Table VII. A_1 Block Symmetry Force Constants

	$AsF_5 \cdot NCCH_3$	$SbF_5 \cdot NCCH_3$	$SbCl_5 \cdot NCCH_3$
F_{11} [a]	4.994 (5) [b]	4.99 (1)	4.936 (8)
F_{22}	18.38 (3)	18.26 (6)	18.00 (4)
F_{33}	0.584 (3)	0.583 (6)	0.570 (2)
F_{44}	5.27 (8)	5.32 (5)	5.30 (3)
F_{55}	4.34 (2)	4.20 (4)	1.78 (2)
F_{66}	5.07 (2)	4.60 (4)	2.48 (3)
F_{77}	1.00 (12)	1.08 (4)	1.08 (3)
F_{88}	1.87 (25)	1.88 (8)	1.09 (2)
F_{28}	−0.25 [c]	−0.25 [c]	−0.25 [c]
F_{34}	−0.41 (2)	−0.41 (1)	−0.38 [c]
F_{78}	0.10 (6)	0.34 (2)	0.17 (22)

[a] The subscripts identify F_{kl} with the corresponding symmetry coordinates k and l defined in Table IV. Force constants F_{33} and F_{77} are in units of mdyn Å/radian² while F_{34} and F_{78} are in units of mdyn/radian. All other force constants are in units of mdyn/Å.
[b] Least-squares standard deviations, given in parentheses, represent the deviation in the last decimal place(s) of a given force constant.
[c] These force constants were constrained during refinement. The other 25 unlisted force constants were constrained to zero.

Table VIII. Potential Energy Distribution[a]

	$AsF_5 \cdot NCCH_3$	$SbCl_5 \cdot NCCH_3$
ν_1	100% V_{11}	99% V_{11}
ν_2	87% V_{22} + 10% V_{44}	87% V_{22} + 11% V_{44}
ν_3	105% V_{33} + 8% V_{44} − 13% V_{34}	104% V_{33} + 8% V_{44} − 13% V_{34}
ν_4	7% V_{22} + 82% V_{44} + 9% V_{88}	8% V_{22} + 83% V_{44}
ν_5	93% V_{55}	85% V_{55} + 9% V_{77} + 8% V_{88}
ν_6	100% V_{66}	100% V_{66}
ν_7	7% V_{55} + 64% V_{77} + 32% V_{88} − 7% V_{78}	11% V_{55} + 7% V_{77} + 85% V_{88} − 8% V_{78}
ν_8	32% V_{77} + 56% V_{88} + 6% V_{78}	86% V_{77} + 6% V_{78}

[a] Contributions less than 6% have been omitted.

sented in Tables V and VI. The PED's presented in Table VIII for $AsF_5 \cdot NCCH_3$ hold approximately for $SbF_5 \cdot NCCH_3$, while those for $SbCl_5 \cdot NCCH_3$ are significantly different.

Registry No. $AsF_5 \cdot NCCH_3$, 17632-27-8; $SbF_5 \cdot NCCH_3$, 19106-78-6; $SbCl_5 \cdot NCCH_3$, 19106-78-6.

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

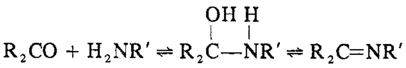
Amide and Fluoroxy Derivatives of *N*-Perfluoroacylhexafluoroisopropylidenimines

KEITH E. PETERMAN and JEAN'NE M. SHREEVE*

Received April 16, 1974 AIC40246R

$LiN=C(CF_3)_2$ readily undergoes metathetical reactions with perfluoroacyl halides to give perfluoroacylimines. The new acylimines, $R_fC(O)N=C(CF_3)_2$ ($R_f = CF_3, C_2F_5$), are susceptible to polar addition of XY (XY = HF, HCl, ClF) across the C=N bond to yield the corresponding secondary and tertiary amides, $R_fC(O)NXCY(CF_3)_2$. Direct fluorination of $CF_3C(O)N=C(CF_3)_2$ under catalytic conditions produces a fluoroamide, $CF_3C(O)NFCF(CF_3)_2$, from saturation of the C=N function and a fluoroxy compound $CF_3CF(OF)NFCF(CF_3)_2$ from further addition across the C=O bond.

