Acknowledgments.—Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We are grateful to Mr. R. A. De Marco for mass spectra. J. M. S. thanks the Alfred P. Sloan Foundation for a fellowship.

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Hexafluoropropylideniminolithium Reactions with Halides

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Received June 10, 1971

Substitution of the hexafluoroisopropylidenimino group for chlorine or fluorine occurs readily when the lithium salt of $(CF_3)_2C{=}NH$ is reacted with inorganic compounds of groups IIIa–VIa. The formation of lithium halide prevents nucleophilic attack on the double bond and allows the new ketimides to be obtained in yields from 38 to 100%. Compounds obtained from reactions with SOX_2 and COX_2 result from extensive rearrangement.

Following the synthesis of the imine of hexafluoroacetone ($(CF_3)_2C{=}NH$) by Knunyants, *et al.*,[2] and the discovery of the facile one-step synthesis from hexafluoroacetone,[3] a number of papers have appeared describing the electrophilic character of this imine.[2-11] The strongly electron-withdrawing CF_3 groups cause the double bond to be electron deficient thus making it susceptible to attack by nucleophiles which give rise to products of unusually high stability. Although isolated compounds are cited[3,6,11] in which the imine functional group is preserved or regenerated during the course of a reaction, it is the stability of the adduct resulting from nucleophilic attack which generally renders direct reaction of the imine with substrate unacceptable for introducing the intact imine group as a ligand.

We have found that the hexafluoroisopropylidenimino group can be readily introduced by a simple metathetical reaction between the lithium salt of the imine and chlorine- or fluorine-containing inorganic compounds of groups IIIa–VIa, as in

$$RX_n + nLiN{=}C(CF_3)_2 \longrightarrow R(N{=}C(CF_3)_2)_n + nLiX$$

where RX_n = BCl_3, $(CH_3)_3SiCl$, PCl_3, PF_2Cl, PF_3, $AsCl_3$, SCl_2, CF_3SCl, or $CF_3S(O)F$. In these cases, the totally substituted compound is obtained as the major reaction product in yields ranging from 38 to 100%. However, reactions with sulfur(IV) compounds which contain more than one labile halogen and with $COCl_2$ and COF_2 produce compounds in which extensive rearrangement has taken place. This rearrangement is rationalized on the basis of stepwise substitution followed by halide migration to a more electropositive center.

While our preliminary report was in press,[12] the synthetic versatility of this general method was further demonstrated[13] by the reaction of hexafluoroisopropylideniminolithium with transition metal chlorides to obtain the expected ketimides.

Experimental Section

Materials.—Hexafluoroisopropylidenimine, $(CF_3)_2C{=}NH$,[3] and $CF_3S(O)F$[14] were prepared according to the literature. *n*-Butyllithium in hexane (Alfa Inorganics) was transferred into small-volume glass bottles in an inert-atmosphere box for ease in handling but otherwise was used as purchased. Sulfur dichloride was redistilled prior to use. All other chemicals were used as received.

General Procedures.—Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon-tube gauge. Volatile starting materials and purified products were measured quantitatively by *PVT* techniques. Reactants and products of lower volatility were weighed. For gas chromatographic separations the columns were constructed of 0.25-in. aluminum or copper tubing packed with 20% Kel-F polymer oil (3M Co.) or 8% SE-30 (Loenco) on Chromosorb W. In most cases, fractional condensation was used to effect crude separation prior to gas chromatography. Vapor pressure studies were run by using the method of Kellogg and Cady[15] or by an isoteniscopic method.

Infrared spectra were recorded with a Perkin-Elmer 457 or Perkin-Elmer 621 spectrometer by using a 5-cm gas cell equipped with KBr windows. Fluorine-19 nmr spectra were obtained with a Varian HA-100 spectrometer using trichlorofluoromethane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Preparation of Hexafluoroisopropylideniminolithium (I).—In an inert-atmosphere box, 8 ml of 2.3 *M* *n*-BuLi in hexane was transferred *via* a syringe into a rigorously dried glass vessel which had been purged with dry nitrogen. The vessel was cooled to −196° and 20 mmol of $(CF_3)_2C{=}NH$ was introduced. The vessel was allowed to warm slowly from −196 to +25°. An exothermic reaction occurred at about 0° which resulted in a detonation in some cases when 2.67 *M* *n*-BuLi in hexane was used. Explosions did not occur when an additional 10 ml of dry pentane was added to the more concentrated *n*-BuLi in the reaction

