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Fluoride-Catalyzed Reactions of Perfluoromethanimine. Novel Chemistry of the Perfluoromethanamine Ion

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Perfluoromethanimine ($CF_2{=}NF$) is readily attacked by the fluorides KF, CsF, and HgF_2 to form an intermediate perfluoromethanamine ion, CF_3NF^-. This ion is a reactive nucleophile which readily attacks $CF_2{=}NF$, forming perfluoro-*N*-methylformamidine, and RC(O)F (R = F, CF_3, C_2F_5), forming perfluoro-*N*-methylformamide, acetamide, and propanamide. With CsF, the intermediate formamidine is cyclized to perfluoro-1-methyldiaziridine. The latter undergoes an unusual isomerization in the presence of Fe, Cr, or Ni to bis(trifluoromethyl)diazene. NMR, IR, and mass spectral and physical data are presented for new compounds.

In unsaturated fluorocarbon systems, fluoride ion as a nucleophile occupies a unique position analogous to that of the proton as an electrophile in unsaturated hydrocarbons.[2,4] Fluoro olefins with a $CF_2{=}$ group are especially reactive toward fluoride ion and this high reactivity apparently extends to some heteroatom systems such as $CF_2{=}O$. For example, $CF_2{=}O$ reacts exothermically with finely powdered fused CsF at 22 °C to form $CsOCF_3$.[5,6] In contrast, $CF_3C(O)F$ is only partially absorbed by excess CsF under the same conditions, although a variety of interesting reactions involving perfluoroalkoxide anions are known for acid fluorides, especially in conjunction with the chemistry of perfluorinated epoxides.[7]

Unsaturated fluorocarbon systems containing nitrogen of the type $CF_2{=}N$ may also exhibit a high degree of reactivity toward fluoride ion, but the difficulty in obtaining the appropriate imines has limited investigaton. A few examples of fluoride ion catalyzed reactions with fluorocarbon nitriles, which may involve intermediate perfluoroalkanamine ions, are known.[8-10] In addition, reactions of CsF with $CF_3N{=}CF_2$,[11] $SF_5N{=}CF_2$,[12] $(CF_3)_2NN{=}CF_2$,[13] $CF_3ON{=}CF_2$, and $(CF_3)_2CFON{=}CF_2$[14] all result in dimerization of the imines, suggesting the same ionic mechanism in each case.

$$RN{=}CF_2 + F^- \rightarrow CF_3NR^- \xrightarrow{RN=CF_2} CF_3RNCF{=}NR + F^- \quad (1)$$

$$R = CF_3,\ SF_5,\ (CF_3)_2N,\ CF_3O,\ (CF_3)_2CFO$$

The recent availability of the simplest perfluorinated imine, $CF_2{=}NF$, provides an opportunity to investigate its reactivity toward fluoride ion.[15] As expected, $CF_2{=}NF$ is very reactive, and the perfluoromethanamine ion is readily formed.[16] Nucleophilic reactions of CF_3NF^- lead to several novel compounds.

Experimental Section

General Methods. Volatile compounds were handled in glass or stainless steel vacuum systems. The glass system employed Teflon-glass valves throughout. Pressures were measured with a Wallace and Tiernan differential pressure gauge (Series 1500). Temperatures were measured with a iron–constantan digital-indicating thermocouple. Amounts of materials were measured by direct weighing or by PVT measurements.

Infrared spectra were recorded on Perkin-Elmer 337, 1330, or 180 spectrometers by using 10-cm glass cells fitted with KCl or AgCl windows. NMR spectra were taken on a Varian XL-100-15 spectrometer with ~80 mol % $CFCl_3$ as the solvent and internal reference. Chemical shifts are negative to higher field of $CFCl_3$ and vice versa. Mass spectra were taken on a Finnigan 4021-C instrument at 70 eV for EI and CI (CH_4). Samples were introduced into the source by direct gas inlet.

Molecular weights were determined by gas density measurements. Melting points were taken by a modified Stock procedure. Vapor pressures were measured by the method of Kellogg and Cady[17] or by means of a small isoteniscope.[18] Data was analyzed by a computer-assisted least-squares fit to linear and quadratic equations, and the best fit is reported.