The acid-catalyzed reaction of aldehydes or ketones with amines has been the most commonly used preparation as a direct one-step route to imines.



$$R_2CO + H_2NR' \rightleftharpoons R_2\overset{OH}{\overset{|}{C}}—\overset{H}{\overset{|}{N}}R' \rightleftharpoons R_2C=NR'$$

Middleton and Krespan[1] employed this facile one-step procedure in the synthesis of hexafluoroisopropylidenimine, $(CF_3)_2C=NH$,[2] and the electrophilic nature of the C=N[1-11] link has been thoroughly elucidated. The electron-withdrawing substituents (CF_3) on the imine carbon enhance the electrophilicity of the C=N bond making it very susceptible to nucleophilic attack. Reactive carbon–nitrogen multiple bonds, however, are not limited to imines as is demonstrated by nucleophilic additions to polar isocyanates ($R–N=C=O \leftrightarrow R–N^{\delta-}–C^{\delta+}=O$)[12,13] and nitriles ($R–C\equiv N \leftrightarrow R–C^{\delta+}=N^{\delta-}$).[14,15] Though other polar carbon–nitrogen multiple bonds are electrophilic also, the imine usually is much more susceptible to addition. Generalized addition to carbon–nitrogen multiple-bond linkages has been illustrated by the reaction of chlorine monofluoride when it reacted as a chlorofluorinating agent.[11,14,16,17] Although studies involving nucleophilic or polar addition have been prevalent in recent years, it is noteworthy that a number of papers have appeared dealing with the direct fluorination of carbon–nitrogen multiple bonds.[5,18-20]

---

(1) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).
(2) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **153**, 1334 (1963).
(3) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1431 (1965).
(4) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).
(5) J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967).
(6) D. M. Gale and C. G. Krespan, *J. Org. Chem.*, **33**, 1002 (1968).
(7) O. Glemser and S. P. von Halasz, *Chem. Ber.*, **102**, 3333 (1969).
(8) K. Niedenzu, K. R. Blick, and C. D. Miller, *Inorg. Chem.*, **9**, 975 (1970).
(9) K. Niedenzu, C. D. Miller, and F. C. Nahm, *Tetrahedron Lett.*, **28**, 2441 (1970).
(10) S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 553 (1970).
(11) R. F. Swindell, L. M. Zaborowski, and J. M. Shreeve, *Inorg. Chem.*, **10**, 1635 (1971).
(12) S. Ozaki, *Chem. Rev.*, **72**, 457 (1972).
(13) G. H. Sprenger, K. J. Wright, and J. M. Shreeve, *Inorg. Chem.*, **12**, 2890 (1973).
(14) J. B. Hynes and T. E. Austin, *Inorg. Chem.*, **5**, 488 (1966).
(15) P. H. Ogden, *J. Org. Chem.*, **33**, 2518 (1968).
(16) D. D. Moldavskii and V. G. Temchenko, *J. Gen. Chem. USSR*, **39**, 1362 (1969).
(17) D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Commun.*, **7**, 395 (1970).
(18) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Amer. Chem. Soc.*, **85**, 1606 (1963).
(19) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Amer. Chem. Soc.*, **86**, 1827 (1964).
(20) J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *J. Amer. Chem. Soc.*, **85**, 83 (1963).

The stability of the adducts which result from nucleophilic attack on $(CF_3)_2C{=}NH$ generally renders direct reaction of this imine with substrates unacceptable for introducing the intact imine group as a ligand. However, it was shown that inorganic compounds of groups IIIa-VIa containing labile chlorine of fluorine reacted readily with $LiN{=}C(CF_3)_2$ to form products containing the hexafluoroisopropylidenimino group.[21] We have used this method to synthesize *N*-perfluoroacylhexafluoroisopropylidenimines, $R_fC(O)N{=}C(CF_3)_2$. While CF_3 or F substituents on imine carbons have been shown to be magnetically nonequivalent from ^{19}F nmr studies,[11,15,17,21-24] we have found only a sharp single resonance for these substituents at temperatures as low as $-60°$ which indicates that rapid stereoisomerization must be occurring about the C=N bond.

We have also found that $R_fC(O)N{=}C(CF_3)_2$ is susceptible to uncatalyzed polar addition at the C=N bond. The parent imine and most of the reported addition compounds are thermally stable except for those formed *via* ClF addition which decompose photolytically or thermally above 50°. In a like manner, catalytic fluorination of the trifluoroacetylimine produced a fluoroamine from saturation of the C=N bond plus a fluoroxy compound as a result of further addition across the C=O bond. While $CF_3C(O)NFCF(CF_3)_2$ was thermally stable, the fluoroxy compound, $CF_3CF(OF)NFCF(CF_3)_2$, decomposed slowly at 25°. Although only double-bond saturation and no -OF fluorination occurred at $-78°$, complete saturation was observed at $-60°$.

Nmr and infrared evidence suggests that the trans conformer is the only isomer present for each of the secondary and tertiary amides at 25°.