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TABLE I

REACTION CONDITIONS AND STOICHIOMETRY

Product	Amt, mmol		Reaction time, hr	Yield, %	Glc conditions	Remarks
	$LiN{=}C(CF_3)_2$	Reactant				
$(CH_3)_3SiN{=}C(CF_3)_2$	13	$(CH_3)_3SiCl$, 10	0.3	100		
$As[N{=}C(CF_3)_2]_3$	15	$AsCl_3$, 4	12	38		Highly water sensitive
$P[N{=}C(CF_3)_2]_3$	20	PCl_3, 5.5	0.5	60	5-ft SE-30 (100°)	Yields increased by running in pentane
	10	PF_2Cl, 3.5	12			No partial substitution observed
	10	PF_3, 30	12			Trace amounts of mono- and disubstitution products observed
$S[N{=}C(CF_3)_2]_2$	12	SCl_2, 5.5	12	83	1.5-ft Kel-F (25°)	Yields increased by running in pentane
$CF_3SN{=}C(CF_3)_2$	12	CF_3SCl, 8	0.5	67	7-ft Kel-F (25°)	
$CF_3S(O)N{=}C(CF_3)_2$	12	$CF_3S(O)F$, 8.2	12	73	2-ft Kel-F (40°)	
$(CF_3)_2C{=}NC(CF_3)_2NSO$	17	$SOCl_2$, 7	12	47	5-ft SE-30 (50°)	Very exothermic—explosion occurred when run without pentane
$(CF_3)_2C(F)NCO$	18	COF_2, 11	0.5		7-ft Kel-F (25°)	$(CF_3)_2C{=}NC(CF_3)_2NCO$ is the major product
$(CF_3)_2C{=}NC(CF_3)_2NCO$	18	$COCl_2$, 8	12		7-ft Kel-F (25°)	Trace of $(CF_3)_2C(Cl)NCO$ identified by mass spectrum
$B[N{=}C(CF_3)_2]_3$	15	BCl_3, 4.5	0.5	40		

TABLE II

INFRARED DATA

$(CH_3)_3SiN{=}C(CF_3)_2$	$As[N{=}C(CF_3)_2]_3$	$P[N{=}C(CF_3)_2]_3$	$Cl_2P[N{=}C(CF_3)_2]_3$	$OP[N{=}C(CF_3)_2]_3$	$S[N{=}C(CF_3)_2]_2$	$CF_3SN{=}C(CF_3)_2$	$CF_3S(O)N{=}C(CF_3)_2$	$(CF_3)_2C{=}NC(CF_3)_2NSO$	$(CF_3)_2C(F)NCO$	$(CF_3)_2C{=}NC(CF_3)_2NCO$	$B[N{=}C(CF_3)_2]_3$
2970 m									2273 s	2273 s	
1770 m	1710 m	1717 m	1742 w	1750 m	1640 sh	1655 w	1675 w	1730 w		1724 w	1810 m
1385 m	1325 s	1328 s	1440 w	1328 s	1625 w	1340 s	1322 s	1335 sh	1493 m	1325 vs	1340 s
1320 s	1300 w	1290 w	1320 m	1270 vs	1340 s	1315 sh	1270 vs	1318 s	1333 . . .	1282 . . .	1280 vs
1253 vs	1258 s	1260 vs	1280 sh	1238 vs	1318 m	1270 vs	1250 vs	1270 s	1282 vs	1205 vs	1245 s
1198 vs	1242 s	1238 vs	1270 s	1220 vs	1260 vs	1205 vs	1228 vs	1250 vs	1266 . . .	1117 s	1220 vs
1072 m	1220 s	1215 vs	1245 sh	975 s	1240 s	1138 vs	1180 sh	1217 s	1235 vs	1093 s	975 s
960 s	970 s	1182 w	1235 s	870 m	1205 vs	990 s	1125 s	1078 w	1190 s	1053 m	930 w
930 m	785 w	1168 w	1215 s	720 m	990 s	825 w	982 s	1003 m	1124 vs	1036 s	758 w
870 s	730 m	972 s	970 m	515 w	810 w	745 m	795 w	982 m	1053 vs	985 s	720 m
855 s		810 w	955 sh		738 m	725 m	750 w	950 w	985 vs	730 s	
760 w		740 w	895 w		725 m	455 w	730 m	732 m	727 s	685 s	
710 m		720 m	720 m				590 w	688 m			
620 w		580 w					432 w	500 w			