Reagents. Chlorine, F_2, ClCN, $(CF_3CO)_2O$, $COCl_2$, CF_3CO_2H, $CF_3CF_2CO_2H$, Hg, CsF, KF, NaF, and SbF_3 were obtained from commercial sources and appropriately purified as needed. Potassium and cesium fluoride were fused in a Pt dish, and then the molten fluoride was allowed to cool in a drybox and ground to a fine powder. The compounds HgF_2,[19] COF_2,[20] $CF_3C(O)F$, $C_2F_5C(O)F$,[20,21] and $CF_2{=}NF$[15] were prepared by literature methods.

Reactions. All reactions were carried out in 100-mL glass bulbs fitted with a glass–Teflon valve and containing a small magnetic stirring bar. The appropriate metal fluoride was added in the drybox, and the reactor was then attached to the vacuum line. After the reactor was evacuated and cooled to −196 °C, the gaseous reactants were added by vacuum transfer. The reactor was then warmed to 22 °C and stirred for an appropriate time. The reactor was then cooled to −196 °C, any non-condensable gases were noted and removed, and the remaining volatile materials were separted by distillation through a series of cold traps. Final purification of new compounds was achieved by GLC on 20 ft × 0.25 in. column packed with perfluorotributylamine on Chromosorb P.

The reactions are summarized in Table I, and the characterization of the new compounds is given below.

$CF_3{}^ANF^BCF^C{=}NF^D$: bp −5.5 °C; glass formation −196 °C; mol wt. 169.2, calcd 166.04; $\log P$ (torr) = 7.8915 − 1341.1/T; ΔH_{vap} = 6.14 kcal/mol; ΔS_{vap} = 22.9 eu; NMR δ −77.1 (dd, A), −69.3 (ddq, B), −64.3 (br m, c), −16.9 (br s, D), J_{AB} = 17 Hz, J_{AC} = 5.5 Hz, J_{AD} = ≤1 Hz, J_{BC} = 27 Hz, J_{BD} = 12.0 Hz, J_{CD} = 16.0 Hz; IR 1675 (s), 1400 (w), 1350 (vs), 1330 (vs), 1280 (vs), 1240 (vs), 1065 (w), 1040 (m), 990 (s), 945 (s), 840 (m), 735 (m), 662 (w), 570 (w) cm^{-1}; MS (EI), major m/z 166 (M^+), 128 ($C_2F_4N_2{}^+$), 69 ($CF_3{}^+$), 64

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Table I. Fluoride-Catalyzed Reactions of $CF_2{=}NF$

reactants[a]	MF[b]	time, h[c]	products[d]
$CF_2{=}NF$ (3.0)	KF (8)	24	$CF_3NFCF{=}NF$ (1.2), <$\mathrm{CF_3\overline{NCF_2N}F}$, CF_3Cl,[d] $CF_3C(O)F$,[d] $CF_3C(O)NFCF_3$ [e]
$CF_2{=}NF$ (3.8)	KF (1.8)	22	$CF_3NFCF{=}NF$ (1.7), other
$CF_2{=}NF$ (5.4)	CsF (8)	13	$\mathrm{CF_3\overline{NCF_2N}F}$ (1.9), N_2 (0.7), other
$CF_2{=}NF$ (3.6)	CsF (1.7)	13	$\mathrm{CF_3\overline{NCF_2N}F}$ (1.3), other
$CF_2{=}NF$ (3.0)	NaF (8)	24	no reaction
$CF_2{=}NF$ (3.0), $CF_3C(O)F$ (3.5)	KF (8)	15	$CF_3C(O)NFCF_3$ (1.8), reactants (2.5)
$CF_2{=}NF$ (2.2), $CF_3C(O)F$ (2.2)[f]	CsF (10)	12	$\mathrm{CF_3\overline{NCF_2N}F}$ (0.9), other
$CF_2{=}NF$ (2.5), $CF_3C(O)F$ (4.0)	CsF (0.8)	3	$CF_3C(O)NFCF_3$ (1.7), reactants (2.3)
$CF_2{=}NF$ (3.0), $C_2F_5C(O)F$ (2.6)	KF (6)	12	$C_2F_5C(O)NFCF_3$ (0.9), $CF_3NFCF{=}NF$, $C_2F_5C(O)F$
$CF_2{=}NF$ (1.9), $C_2F_5C(O)F$ (1.9)	CsF (6)	13	$C_2F_5C(O)NFCF_3$ (0.4), $CF_3NFCF{=}NF$, $\mathrm{CF_3\overline{NCF_2N}F}$, $C_2F_5C(O)F$
$CF_2{=}NF$ (2.8), COF_2 (3.0)	CsF (1.5)	7	$CF_3NFC(O)F$[g] (2.6), <other
$CF_2{=}NF$ (4.1), COF_2 (2.0)	CsF (2.1)	11	$CF_3NFC(O)F$/$\mathrm{CF_3\overline{NCF_2N}F}$ (2.5), other
$CF_2{=}NF$ (1.5), $CH_3C(O)F$ (1.3)	CsF (1.3)	9	$\mathrm{CF_3\overline{NCF_2N}F}$ (0.7), $CH_3C(O)F$, other
$CF_2{=}NF$ (3.8)	HgF_2 (4)	10	$CF_3NFCF{=}NF$ (0.8), N_2, $CF_2{=}NF$, other