Experimental Section

Materials. $LiN{=}C(CF_3)_2$[21] and its precursor $HN{=}C(CF_3)_2$[1] were prepared according to literature methods. $CF_3C(O)Cl$ (PCR, Inc.), $C_2F_5C(O)Cl$ (K & K Laboratories, Inc.), ClF (Ozark-Mahoning Co.), and HCl and HF (Matheson) were used as received without further purification. KF and NaF (General Chemical) were dried at 300° and activated with fluorine. CsF (ROC/RIC) was dried *in vacuo* at 135° and activated with fluorine.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. HF was handled in a similar Monel vacuum apparatus. All starting materials and products were measured quantitatively by *PVT* techniques. Products were purified by trap-to-trap distillation. Vapor pressure studies were made by using the method of Kellogg and Cady.[25] Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer by using a 50-mm cell equipped with KBr windows. ^{19}F nmr spectra were obtained on a Varian HA-100 spectrometer by using CCl_3F as an internal standard. ^1H nmr spectra were obtained on either a Varian A-60 spectrometer or a Varian HA-100 spectrometer by using tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Gottingen, Germany. Oxidizing equivalents of the fluoroxy compound were determined by condensing a weighed sample of the compound into an acidic iodide solution and titrating the liberated iodine with standard sodium thiosulfate.

Preparation of $R_fC(O)N{=}C(CF_3)_2$. $LiN{=}C(CF_3)_2$ was prepared according to the literature method[21] in a rigorously flame-dried 100-ml Pyrex vessel fitted with a Teflon stopcock. Then $R_fC(O)Cl$ was condensed onto the dry lithium salt at $-196°$ and allowed to warm slowly to 25° in a cold dewar. The volatile products were separated by trap-to-trap distillation. Reaction conditions are summarized in Table I, infrared data in Table II, ^{19}F and ^1H nmr data in Table III, and elemental analyses and thermodynamic data in Table IV.

Preparation of $R_fC(O)NClCF(CF_3)_2$. Into a 100-ml Pyrex vessel at $-196°$, ClF and $R_fC(O)N{=}C(CF_3)_2$ were condensed. The vessel was immersed in a bath at $-78°$ for 18 hr after which the volatile products were separated by trap-to-trap distillation.

Preparation of $R_fC(O)NHCCl(CF_3)_2$. Condensed into a 100-ml Pyrex vessel at $-196°$ were HCl and $R_fC(O)N{=}C(CF_3)_2$ which were allowed to warm slowly to 25° in a cold dewar. The products were cooled to $-30°$ and excess HCl was removed under vacuum. $C_2F_5C(O)NHCCl(CF_3)_2$ was purified by trap-to-trap distillation.

Preparation of $R_fC(O)NHCF(CF_3)_2$. (a) HF and $R_fC(O)N{=}C(CF_3)_2$ were condensed into a 75-ml Hoke bomb at $-196°$ and allowed to warm slowly at 25°. The vessel was then cooled to $-50°$ and excess HF was removed under vacuum. The volatile products were transferred to a second 75-ml Hoke bomb which contained NaF. This vessel was shaken for 10 min at 25° to remove remaining traces of HF. The volatile products were purified by trap-to-trap distillation.

(b) HCl and $R_fC(O)NClCF(CF_3)_2$ were condensed into a 100-ml Pyrex vessel at $-196°$ and allowed to warm slowly to 25°. The volatile products were separated by trap-to-trap distillation. Chlorine was obtained quantitatively.

Preparation of $CF_3C(O)NFCF(CF_3)_2$ and $CF_3CF(OF)NFCF(CF_3)_2$. Into a 75-ml Hoke vessel containing KF, $CF_3C(O)N{=}C(CF_3)_2$ was condensed. While the system was at $-183°$, gaseous fluorine was added until the pressure reached 1 atm. Unreacted fluorine was removed under dynamic vacuum after completion of the reaction. The products were separated by trap-to-trap distillation.

Results

Hexafluoropropylideniminolithium readily undergoes simple metathetical reactions with perfluoroacyl halides to produce acylimines. Preliminary evidence for the reaction having occurred is the shift of $\nu_{C=O}$ to a lower wave number than that of the reacting perfluoroacyl halide with a concomitant appearance of the C=N stretching frequency at 1750 cm^{-1}. At normal pressures, the C=N band is absent in the gas-phase infrared spectrum of $HN{=}C(CF_3)_2$[1] (the precursor of $LiN{=}C(CF_3)_2$).[21] The new *N*-perfluoroacylhexafluoroisopropylidenimines and most of their derivatives are easily purified by trap-to-trap fractionation. The only separation difficulties occurred in the direct fluorination reaction of $CF_3C(O)N{=}C(CF_3)_2$. This reaction yielded six products under most experimental conditions tried.

$$CF_3C(O)N{=}C(CF_3)_2 + F_2(\text{excess}) \xrightarrow[\text{low temp}]{\text{KF or CsF}}$$
$$CF_3C(O)NFCF(CF_3)_2 + CF_3C(O)F + (CF_3)_2C{=}NF \xrightarrow{F_2}$$
$$CF_3CF(OF)NFCF(CF_3)_2 + C_2F_5OF + (CF_3)_2CFNF_2$$

