloimines at or below 22° in all cases. It may be argued that metal fluorides on the surface of the 304 stainless steel reactor catalyze this addition in the six cases where addition occurred. However, this is very unlikely because $CF_3CF{=}NF$ did not react. If this imine is an intermediate in the fluorination of CF_3CN by CsF/F_2, it clearly undergoes a rapid catalyzed reaction with F_2, even at -78°.[10] It would appear unreasonable to suggest that the first six compounds in Table 1 are catalytically fluorinated but that this same unknown catalyst (fluoride on the walls of the reactor) fails to work for $CF_3CF{=}NF$ and $(CF{=}NF)_2$.

We believe our results can be rationalized in the following way, as illustrated for $CF_2{=}NF$.

$$CF_2{=}NF + F_2 \rightarrow CF_3NF\cdot + F\cdot$$

$$CF_3NF\cdot + F\cdot + M \rightarrow CF_3NF_2 + M$$

$$CF_3NF\cdot + F_2 \rightarrow CF_3NF_2 + F\cdot$$

The observed products and qualitative reaction rates imply that the first reaction is slow compared to the other two reactions. The low reactivity of $CF_3CF{=}NF$ and $(CF{=}NF)_2$ is very curious and we have no explanation for this. The explosive reactions of $(CF_3)_2C{=}NF$ and $CF_3CF_2CF{=}NF$ can be rationalized on the basis that the intermediate radicals $(CF_3)_2CFNF\cdot$ and $CF_3CF_2CF_2NF\cdot$ are unstable. An analogy can be drawn with the stability of O-F compounds of the type R_fOF and $R_fCF(OF)_2$, which presumably decompose by radical mechanisms. Increasing the carbon number of R_f or the introduction of carbon branching in R_f leads to low stability and pronounced explosiveness. For example $CF_3CF(OF)_2$ has much higher thermal stability and is far less prone to explosive decomposition than either $(CF_3)_2C(OF)_2$ or $CF_3CF_2CF(OF)_2$.[16] The fact that $(CF_3)_2C{=}NF$ and presumably $CF_3CF_2CF{=}NF$ are readily converted to the amines in the presence of CsF/F_2 is reasonable based on the expected nucleophilicity of such compounds leading to the fluorination of an anion $R_fCF_2NF^-$ in the presence of CsF.[17]

Finally, it can be noted that CF_2=NF fails to react with Cl_2 or Br_2, even when heated. Similar behavior is expected for other R_fCF=NF derivatives but they have not been examined. It should be of interest to investigate these and other reactions in the presence of CsF.

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