[a] Amounts in millimoles in parentheses. [b] Amounts in grams in parentheses. [c] At ~22 °C. [d] Impurities in $CF_2{=}NF$, which were present in small amounts in nearly all the reactions carried out. [e] Formed by reaction with $CF_3C(O)F$ impurity in the starting material. Small amounts of this product were probably formed in nearly all reactions of $CF_2{=}NF$ involving KF or CsF. [f] $CF_3C(O)F$ (4 mmol) was stirred for 24 h at 22 °C with the CsF. The unabsorbed $CF_3C(O)F$ was then removed, and $CF_2{=}NF$ was added. [g] This compound was identical with that reported by: Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1979**, *18*, 919.

(CF_2N^+), 59 (CFN_2^+), 50 (CF_2^+); MS (CI), *m/e* 167 (MH^+).

$\mathrm{CF_3{}^{A}\overline{NCF^{B}F^{C}N}F^{D}}$: bp −17.2 °C; glass formation −141.4 °C; mol wt 167.9, calcd 166.04; log *P* (torr) = 7.6514 − 1220.99/*T*; ΔH_{vap} = 5.57 kcal/mol; ΔS_{vap} = 21.8 eu; NMR (second-order M_3ABX type) δ −62.9 (br d, A), −113.1 (m, B), −111.8 (br m, C), −12.4 (br s, D), J_{AB} = 9.5 Hz, $J_{AC} \leq$ 2 Hz, $J_{AD} \leq$ 2 Hz, J_{BC} = 41.5 Hz, J_{BD} = 9.5 Hz, J_{CD} = 17.5 Hz; IR 2480 (vw), 2280 (vw), 2075 (vw), 1600 (vw), 1435 (vs), 1380 (w), 1312 (vs), 1240 (vs), 1190 (vw), 1100 (vw), 1054 (m), 966 (s), 906 (m), 830 (m), 763 (m), 710 (s), 585 (w), 520 (w) cm^{-1}; MS (EI), major *m/z* 69 (CF_3^+), 64 (CF_2N^+), 59 (CFN_2^+), 50 (CF_2^+);MS (CI), *m/e* 167 (MH^+), 147 ($C_2F_5N_2^+$), 69 (CF_3^+).

$\mathrm{CF_3{}^{A}C(O)NF^{B}CF_3{}^{C}}$: bp −6.0 °C; mp −89 °C; mol wt 199.3, calcd 199.04; log *P* (torr) = 7.0243 − 922.25/*T* − 65521/T^2; ΔH_{vap} = 6.37 kcal/mol; ΔS_{vap} = 22.8 eu; NMR −66.8 (d, A), −82 (br s, A), −74.1 (d, C), J_{AB} = 11.0 Hz, J_{BC} = 22.0 Hz; IR 3581 (vw), 1805 (s), 1760 (w), 1336 (s), 1285 (vs), 1260–1190 (vs), 1163 (vs), 1054 (m), 926 (w), 880 (s), 762 (m), 730 (w), 697 (s), 660 (m), 606 (w), 564 (m), 527 (w) cm^{-1}; MS (EI), major *m/z* 152 ($C_2F_6N^+$), 130 ($C_2F_4NO^+$), 97 (CF_3CO^+), 92 ($C_2F_2NO^+$), 69 (CF_3^+), 64 (CF_2N^+), 50 (CF_2^+), 47 (FCO^+); MS (CI), *m/e* 200 (MH^+), 167 ($C_3F_6OH^+$).