The yields of each individual species have been found to be extremely sensitive to condition of catalyst, temperature, and $F_2{:}CF_3C(O)N{=}C(CF_3)_2$ molar ratio. The two new compounds which resulted from the fluorination reaction, $CF_3C(O)NFCF(CF_3)_2$ and $CF_3CF(OF)NFCF(CF_3)_2$, could not be separated by conventional fractionation techniques and gas chromatography was not feasible due to the instability of the fluoroxy compound. Therefore, of the many reaction conditions tried, we chose those which generally provide the new compounds independent of one another while minimizing cleavage of the amide bond C(O)-N. Although CsF is generally the preferred catalyst in the synthesis of fluoroxy compounds[26] or direct fluorination reactions, it was found to be too active and extensive cleavage of the amide bond resulted with a concomitant reduction in the yields of the desired products. On the other hand, KF proved to be a good source of fluoride ion while remaining relatively inactive toward the amide bond. The formation

---

(21) R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, **11**, 242 (1972).

(22) P. H. Ogden and G. V. D. Tiers, *Chem. Commun.*, 527 (1967).

(23) P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, **89**, 3868 (1967).

(24) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(25) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

(26) M. Lustig and J. M. Shreeve, *Advan. Fluorine Chem.*, **7**, 175 (1973).

Table I. Reaction Conditions and Stoichiometry

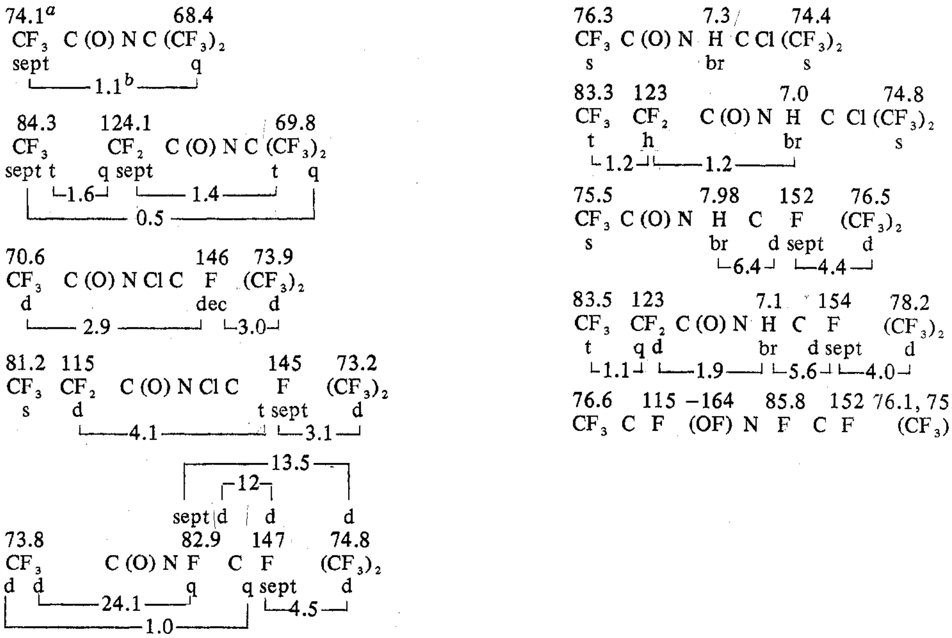
Products	Reactants (mmol)	Reaction time, hr	Reaction temp, °C	Yield, %	Trap,[a] °C
$CF_3C(O)N{=}C(CF_3)_2$ (I)	$LiN{=}C(CF_3)_2$ (7), $CF_3C(O)Cl$ (6)	16	25	55	−98/−65
$C_2F_5C(O)N{=}C(CF_3)_2$ (II)	$LiN{=}C(CF_3)_2$ (10), $C_2F_5C(O)Cl$ (8)	16	25	35	−78/−45
$CF_3C(O)NClCF(CF_3)_2$	I (4), ClF (6)	16	−78	99	−50/−30
$C_2F_5C(O)NClCF(CF_3)_2$	II (5), ClF (6)	16	−78	74	−45/−30
$CF_3C(O)NHCCl(CF_3)_2$	I (5), HCl (6)	16	25	94	−30[b]
$C_2F_5C(O)NHCCl(CF_3)_2$	II (3), HCl (3.6)	16	25	99	−40/−20
$CF_3C(O)NHCF(CF_3)_2$	I (5), HF (5.6)	10	25	99	−35/0
$CF_3C(O)NHCF(CF_3)_2 + Cl_2$	$CF_3C(O)NClCF(CF_3)_2$ (5), HCl (6)	16	25	99	
$C_2F_5C(O)NHCF(CF_3)_2$	II (1), HF (1.3)	10	25	99	−35/0
$C_2F_5C(O)NHCF(CF_3)_2 + Cl_2$	$C_2F_5C(O)NClCF(CF_3)_2$ (2.6), HCl (3.5)	16	25	99	
$CF_3C(O)NFCF(CF_3)_2$[c]	I (4), F_2 (10), KF (9 g)	4.5	−78	85	−75/−60
$CF_3CF(OF)NFCF(CF_3)_2$[c]	I (2), F_2 (10), KF (9 g) or	4	−60	27	−75/−60
	$CF_3C(O)NFCF(CF_3)_2$ (3), F_2 (10), CsF (9 g)	0.75	−78	40	