vessel before the imine was added. *n*-Butane, hexane, and excess $(CF_3)_2C{=}NH$ were pumped off after standing at 25° for 30 min leaving a brown amorphous solid which darkens on standing but is stable in glass under vacuum for several days. Based on the butane recovered, the conversion to I was about 98% complete.

Preparative Method of Imine Derivatives.—Generally, the new imines were prepared by the following procedure. The halogen-containing parent was distilled onto an excess of I at −196° and allowed to warm slowly to 25° in a cold dewar. Although all the reactions were carried out without a solvent, in some cases reaction was so violent (a detonation occurred with $SOCl_2$) that a few milliliters of pentane was added as a heat sink to moderate the reaction. After reaching 25° the products were separated by trap-to-trap fractionation followed by gas chromatographic purification, although in some cases the latter was not necessary. Reaction conditions are summarized in Table I, infrared data in Table II, major mass spectral ions in Table III, ^{19}F nmr data in Table IV, and elemental analyses and thermodynamic data in Table V.

Preparation of $Cl_2P[N{=}C(CF_3)_2]_3$.—$P[N{=}C(CF_3)_2]_3$ (1.50 mmol) and Cl_2 (1.53 mmol) were condensed into a glass vessel at −196°, warmed slowly to 25°, and allowed to stand at room temperature for 90 min. The vessel was cooled to −30° and excess Cl_2 (about 0.25 mmol) was removed under vacuum. $Cl_2P[N{=}C(CF_3)_2]_3$ was obtained in 75% yield after separation by gas chromatography using a 5-ft SE-30 column heated to 110°.

Reaction of $P[N{=}C(CF_3)_2]_3$ and O_2.—$P[N{=}C(CF_3)_2]_3$ (2.34 mmol) was condensed into a 30-ml Pyrex vessel equipped with a Teflon stopcock and an excess of oxygen was added. The vessel was heated in a water bath to 100° for 20 min during which time the yellow color of the reacting phosphine became very pale. On cooling to 25° large colorless crystals formed on the vessel walls. Excess oxygen was removed and the vessel and the crystalline compound were reweighed. The increased mass of 0.0380 g corresponds to an uptake of 2.37 g-atom of atomic oxygen. Pure crystals are obtained by holding the vessel at 0° and removing the volatiles under dynamic vacuum. A sample of the pure material was stored in glass for 68 days after which its mass spectrum was recorded (see Table III). Solution molecular weights were run in acetone and chloroform. In acetone values of 521 and 530 were obtained, while in chloroform values of 590, 1132, and 1700 were found. The molecular weight of the monomer is calculated to be 539.

Results and Discussion

Reactions of hexafluoroisopropylideniminolithium with labile halides provides a straightforward means of replacing the halide with the intact imine moiety. The reactions are rapid and exothermic and are usually complete at, or below, room temperature. Evidence for reaction having occurred is the appearance of a characteristic C═N stretching frequency between 1600 and 1800 cm^{-1} in the infrared spectra. This band is not observed in the gas-phase infrared spectrum of the parent imine at normal pressures. Separation of the products by gas chromatography usually revealed a large number of minor products, but only in the cases of reaction with excess PF_3 and $C(O)X_2$