$\mathrm{CF_3{}^{A}CF_2{}^{B}C(O)NF^{C}CF_3{}^{D}}$: bp 32.9 °C; mp − 123.5 °C; mol wt 246.9, calcd for 249.05; log *P* (torr) = 7.4040 − 1384.5/*T*; ΔH_{vap} = 6.33 kcal/mol; ΔS_{vap} = 20.7 eu; NMR −82.5 (dt, A), −120.2 (dqq, B), −81.0 (br s, C), −66.7 (dm, D), J_{AB} = 1.0 Hz, J_{AC} = 7.5 Hz, J_{BC} = 29.0 Hz, J_{BD} = 1.0 Hz, J_{CD} = 10.5 Hz; IR 3560 (w), 1790 (s), 1415 (w), 1350 (sh), 1310–1275 (s), 1250–1190 (vs), 1160 (vs), 1065 (s), 1030 (s), 1010 (s), 940 (w), 859 (m), 837 (m), 756 (m), 734 (w), 700 (s), 680 (sh), 613 (m), 586 (m), 531 (m) cm^{-1}; MS (EI), major *m/z* 147 ($C_2F_5CO^+$), 119 ($C_2F_5^+$), 69 (CF_3^+), 50 (CF_2^+); MS (CI), *m/e* 250 (MH^+), 200 ($C_3F_7CONH^+$), 167 ($C_3F_6OH^+$), 147 ($C_3F_5O^+$), 69 (CF_3^+).

Results and Discussion

The fluoride-catalyzed reactions of $CF_2{=}NF$ are summarized in Table I. Most of the reactions were repeated several times, and typical cases are presented in this table. The results clearly show that KF, CsF, and HgF_2 are effective in the formation of the perfluoromethanamine ion CF_3NF^-, whereas NaF is not. All the reactions can be explained by the initial step shown in eq 2. The CF_3NF^-

$$\mathrm{MF + CF_2NF \rightarrow M^+\ FNCF_3{}^-} \qquad (2)$$

anion then functions as a reactive nucleophile in competition with the excess fluoride. Because the reactions are heterogeneous, the observed products and yields are variable depending on the fluoride ion activity, amount of MF, scale of the reaction, and other factors.

The first reaction observed with CF_3NF^- was the reaction with $CF_2{=}NF$ to form perfluoro-*N*-methylformamidine in the presence of KF (eq 3). The formamidine

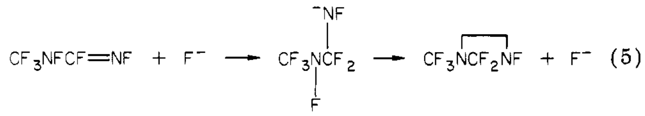
$$\mathrm{CF_3NF^- + CF_2{=}NF \xrightarrow[-F^-]{KF} CF_3NFCF{=}NF\ (80\text{–}90\%)} \qquad (3)$$

was also formed with HgF_2 but in lower yield. In this case, in contrast to KF, considerable $CF_2{=}NF$ is absorbed by the HgF_2. The HgF_2 residue may then have contained $(CF_3NF)_2Hg$, but this was not identified.

With CsF, the reaction of $CF_2{=}NF$ gives only traces of the linear formamidine dimer, and the major product is a novel perfluoro-1-methyldiaziridine (eq 4). The origin

$$\mathrm{CR_3NF^- + CF_2{=}NF \xrightarrow[-F^-]{CsF} CF_3\overline{NCF_2N}F\ (70\%)} \qquad (4)$$

of the diaziridine is believed to be the further reaction of the initially formed $CF_3NFCF{=}NF$ with CsF. Formation of the formamidine first with KF followed by treatment with CsF results in the same product. The increased activity of the CsF results in further fluoride ion attack and an internal nucleophilic displacement of fluoride from nitrogen[22] (eq 5). Precedent for such a reaction is available