[a] Under dynamic vacuum, the product passed through a trap at the higher temperature and was retained in the colder trap. [b] Solid at 25°.
[c] Other products included varying yields of $CF_3C(O)F$, $(CF_3)_2C{=}NF$, $(CF_3)_2CFNF_2$, and C_2F_5OF.

Table II. Infrared Data

$CF_3C(O)N{=}C(CF_3)_2$	1790 s, 1750 m, 1340 s, 1318 m, 1270 vs, 1225 vs, 1200 s, 1083 s, 990 s, 828 w, 800 w, 761 w, 727 w, 700 m, 585 w
$C_2F_5C(O)N{=}C(CF_3)_2$	1782 s, 1750 m, 1339 s, 1280 vs, 1225 vs, br, 1200 m, 1178 m (pqr), 1125 m, 1002 s, 985 s, 810 w, 785 w, 760 w, 736 m, 700 m, 546 w
$CF_3C(O)NClCF(CF_3)_2$	1778 s, 1367 m, 1315 m, 1278 s, 1250 vs, 1193 vs, 1160 s, 1111 s, 990 s, 938 w, 734 m, sh, 707 m, 550 w
$C_2F_5C(O)NClCF(CF_3)_2$	1761 s, 1355 s, sh, 1302 s, 1250 vs, sh, 1230 vs, 1180 s, 1161 s, 1110 vs, 1049 s, 980 s, 917 w, 760 w, 735 m, 695 m, 668 w, 540 w
$CF_3C(O)NHCCl(CF_3)_2$	3460 m, 1800 s, 1540 s, 1340 m, 1300 vs, 1270 vs, br, 1242 vs, br, 1190 s, 1108 s, 1088 w, 1008 s, 950 m, 769 w, 710 m, 670 w, 522 w
$C_2F_5C(O)NHCCl(CF_3)_2$	3455 m, 1792 s, 1539 s, 1350 m, 1300 vs, 1240 vs, br, sh, 1173 m, 1150 s, 1117 s, 1040 m, 982 s, 949 m, 833 w, 761 w, sh, 710 m, 665 w, 528 w
$CF_3C(O)NHCF(CF_3)_2$	3465 m, 1809 s, 1540 m, 1331 m, 1292 vs, 1260 vs, br, 1190 vs, 1137 m, 1100 m, 1019 s, 770 w, 724 m, 685 m, 550 w
$C_2F_5C(O)NHCF(CF_3)_2$	3465 m, 1797 s, 1538 s, 1313 vs, 1255 vs, br, 1220 vs, 1182 s, 1165 s, sh, 1115 s, 1036 m, 1002 s, 750 w, 726 m, 682 m, 540 w
$CF_3C(O)NFCF(CF_3)_2$	1799 s, 1362 w, 1310 s, 1250 vs, 1201 vs, 1187 sh, 1165 sh, 1030 w, 992 s, 979 s, 830 w, 738 s, 713 m, 690 m, 530 w
$CF_3CF(OF)NFCF(CF_3)_2$	1260 vs, 1208 s, 1180 s, 1130 m, 1107 m, 1067 w, 1015 w, 975 m, 902 w, 884 vw, 847 vw, 810 vw, 737 m, 675 w, 542 w

Table III. ^{19}F and ^1H Nmr Data[c]



74.1[a] 68.4
CF_3 C (O) N C $(CF_3)_2$
sept q
1.1[b]

84.3 124.1 69.8
CF_3 CF_2 C (O) N C $(CF_3)_2$
sept t q sept t q
1.6 1.4
0.5

70.6 146 73.9
CF_3 C (O) N Cl C F $(CF_3)_2$
d dec d
2.9 3.0

81.2 115 145 73.2
CF_3 CF_2 C (O) N Cl C F $(CF_3)_2$
s d t sept d
4.1 3.1

13.5
12
sept d d d
73.8 82.9 147 74.8
CF_3 C (O) N F C F $(CF_3)_2$
d d q q sept d
24.1 4.5
1.0

76.3 7.3 74.4
CF_3 C (O) N H C Cl $(CF_3)_2$
s br s

83.3 123 7.0 74.8
CF_3 CF_2 C (O) N H C Cl $(CF_3)_2$
t h br s
1.2 1.2

75.5 7.98 152 76.5
CF_3 C (O) N H C F $(CF_3)_2$
s br d sept d
6.4 4.4

83.5 123 7.1 154 78.2
CF_3 CF_2 C (O) N H C F $(CF_3)_2$
t q d br d sept d
1.1 1.9 5.6 4.0

