Acknowledgment. The group from Rocketdyne is grateful to the Office of Naval Research, Power Branch, for financial support and to Drs. L. R. Grant, C. J. Schack, and I. B. Goldberg for helpful discussions.

Registry No. $NF_4^+SbF_6^-$, 16871-76-4; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4; $\dot{N}F_3^+$, 54384-83-7; $Sb\dot{F}_6$, 54384-84-8.

References and Notes

(1) K. O. Christe, J. P. Guertin, and A. E. Pavlath, U.S. Patent 3,503,719 (1970).
(2) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discuss. Faraday Soc.*, **35**, 201 (1963).
(3) J. N. Wilson, paper presented at the Symposium on Advanced Propellant Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.
(4) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).
(5) J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).
(6) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Chem. Lett.*, **2**, 79 (1966).
(7) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Chem.*, **6**, 1156 (1967).
(8) C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, and J. N. Wilson, *Inorg. Chem.*, **11**, 1696 (1972).
(9) K. O. Christe, R. D. Wilson, and A. E. Axworthy, *Inorg. Chem.*, **12**, 2478 (1973).
(10) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).
(11) J. Maruani, J. A. R. Coope, and C. A. McDowell, *Mol. Phys.*, **18**, 165 (1970).
(12) J. Maruani, C. A. McDowell, H. Nakajima, and P. Raghunathan, *Mol. Phys.*, **14**, 349 (1968).
(13) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, **10**, 2803 (1971).
(14) W. E. Tolberg, private communication.
(15) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).
(16) J. A. R. Coope, *Chem. Phys. Lett.*, **3**, 589 (1969).
(17) Calculated from the data of C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966).
(18) S. P. Mishra and M. C. R. Symons, unpublished results.
(19) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966).
(20) F. G. Herring, J. H. Hwang, and W. C. Lin, *J. Phys. Chem.*, **71**, 2086 (1967).
(21) M. C. R. Symons, *J. Chem. Soc. A*, 2393 (1971).
(22) S. Subramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. A*, 1239 (1970).

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

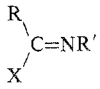
F-N-Isopropylacetimidoyl Chloride: a Precursor to Totally and Partially Fluorinated Imido Esters and Imido Thio Esters [1]

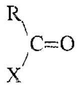
KEITH E. PETERMAN and JEAN'NE M. SHREEVE*

Received September 16, 1974 AIC40652A

The imidoyl chlorine of $CF_3CCl{=}NCF(CF_3)_2$ is susceptible to base-catalyzed nucleophilic attack by alcohols (ROH; R = $(CF_3)_3C$, $(CF_3)_2CH$, CF_3CH_2) and thiols (R'SH; R' = CF_3, CH_3, C_2H_5) to produce the corresponding imido esters, $CF_3(RO)C{=}NCF(CF_3)_2$, and imido thio esters, $CF_3(R'S)C{=}NCF(CF_3)_2$. Two other imido thio esters, $CF_3(R'S)C{=}NCH(CF_3)_2$ (R' = CH_3, C_2H_5), result in the reaction of the imidoyl chloride with the hydrogenated thiols *via* a complex mechanism. These two imido thio esters exist as a mixture of syn and anti isomers at 30°. Syn and anti conformers of $CF_3(CF_3S)C{=}NCF(CF_3)_2$ and $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$ were resolved at low temperature using ^{19}F nmr spectra. Each of the imido esters exists in the anti configuration with no evidence of stereoisomerization about the C=N bond on the infrared or nmr time scale.

A halo group attached to the carbon atom of >C=N– characterizes a class of reactive compounds known as imidoyl halides. Electronic assistance from a heteroatom attached to the carbon atom bonded to the halo group greatly increases the reactivity of the halide as evidenced by the high reactivity of acid halides where the halo group is attached directly to the carbonyl carbon. In a like manner, the C=N double bond increases the reactivity of an imidoyl halide (I) comparable to that of an acid halide (II).