$$\mathrm{CF_3NFCF{=}NF + F^- \longrightarrow CF_3N\underset{F}{\overset{^-NF}{C}}F_2 \longrightarrow CF_3\overline{NCF_2N}F + F^-} \qquad (5)$$

from the synthesis of the diaziridine $\mathrm{\overline{CF_2N{=}N}}$ from the

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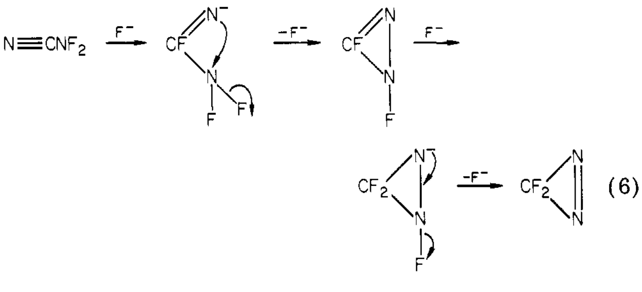
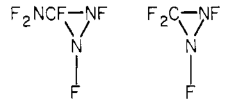
(22) A referee suggested the following alternative mechanism for the formation of the diaziridine which cannot be ruled out by this work.

$$\mathrm{CF_3NFCF{=}NF \overset{F^-}{\rightleftharpoons} CF_3N{=}CFNF_2 \xrightarrow{F^-} CF_3NCF_2NF_2{}^- \xrightarrow{-F^-} CF_3\overline{NCF_2N}F}$$

reaction of $N{\equiv}CNF_2$ with CsF, which may proceed by a two-sequence process of the above[23,24] (eq 6). Similar



results were also found for the reaction of $(F_2N)_2C{=}NF$ and $F_2NCF{=}NF$ with CsF, resulting in the formation of I and II, respectively.[25] However, our result is apparently



I II

the first example of this process not involving the elimination of fluoride ion from an NF_2 group and serves to confirm the generality of this rearrangement. Other work by us also shows that the substituent on the terminal nitrogen of the formamidine can be chlorine.[26]

The reactivity of CF_3NF^- as a nucleophile was further demonstrated by reactions with carbonyl fluorides (eq 7).

$$CF_2{=}NF + F^- \xrightarrow{KF} CF_3NF^- \xrightarrow{RC(O)F} CF_3NFC(O)R + F^- \quad (7)$$

$$R = F,\ CF_3,\ C_2F_5,\ CH_3$$

The yield varied rather drastically as a function of R with F (93%), CF_3 (68%), C_2F_5 (30%), and CH_3 (0%). The competing reaction of CF_3NF^- with $CF_2{=}NF$ increased as $R_fC(O)F$ became less reactive, and with $CH_3C(O)F$, this was the only reaction observed. Similarly, an attempt to substitute $CF_3NFCF{=}NF$ a second time with CF_3NF^- was unsuccessful. The excess $CF_2{=}NF$ in a reaction with CsF and COF_2 was converted to the diaziridine with no evidence for $(CF_3NF)_2C{=}NF$. A preliminary report claiming the formation of $C_2F_5OCF{=}NF$ by reaction of $CF_2{=}NF$ with $CF_3C(O)F$ and CsF was in error.[27] The reaction of $CF_3C(O)F$ absorbed on CsF with $CF_2{=}NF$ produces only the diaziridine.

In all reactions involving CsF, small amounts of $CF_2{=}NF$ are absorbed by the CsF and not found as volatile nitrogen-containing products. Heating the CsF to ~150 °C does not result in recovery of the $CF_2{=}NF$. On occasion, larger scale reactions resulted in a sticky–wet coating on the CsF. The identity of these products is unknown, and our observations may suggest that formation of some polymeric material.[28]

The characterization of the new compounds by IR, NMR, and mass spectral and physical data is given in the Experimental Section. In each case the interpretation is straightforward. Intense parent ions are observed in the CI mass spectrum of each compound, and the infrared spectra contain characteristic absorptions for the C=N in $CF_3NFCF{=}NF$ (1675 cm^{-1}), for $\overline{NCN}$ in $CF_3\overline{NCF_2N}F$ (1435 cm^{-1}), and for C=O in $CF_3C(O)NFCF_3$ and $C_2F_5C(O)NFCF_3$ (~1800 cm^{-1}).