76.6 115 −164 85.8 152 76.1, 75.5
CF_3 C F (OF) N F C F $(CF_3)_2$

[a] ϕ, ppm. [b] *J*, Hz. [c] Key: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; h, hextet; sept, septet; dec, dectet. Reference: internal $CFCl_3$ and $(CH_3)_4Si$.

of $CF_3C(O)NFCF(CF_3)_2$ is indicated by the disappearance of the C=N stretching frequency and shift of $\nu_{C=O}$ to a higher wave number. Infrared evidence for the fluoroxy compound is the disappearance of the C=O stretching frequency accompanied by the appearance of an O–F band at 902 cm^{-1}. The high-resolution nmr (Table III) of $CF_3C(O)NFCF(CF_3)_2$ showed extensive through-bond and through-space spin–spin coupling. The nmr of $CF_3CF(OF)NFCF(CF_3)_2$ is of particular interest since it is the only compound which showed possible magnetic nonequivalence of

Table IV. Elemental Analyses and Thermodynamic Data

	Elemental analyses, %										Thermodynamic data				
	C		N		F		H		Cl					$\log P_{\mathrm{Torr}} = A - B/T$	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Bp, °C	ΔH_{vap}, kcal/mol	ΔS_{vap}, eu	A	B
$CF_3C(O)N{=}C(CF_3)_2$	22.98	22.81	5.36	5.48	65.5	65.1					45.6	7.68	24.09	8.15	1678
$C_2F_5C(O)N{=}C(CF_3)_2$	23.15	23.09	4.50	4.63	67.2	67.1					64.7	7.81	23.13	7.94	1707
$CF_3C(O)NClCF(CF_3)_2$	19.01	19.02	4.43	4.32	60.2	60.2			11.25	11.06	44[a]				
$C_2F_5C(O)NClCF(CF_3)_2$	19.56	19.70	3.92	3.83	62.4	62.4			9.53	9.71	283[b]				
$CF_3C(O)NHCCl(CF_3)_2$	20.16	20.02	4.70	4.72	57.5	57.6	0.33	0.31	11.93	11.84	10[c]				
$C_2F_5C(O)NHCCl(CF_3)_2$	20.72	20.83	4.03	4.15	60.1	60.5	0.29	0.33	10.22	10.20	107.5	9.76	25.6	8.48	2132
$CF_3C(O)NHCF(CF_3)_2$	21.35	21.48	4.98	5.05	67.6	67.8	0.36	0.43			93.6	10.12	27.59	8.91	2211
$C_2F_5C(O)NHCF(CF_3)_2$	21.75	21.75	4.23	4.38	68.9	68.6	0.30	0.35			95.3	9.87	26.80	8.74	2158
$CF_3C(O)NFCF(CF_3)_2$	20.07	20.16	4.68	4.53	69.9	69.9					59.0	7.79	23.4	8.00	1701
$CF_3CF(OF)NFCF(CF_3)_2$					2.0	1.9[d]									

[a] Vapor pressure (Torr) at 26° (decomposes at elevated temperatures). [b] Vapor pressure at 76.5° (decomposes at elevated temperatures). [c] Sublimation pressure at 25° (mp 34–35°). [d] Oxidizing equivalents.

the $(CF_3)_2$ groups even at low resolution. However, the complete coupling scheme could not be resolved since the compound decomposed slowly above 0°, and at temperatures below 0° broadening of many of the peaks caused a loss of the hyperfine splitting pattern.

All of the polar addition reactions proceeded in quantitative or nearly quantitative one-step additions to produce a variety of secondary and tertiary amides.

$$R_fC(O)N{=}C(CF_3)_2 + XY \rightarrow R_fC(O)NXCY(CF_3)_2$$

$$(R_f = CF_3, C_2F_5; XY = HF, HCl, ClF)$$

As in the case of the fluoroamine, the completion of reaction could readily be ascertained from the infrared spectrum due to the disappearance of the C=N stretching frequency. Also, further infrared evidence for the secondary amides was the appearance of the N–H peak at 3455–3465 cm^{-1} and a strong amide II band at approximately 1540 cm^{-1}. Although a recent report has shown that a class of *N*-chloroamines ($R_fNClC(O)R_f'$) can be photolyzed to form a new family of hydrazines,[27] we have found that our analogous ClF addition compounds are thermally and photolytically unstable.