TABLE III

MAJOR MASS SPECTRUM IONS

$(CH_3)_3SiN{=}C(CF_3)_2$	M^+, 9;[a] $(M - CH_3)^+$, 0.4; $(M - C_2H_3F_2)^+$, 34; $(M - CF_3)^+$, 25; $SiNC_4F_3^+$, 28; $F_2Si(CH_3)_2^+$, 18; $(CH_3)_2SiF^+$, 100; $Si(CH_3)_3^+$, 68; CF_3^+, 16 (silicon-containing fragments give the correct isotopic ratios)
$As[N{=}C(CF_3)_2]_3$	$AsN_2C_6F_{12}^+$, 0.1; $AsN_3C_7F_6^+$, 0.6; $AsN_3C_6F_3^+$, 0.2; $C_3F_5NH^+$, 4; $C_3F_5N^+$, 2; $C_2F_3NH^+$, 100; $C_2F_2NH^+$, 4; CF_3^+, 79; CF_2^+, 42
$P[N{=}C(CF_3)_2]_3$	M^+, 1; $(M - F)^+$, 0.5; $(M - CF_3)^+$, 0.1; $(M - C_2F_5)^+$, 0.1; $(M - C_2F_6)^+$, 0.1; $(M - C_3F_6N)^+$, 11; $PNC_3F_9^+$, 1; $PNC_3F_7^+$, 17; $PNC_3F_6^-$, 1; $PNC_3F_5^+$, 6; $C_3F_6N^+$, 39; $PNC_3F_2^+$, 12; PCF_3^+, 2; $PNCF_2^+$, 38; $PNCF^+$, 14; CF_3^+, 100
$OP[N{=}C(CF_3)_2]_3$	M^+, 1; $(M - F)^+$, 6; $(M - CF_3)^+$, 1; $(M - C_3F_6N)^+$, 19; $(M - C_4F_8N)^+$, 17; $OPN_2C_5F_5^+$, 27; $OPNC_3F_6^+$, 1; $OPN_2C_4F_3^+$, 43; $C_2F_3NH^+$, 36; CF_3^+, 100; OP^+, 40
$S[N{=}C(CF_3)_2]_2$	M^+, 100; $(M - F)^+$, 22; $(M - CNF)^+$, 54; $CF_3SNC_3F_6^+$, 22; $CF_2SNC_3F_6^+$, 22; $FSNC_3F_6^+$, 39; $SNC_3F_6^+$, 46; $SNC_3F_5^+$, 66; $SNC_2F_2^+$, 84; SCF_3^+, 51; $C_2F_2N^+$, 34; CF_3^+, 68; SF^+, 34; CF_2^+, 31; SN^+, 46
$CF_3SN{=}C(CF_3)_2$	M^+, 65; $(M - F)^+$, 29; $SNC_3F_6^+$, 63; $SNC_3F_5^+$, 21; $SNC_2F_4^+$, 4; $SNC_2F_3^+$, 10; $SNC_2F_2^+$, 14; SCF_3^+, 74; SCF_2^+, 11; $C_2F_2N^+$, 10; CF_3^+, 100; SCF^+, 8
$CF_3S(O)N{=}C(CF_3)_2$	M^+, 2; $(M - CF_3)^+$, 25; $(M - OCF_3)^+$, 6; $OSNC_2F_4^+$, 6; $SNC_2F_4^+$, 2; $OSNC_2F_3^+$, 3; $OSCF_4^+$, 2; SCF_4^+, 18; $OSCF_3^+$, 6; $SNC_2F_2^+$, 2; SCF_3^+, 18; $OSCF_2^+$, 4; SCF_2^+, 11; $C_2F_2N^+$, 31; CF_3^+, 100; OSF^+, 24; SF^+, 14; OS^+, 32
$(CF_3)_2C{=}NC(CF_3)_2NSO$	$(M - F)^+$, <0.1; $(M - NSO)^+$, 19; $(M - CF_3)^+$, 13; $(M - NC_3F_6)^+$, 98; $OSN_2C_3F_3^+$, 11; $OSNC_2F_4^+$, 22; $NC_3F_4^+$, 11; $C_3F_4^+$, 22; $C_2F_3NH^+$, 16; CF_3^+, 100; OSF^+, 55
$(CF_3)_2C(F)NCO$	$(M - F)^+$, 12; $(M - CF_3)^+$, 98; $C_2F_4^+$, 3; $C_2F_3NH^+$, 8; CF_2NCO^+, 100; CF_2NC^+, 4; $FCNCO^+$, 3; CF_3^+, 49; CF_2^+, 13
$(CF_3)_2C{=}NC(CF_3)_2N{=}C{=}O$	$(M - F)^+$, 3; $(M - NCO)^+$, 13; $(M - CF_3)^+$, 16; $C_7N_2F_8^+$, 10; $C_6N_2F_6^+$, 11; $OCNC_3F_6^+$, 68; $OCNC_2F_4^+$, 47; $OCNCF_2^+$, 82; $C_2F_2N^+$, 10; CF_3^+, 100
$B[N{=}C(CF_3)_2]_3$	M^+, 9; $(M - CF_3)^+$, 26; $(M - NC_3F_6)^+$, 11; $(M - NC_4F_9)^+$, 22; $BN_2C_4F_7^+$, 88; $BNC_3F_7^+$, 85; $BNC_3F_6^+$, 11; $BN_2C_4F_3^+$, 89; $BN_2C_4F_2^+$, 68; BCF_4^+, 64; $C_2F_3NH^+$, 100; CF_3^+, 44; $BNCF^+$, 16; CF_2^+, 42; BF_2^+, 59 (boron-containing fragments give the correct isotopic ratios)