The ^{19}F NMF shows the expected number of different resonances in each case with the appropriate relative areas. In $CF_3{}^ANF^BCF^C{=}NF^D$, the resonance for D can be assigned on the basis of the large line width, typical for *N*-fluoro imines.[28] The distinction between B and C, both of which are somewhat broadened, is based mainly on the magnitude of J_{AB} which is typically greater than 10 Hz in a variety of CF_3NF derivatives.[30,31] By homonuclear decoupling, all the coupling constants could be determined. The J_{CD} value of only 16.0 Hz implies that fluorines C and D are syn.

In $CF_3{}^A\overline{NCF^BF^CN}F^D$ the nitrogen atoms may be nearly planar. However, for the purpose of discussing the ^{19}F NMR, a reasonable model is to assume the $CF_3{}^A$ group and F^B extend above the plane of the ring and F^C and F^D below the plane. The relative magnitude of the coupling constants $J_{AB} > J_{AC}$ and $J_{CD} > J_{BD}$ would then be reasonable on the basis of the expected nonbonded distances. The relative magnitude of $J_{AB} > J_{AC}$ is similar in $CF_3{}^A\overline{NCF^BF^CO}$,[32] with B having a smaller line width than C, as in the diaziridine, where B is considerably less broad than C. However, J_{BC} is much larger and ΔBC much smaller in the diaziridine.

The new compounds are all thermally stable at 22 °C in dry glass. However, $R_fC(O)NFCF_3$ compounds are moisture sensitive and readily hydrolyze to corresponding amine and acid. This was previously shown for $FC(O)NFCF_3$,[33] and when $CF_3C(O)NFCF_3$ was treated with H_2O in glass it readily formed the amine as shown by IR (see eq 8 and 9). Perfluoro-1-methyldiaziridine, while stable

$$FC(O)NFCF_3 + H_2O \xrightarrow{22\ °C} CO_2 + HF + CF_3NHF \quad (8)$$

$$CF_3C(O)NFCF_3 + H_2O \xrightarrow{22\ °C} CF_3CO_2H + CF_3NHF \quad (9)$$

in glass, was found to be sensitive to metal. In metal systems of 304 and 316 stainless steel which had been treated with F_2, $CF_3\overline{NCF_2N}F$ underwent an unusual isomerization to bis(trifluoromethyl)diazene[34,35] (eq 10).

$$CF_3\overline{NCF_2N}F \xrightarrow{22\ °C} CF_3N{=}NCF_3\ (>95\%) \quad (10)$$

A 2.5-mmol sample standing in a small-volume vacuum system for 1 day at 22 °C was completely isomerized, and no other significant products were formed. This isomerization is presumably caused by transition-metal fluorides on the surface of the stainless steel. The 304 and 316 stainless steels used in our work contain mainly Fe, Cr, and Ni. Therefore, an attempt was made to check the above presumption. Small amounts (~0.2 g) of small Ni shot, small pieces of Cr, and 200-mesh Fe powder were treated each separately in a 50-mL glass vessel for a brief time with

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(27) See ref 16. Considerable effort was expanded to repeat this result. After repeated failures under a variety of conditions, the problem was traced to a mislabeled sample of $CF_3CF_2CF{=}NF$ which was originally chromatographed as the reaction product from $CF_2{=}NF/CF_3C(O)F/CsF$. The properties (IR and ^{19}F NMR) of $C_2F_5CF{=}NF$ closely resemble those expected for $C_2F_5OCF{=}NF$ (see ref 15).

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~700 torr of F_2. The diaziridine (0.3 mmol) was then added to the evacuated flask and allowed to stand for 12 h. After this time, nearly complete isomerization was observed in each case. The Ni metal appeared to be the most reactive.

The possibility that the metal alone is responsible for the isomerization was then checked with the 200-mesh iron powder. Surprisingly, the rate of isomerization was qualitatively the same as with the fluorine-treated powder. This result clearly leaves the identity of the catalytic species open. It may be that small amounts of the Fe surface were first fluorinated by the N–F bond and that indeed metal fluorides are the catalytic species. However, the only conclusion that can be drawn at this time is that the isomerization is caused by Fe, Ni, and Cr and/or certain compounds of these elements.