$$R_fC(O)NClCF(CF_3)_2 \xrightarrow[\text{or } \Delta]{h\nu} R_f\cdot + Cl\cdot + O{=}\dot{C}{-}\dot{N}CF(CF_3)_2 \rightarrow$$

$$R_fCl + (CF_3)_2CFNCO$$

The resulting isocyanate had previously been identified as a minor product in the reaction of COF_2 with $LiN{=}C(CF_3)_2$.[21] Therefore, decomposition of $R_fC(O)NClCF(CF_3)_2$ provides a new route to $(CF_3)_2CFNCO$ in quantitative yields. The polar nature of the nitrogen-chlorine bond ($N^{\delta-}$—$Cl^{\delta+}$) has been demonstrated by its reaction with HCl to give the secondary amine and chlorine gas. The secondary amines can also be synthesized directly by addition of HX (X = F, Cl) across the C=N bond. $CF_3C(O)NHCCl(CF_3)_2$ is a white sublimable solid at 25° while its heavier analog $C_2F_5C(O)NHCCl(CF_3)_2$ is unexpectedly a liquid at the same temperature. It is likely that the bulkier C_2F_5 substituent gives rise to packing difficulties which prohibit the crystallization of this species at 25°.

The influence of electron-withdrawing groups on a carbonyl is to reduce the C=O dipole and increase the extent of covalent π bonding which causes the $\nu_{C=O}$ to increase.[4] The two series $R_fC(O)X$ ($R_f = CF_3, C_2F_5$; $X = N{=}C(CF_3)_2$, $NClCF(CF_3)_2$, $NHCCl(CF_3)_2$, $NHCF(CF_3)_2$) accordingly illustrate that the $\nu_{C=O}$ occurred at higher wave numbers for the CF_3 than for the C_2F_5 analog. Also, within a given series similar reasoning can be applied to the C=O band. For $CF_3C(O)NXCF(CF_3)_2$ (X = F or Cl), the carbonyl stretching frequency increased when fluorine replaced chlorine. The carbonyl stretching frequency for both the HF and HCl addition compounds is markedly dependent on the phase examined. The rather high C=O vibration in the gas-phase (10 Torr) infrared spectrum is found to shift to lower frequency by about 40 cm^{-1} when observed as a liquid. This is a function of the increase in hydrogen bonding present in the pure liquid. The single sharp infrared N–H stretching vibrations (3455–3465 cm^{-1}) observed in the gas-phase spectrum of the secondary amides is replaced by broadened, multiple bands at lower frequency for the pure liquids, which is characteristic of trans-configuration amides polymerizing *via* hydrogen bonding.[28]

---

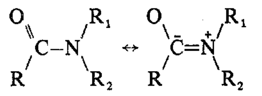
(27) G. H. Sprenger and J. M. Shreeve, *J. Amer. Chem. Soc.*, **96**, 1770 (1974).

(28) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 94.

Hydrogen bonding is also indicated by the high Trouton constants (Table IV) obtained for each of the secondary amides.

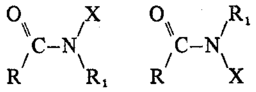
Both of the parent imines, $R_fC(O)N{=}C(CF_3)_2$, show spin-spin coupling of the acyl CF_3 with the two terminal CF_3 groups. However, saturation of the imine function eliminates this coupling. In many instances, identical substituents on imine carbons have been shown to be magnetically nonequivalent by ^{19}F nmr with their coalescence temperatures well above 25° (*i.e.*, $-N{=}C(R_f)_2$; $R_f = CF_3$, F).[11,15,17,21-24] The ^{19}F nmr of the imines reported here show no such coupling even at temperatures down to −60°. Rotation of inversion around the C=N bond causes rapid stereoisomerization,[29] rendering magnetically equivalent (on the nmr time scale) the F atoms of the $-N{=}C(CF_3)_2$.

The ^1H and ^{19}F nmr resonances for the N substituent (H or F) of the new secondary amides and fluoroamides are very broad as a result of the chiral nitrogen center. No geometrically nonequivalent resonances have been observed for the amide function of the form $-C(O)\dot{N}-CX(CF_3)_2$ (X = F or Cl) and the $(CF_3)_2$ groups remain magnetically equivalent. A recent nmr study of amides[30] has expanded the confirmed postulate that partial double-bond character of the C(O)-N amide bond can arise from the contribution of resonance structure A to the amide ground state.



A

Consequently, a stiff, approximately planar, framework may exist which can lead to, among other things, long-range spin-spin coupling from R with R_1 and R_2 and a large barrier to rotation about the C(O)-N bond. Thus, one often finds two conformers for substituted amides.