[a] Numbers are relative intensities.

were sufficient amounts of the minor products obtained to be identified by mass spectra as the partially substituted products.

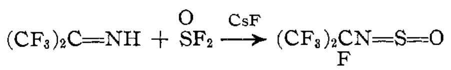
The only product obtained in quantitative yields resulted from reaction of the lithium salt with $(CH_3)_3SiCl$ to give $(CH_3)_3SiN{=}C(CF_3)_2$. This surprisingly stable compound undergoes no reaction with SF_4, PF_3, or $CF_3S(O)F$ even when heated at 80 or 180° (for $CF_3S(O)F$) for extended periods. Hydrolysis does not occur when moist air is added to the pure compound in an infrared gas cell. The stability probably accounts for the observed yield in that this compound does not undergo thermal degradation and side reactions during formation.

The great reactivity of the lithium salt is exemplified by its nonspecificity in removing labile halogens. Reactions with PCl_3, PF_3, and PF_2Cl resulted always in the totally substituted compound as the major product even when widely different conditions of stoichiometry were employed. The fact that virtually no partial substitution occurs even when a large excess of PF_3 was used can be rationalized on the basis of product volatility. As one fluorine atom in PF_3 is replaced by an imine group, the marked decrease in volatility preferentially keeps this molecule in contact with the solid lithium salt and successive substitutions rapidly occur. Presumably partial substitution would predominate in solution but as yet no attempt has been made to verify this. $P[N{=}C(CF_3)_2]_3$ is readily oxidized by Cl_2 to $Cl_2P[N{=}C(CF_3)_2]_3$. The imine groups do not all occupy the equatorial positions of a trigonal bipyramid since two distinct CF_3 resonances in the ratio of 2:1 are observed in the ^{19}F nmr spectrum. No phosphorus–fluorine spin–spin coupling is observed.

A quantitative uptake of oxygen occurs when $P[N{=}C(CF_3)_2]_3$ is heated at 100° for 10 min in the presence of excess oxygen. The readily sublimable crystalline solid which results has an infrared spectrum remarkably similar to that of the parent phosphine; the only major difference is a shift of the C=N stretching frequency to higher energy by about 30 cm^{-1} and the appearance of a new band of medium intensity at 870 cm^{-1}. Only one CF_3 resonance at ϕ 69.9 split into a doublet by phosphorus ($J_{CF_3-P} = 1.9$ cps) is seen in the ^{19}F nmr spectrum. Solution molecular weights have been run on different samples of the compound in different solvents and the results are inconsistent even though infrared spectra prior to the molecular weight determinations were identical. The experimentally obtained molecular weights indicate that possibly monomeric, dimeric, and trimeric species may exist in solution. No mass fragments larger than a parent ion for the monomer have been detected in the mass spectrum. The P=O stretching frequency is normally found in the infrared region between 1415 and 1200 cm^{-1} but it is possible that CF_3 activity has obscured this normally strong band. The new band appearing at 870 cm^{-1} could correspond to a P—O—P stretching frequency[16] and it is hoped that future work using ^{17}O labeling and high-resolution infrared spectroscopy will be useful in determining the degree of molecular association in the solid.