In conclusion, fluoride-catalyzed reactions of $CF_2{=}NF$ provide a facile route to a variety of *N*-fluoro compounds. Reactions of CF_3NF^- as a nucleophile can clearly by extended to other substrates which are at least as susceptible to nucleophilic attack as $CF_2{=}NF$. Finally, the isomerization sequence $CF_3NFCF{=}NF \rightarrow CF_3\overline{NCF_2N}F \rightarrow CF_3N{=}NCF_3$ is a fascinating example of the propensity of fluorocarbon nitrogen–fluoride derivatives to undergo fluorine shifts and skeletal rearrangements.

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Registry No. $CF_2{=}NF$, 338-66-9; $CF_3C(O)F$, 354-34-7; $C_2F_5C(O)F$, 422-61-7; COF_2, 353-50-4; $CH_3C(O)F$, 557-99-3; KF, 7789-23-3; CsF, 13400-13-0; NaF, 7681-49-4; HgF_2, 7783-39-3; $CF_3NFCF{=}NF$, 41409-49-8; $CF_3C(O)NFCF_3$, 82241-74-5; $C_2F_5C(O)NFCF_3$, 84602-24-4; $CF_3NFC(O)F$, 68986-54-9; CF_3NF^-, 82241-77-8; $CF_3N{=}NCF_3$, 372-63-4; perfluoro-1-methyldiaziridine, 82241-73-4.

Versatile Syntheses of Quinolines by Annulation of Pyridines. Synthesis of Furo[2,3-*g*]- and -[3,2-*g*]quinolines

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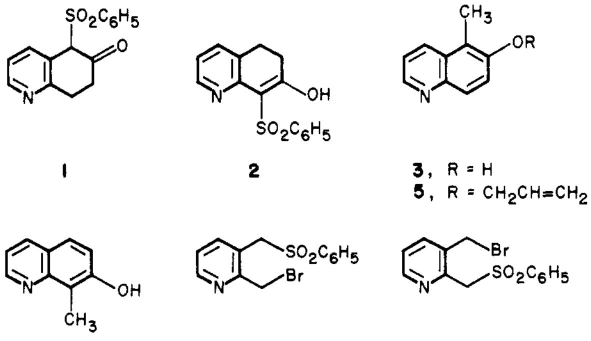
A new, versatile annulation route for the synthesis of substituted quinolines has been developed by using regioisomeric bifunctional pyridine derivatives with vicinal bromomethyl and (phenylsulfonyl)methyl groups. The sequence consists of (a) alkylation of substituted diethyl malonates with these (bromomethyl)pyridines and (b) intramolecular acylation with concomitant decarboxylation and leads to quinoline derivatives variously substituted in the carbocycle. A simultaneous desulfurization–aromatization of the carbocycle has been developed for these cyclized sulfones. 5-(Phenylsulfonyl)-7-allyl-6-quinolinol (**30**), obtained via this cyclization and dehydrogenation, was then used for the preparation of furo[2,3-*g*]quinoline derivatives. The novel parent systems furo[2,3-*g*]- and -[3,2-*g*]quinoline (**38** and **40**) were obtained in good yield in a one-operation acid-induced cyclization–elimination sequence from the bicyclic annulation products **22** and **28**, respectively.

Among the various methods available for synthesis of quinolines, the approach based on the annulation of pyridine derivatives has usually been ineffective and of minor synthetic importance or applicability, for reasons mentioned previously.[1] At the same time, the major routes leading to quinolines,[2] including newer methods,[3] impose limitations on the introduction of certain more complex substituents such as functionalized side chains at the various sites of the carbocycle. Development of new routes leading to quinolines via annulation of pyridines could possibly overcome these limitations and thus broaden the range of available quinoline derivatives, which are compounds of major biological and medicinal importance. Progress toward this goal has been recently reported by us[1] and subsequently by others.[4] The previously obtained bicyclic compounds 1 and 2 were, however, resistant to further substitution in the carbon ring (see below). Hence we have continued our efforts to develop a simple and more general annulation route which would extend the existing methodology by leading to variously substituted quinolines and providing new pathways to pyridine-fused polycyclic systems. We now describe the results of these efforts.

Chart I



1 **2** **3**, R = H
5, R = $CH_2CH{=}CH_2$
4 **6** **7**

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