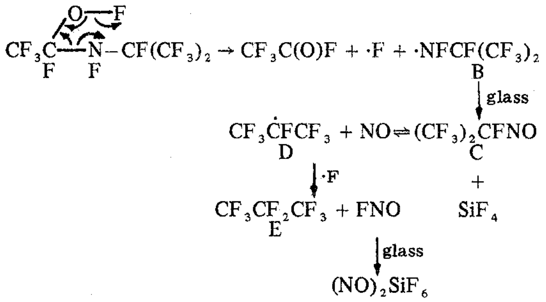


While sterically active groups which cannot be accomodated in the amide plane tend to decrease the height of the rotation barrier *via* loss of delocalization energy, this effect is small since the amides are in a trans configuration only (as confirmed by infrared below). Also, since electron-withdrawing substituents are attached to each end of the amide bond, the net inductive effect should not reduce the contribution from resonance structure A. Observance of a single ^{19}F resonance when $R_1 = CF_3$ and of the two expected resonances when $R_1 = CF_3CF_2$ suggests that only one conformer exists at 25°.

This conformer exists in the trans configuration for the secondary amides since a strong amide II band is observed in the infrared spectrum. The amide II band is an absorption involving the coupling of the N-H bending and other fundamental vibrations and it requires a trans configuration.[28] By analogy, the tertiary amides, for steric reasons, likely exist in the trans configuration also. Presumably, an in-depth nmr investigation of these amides, which has as yet not been undertaken, would be fruitful.

The numerous intense ion fragments in the mass spectrum verify and support the structures. The cracking pattern of the ClF adduct was found to be very sensitive to the chamber temperature of the mass spectrometer with the Cl-containing fragments appearing at higher chamber temperatures. Mass spectra are often not very revealing for fluoroxy compounds as they exhibit patterns of the precursor and thermal decomposition products.[26] We found a similar behavior for $CF_3CF(OF)NFCF(CF_3)_2$. A molecular ion was observed for $CF_3C(O)N{=}C(CF_3)_2$ only.

The fluoroxy compound was found to be thermally unstable at 25°. When decomposition occurred in glass, a complex mixture of products was obtained. The major components of the mixture after complete decomposition had occurred were $CF_3C(O)F$, SiF_4, C_3F_8, $(NO)_2SiF_6$, and R_fNO_2 (G).[31] The principal mode of decomposition is believed to proceed *via* a free-radical mechanism (eq 1). Homolytic



(1)

cleavage of the O-F bond initiates the reaction sequence to produce $CF_3C(O)F$ and the reactive nitrene intermediate B which readily attacks glass to produce the nitroso compound C. The deep blue 2-nitrosoheptafluoropropane (C)[32] can be isolated as a stable species. The equilibrium of C with radical D and nitrogen oxide has been established by Andreades.[24] Thus in the presence of ·F, C is gradually consumed since the radical D is converted to octafluoro-*n*-propane and NO couples with ·F to produce FNO. The rapid reaction of FNO with glass produces a white silicate precipitate

$$6NOF + SiO_2 \rightarrow (NO)_2SiF_6 + 2NO + 2NO_2$$

Oxidizing equivalents of the hypofluorite were found to be 1.9 which agrees reasonably well with the theoretical two-electron change.

Acknowledgment. Fluorine research at Idaho is supported by the Office of Naval Research and the National Science Foundation. We thank Mr. N. R. Zack for mass spectra and Mr. C. Srivanivit for high-resolution ^{19}F nmr spectra.

Registry No. $LiN{=}C(CF_3)_2$, 31340-36-0; $CF_3C(O)Cl$, 354-32-5; $C_2F_5C(O)Cl$, 422-59-3; $CF_3C(O)N{=}C(CF_3)_2$, 52225-57-7; $C_2F_5C(O)N{=}C(CF_3)_2$, 52225-58-8; ClF, 7790-89-8; $CF_3C(O)NClCF(CF_3)_2$, 52225-59-9; $C_2F_5C(O)NClCF(CF_3)_2$, 52225-60-2; HCl, 7647-01-0; $CF_3C(O)NHCCl(CF_3)_2$, 52225-61-3; $C_2F_5C(O)NHCCl(CF_3)_2$, 52225-62-4; HF, 7664-39-3; $CF_3C(O)NHCF(CF_3)_2$, 52225-63-5; $C_2F_5C(O)NHCF(CF_3)_2$, 52225-64-6; $CF_3C(O)NFCF(CF_3)_2$, 52225-65-7; $CF_3CF(OF)NFCF(CF_3)_2$, 52322-49-3.

---

(29) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

(30) W. E. Stewart and T. H. Siddall III, *Chem. Rev.*, **70**, 517 (1970).

(31) Product G had a strong absorption in the infrared spectrum at 1580 cm^{-1} and condenses as a white solid suggesting the $-NO_2$ group. Due to the difficulty of purifying G and lack of reported literature data for fluorinated nitro and nitrito compounds we could not unequivocally assign its structure.

(32) I. L. Knunyants, E. G. Bykhovshaya, V. N. Frosin, and Y. M. Kisel, *Dokl. Akad. Nauk. SSSR, Ser. Khim.*, **132**, 123 (1960).