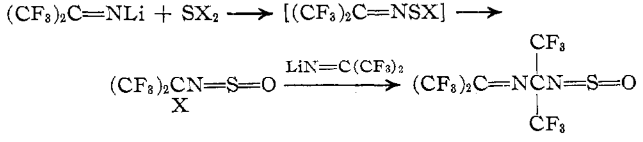
It has not been possible to prepare the symmetrical sulfinyl compound by allowing $S(O)X_2$ (X = Cl, F) to react with $LiN{=}C(CF_3)_2$. In all attempts $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}O$ is the major product with no evidence for the isomer $(CF_3)_2C{=}NS(O)N{=}C(CF_3)_2$.

von Halasz and Glemser[9] have reported that



$$(CF_3)_2C{=}NH + \overset{O}{SF_2} \xrightarrow{CsF} (CF_3)_2\underset{F}{C}N{=}S{=}O$$

On the basis of this reaction, reactions with $C(O)X_2$, and our present work with the lithium salt and SF_4,[17] the following mechanism involving halide ion migration to the highly electropositive isopropyl carbon is proposed



$$(CF_3)_2C{=}NLi + \overset{O}{SX_2} \longrightarrow [(CF_3)_2C{=}N\overset{O}{S}X] \longrightarrow (CF_3)_2\underset{X}{C}N{=}S{=}O \xrightarrow{LiN{=}C(CF_3)_2} (CF_3)_2C{=}N\overset{CF_3}{\underset{CF_3}{C}}N{=}S{=}O$$

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(17) R. F. Swindell and J. M. Shreeve, to be submitted for publication.

TABLE IV

^{19}F NMR DATA (ϕ)[a]

$(CH_3)_3SiN{=}C(CF_3)_2$	71.4 s	$CF_3SN{=}C(CF_3)_2$	53.6 s (1), 68.7 s (2)
$As[N{=}C(CF_3)_2]_3$	68.8 s	$CF_3S(O)N{=}C(CF_3)_2$	65.4 s (2), 72.6 s (1)
$P[N{=}C(CF_3)_2]_3$	68.6 d ($J_{CF_3-P} = 18.2$ cps)	$(CF_3)_2C{=}NC(CF_3)_2NSO$[b]	
$Cl_2P[N{=}C(CF_3)_2]_3$	69.0 s (2), 77.4 s (1)	$(CF_3)_2C(F)NCO$	81.6 d ($J_{CF_3-F} = 5$ cps), 139.5 h ($J_{F-CF_3} = 5$ cps)
$OP[N{=}C(CF_3)_2]_3$	69.9 d ($J_{CF_3-P} = 1.9$ cps)	$(CF_3)_2C{=}NC(CF_3)_2NCO$	59.1 b (1), 69.5 b (1), 78.5 c (2)
$S[N{=}C(CF_3)_2]_2$	69.9 s	$B[N{=}C(CF_3)_2]_3$	71.5 c (+30°), 71.5 s (−30°)

[a] Key: s, singlet; d, doublet; h, heptet; c, complex; b, broad; parentheses denote relative peak areas. [b] See Results and Discussion

TABLE V

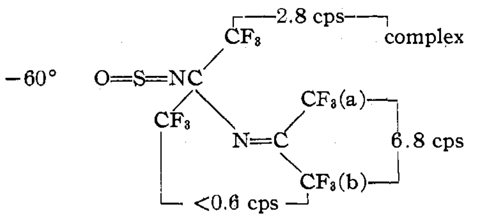
ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

	Elemental analyses, %														
	C		H		F		N		M		Bp,	ΔH_{vap}, kcal/	ΔS_{vap},	Log P_{Torr} = $A - B/T$	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	°C	mol	eu	A	B
$(CH_3)_3SiN{=}C(CF_3)_2$	30.4	30.43	3.8	3.94	48.0	48.0	5.9	5.91			84.7	7.3	20.3	7.30	1581
$As[N{=}C(CF_3)_2]_3$	19.05	19.00			60.3	60.2	7.40	7.50	13.20	13.08	24[b]				
$P[N{=}C(CF_3)_2]_3$	20.6	20.62			65.4	65.3	8.0	8.19	5.9	6.08	146.8	11.2	26.7	8.74	2460
$Cl_2P[N{=}C(CF_3)_2]_3$	18.20	18.28	11.95[a]	11.84[a]	57.55	57.6	7.08	7.10	5.22	5.22					
$OP[N{=}C(CF_3)_2]_3$	20.01	19.92			63.5	63.8	7.80	7.84	5.75	5.88	44[b]				
$S[N{=}C(CF_3)_2]_2$	20.01	20.14			63.31	63.0	7.78	7.96	8.90	8.97	117.9	9.7	24.8	8.16	2068
$CF_3SN{=}C(CF_3)_2$	18.12	17.95			64.5	64.8	5.28	5.38	12.09	12.12	51.3	7.5	23.3	7.76	1584
$CF_3S(O)N{=}C(CF_3)_2$	17.07	17.23			60.9	61.1	4.98	5.02	11.38	11.58	87.6	8.7	24.2	8.21	1922
$(CF_3)_2C{=}NC(CF_3)_2NSO$	19.15	19.26			60.64	61.2	7.45	7.50	8.51	8.56	102.3	9.4	25.2	8.38	2068
$(CF_3)_2CFNCO$	22.75	22.52			63.03	63.2	6.63	6.53							
$B[N{=}C(CF_3)_2]_3$	21.49	21.92			68.00	67.2	8.36	8.39	2.15	2.00					

[a] Cl analysis. [b] Melting points.

The proposed rearranged intermediates were not isolated in this case. The ^{19}F nmr spectrum was of particular use in establishing the above formula. At room temperature ^{19}F nmr shows a broad structureless resonance at ϕ 65.5 and a complex resonance of equal area centered at ϕ 74 (Figure 1). Lowering the temperature to −60° resolves the initial resonance into a complex multiplet at ϕ 60.5 and a quartet at ϕ 70.5 ($J_{ab} = 6.8$ cps). The resonance at ϕ 74 simplifies to a quartet ($J_{ac} = 2.8$ cps). Heating to 90° sharpens the resonance at ϕ 65.5 shifting it to ϕ 66.1. Under high resolution, the latter resonance and the resonance at ϕ 74 are seen as multiplets.

The observed spectra can be explained if the fluorine atoms of CF_3(a) and CF_3(b) are magnetically nonequivalent even at temperatures as high as 90°. At −60°, the isomerization is slowed sufficiently that on an nmr time scale the molecule exists in essentially one configuration giving rise to the interactions



At higher temperatures rapid stereoisomerization about the C=N bond is occurring which causes CF_3(a) and CF_3(b) to become more nearly equivalent. Examples of temperature dependent spectra arising from isomerization about C=N have been previously reported.[18-21]

Reaction of the lithium salt with $C(O)Cl_2$ and $C(O)F_2$ produces the carbon-containing analog of the sulfinyl compound. No ^{19}F nmr temperature study was undertaken in this case but the room-temperature spectrum correlates with that observed in $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}O$ at −20°. Also observed are the partially substituted rearranged products $(CF_3)_2C(Cl)N{=}C{=}O$ and $(CF_3)_2C(F)N{=}C{=}O$, which argue favorably for the mechanism proposed in the reaction with $S(O)Cl_2$ and $S(O)F_2$.

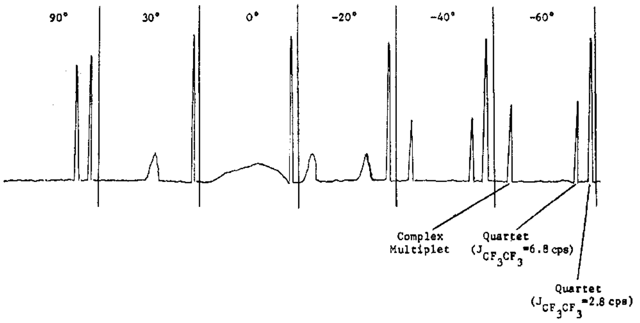


Figure 1.—Temperature dependence of ^{19}F nmr for $(CF_3)_2C{=}NC(CF_3)_2NSO$.

Room-temperature stereoisomerization is also observed in $B[N{=}C(CF_3)_2]_3$. The CF_3 groups are magnetically nonequivalent at 30° but at −30° a single sharp CF_3 resonance is observed at ϕ 71.5. The observed nonequivalence is somewhat surprising since it is noted that the BN=C< moiety is isoelectronic with allene and Lewis acid–base considerations argue for extensive multiple-bond character between boron and nitrogen which should preclude stereoisomerization.

Acknowledgment.—Fluorine chemistry research at the University of Idaho is sponsored by the Office of Naval Research and the National Science Foundation. We thank Mr. R. A. De Marco for mass spectra.

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