I


II

Imidoyl halides have been known since 1876 and since that time have proved to be excellent precursors to a wide variety of hydrogenated nitrogen compounds.[2-5] The chloro substituent in hydrogenated imidoyl chlorides is readily displaced by nucleophilic reagents; however, similar reactions of the fluorinated analogs are rare[6-8] or obscured in the literature. We have found that $CF_3CCl{=}NCF(CF_3)_2$ is very susceptible to nucleophilic attack by OR_f^-, SR^-, and SR_f^-. Generally, the imido esters and imido thio esters are formed *via* a straightforward nucleophilic attack at the reactive site by the nucleophile; however, in the case of SR^- a more complex mechanism is operative.

Compounds containing the C=N function may exist as geometrical isomers (syn and anti); however, rotation or inversion about the C=N bond[9] may cause rapid stereoisomerization which renders equivalent the two isomers on the infrared or nmr time scale. By comparison, hydrogenated imines seem to have a much greater configurational stability than similar fluorinated compounds such that the latter often exhibit a temperature-dependent nmr spectrum.[10-15] Stereoisomerism of imines and the possibility of syn and anti isomers is an intriguing subject and both nmr and infrared spectroscopies are useful for the assignment of structure. We have observed *via* ^1H and ^{19}F nmr spectral studies that a mixture of the syn and anti isomers of $CF_3(RS)C{=}NCH(CF_3)_2$ (R = CH_3, C_2H_5) exists at 30°, and through a consideration of peak areas the syn:anti ratios have been determined. None of the other imido thio esters stereoisomerizes at a rate which is slow enough to permit observation of the individual isomers at ambient temperature in the nmr. However, at 25° while $CF_3(CF_3S)C{=}NCF(CF_3)_2$ is just above its nmr coalescence temperature, the individual conformers are observed in the infrared spectra. Low-temperature nmr spectral studies of $CF_3(CF_3S)C{=}NCF(CF_3)_2$ and $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$ showed that the syn and anti conformers could be resolved at low temperature with the major species existing in the anti configuration. A low-temperature nmr spectral study of $CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$ indicated no conformational changes down to −115°. The absence of syn and anti mixtures at low temperature and the nature of the ^{19}F and ^1H nmr coupling patterns suggest that each of the imido esters exist in the anti configuration at ambient temperature with no evidence of stereoisomerization

Table I. Infrared Spectra (cm^{-1})

$CF_3[(CF_3)_3CO]C{=}NCF(CF_3)_2$	1764 s, 1332 s, 1282 vvs, 1256 vvs, 1239 vs, 1208 s, 1133 s, 1094 ms, 992 s, 857 m, 754 ms, 734 ms
$CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$	2990 w, 1754 s, 1385 ms, 1365 ms, 1329 ms, 1295 vs, 1247 vs, 1213 s, 1144 s, 1120 ms, 1095 ms, 993 ms, 913 ms, 851 w, 752 ms, 734 ms, 695 m
$CF_3(CF_3CH_2O)C{=}NCF(CF_3)_2$	2983 vw, 1740 s, 1423 m, 1346 ms, 1326 ms, 1277 vs, 1245 vs, 1206 s, 1185 s, 1144 vs, 1092 ms, 990 s, 903 ms, 852 w, 748 ms, 734 ms
$CF_3(CF_3S)C{=}NCF(CF_3)_2$	1701 ms, 1672 m, 1319 ms, 1255 vs, 1241 s, 1205 s, 1182 s, 1133 ms, 1103 s, 1082 ms, 990 ms, 955 ms, 761 m, 745 m, 731 ms, 701 m
$CF_3(CH_3S)C{=}NCF(CF_3)_2$	2943 vs, 1672 s,[a] 1318 ms, 1298 m, 1280 s, 1249 vs, 1221 ms, 1202 vs, 1164 m, 1141 ms, 1092 ms, 989 s, 957 m, 730 m, 702 m
$CF_3(C_2H_5S)C{=}NCF(CF_3)_2$	2985 vw, 2945 vw, 1668 ms,[a] 1320 m, 1268 ms, 1249 s, 1203 s, 1163 w, 1142 m, 1093 m, 984 ms, 732 m, 702 w
$CF_3(CH_3S)C{=}NCH(CF_3)_2$	1940 vw, 1641 ms,[a] 1362 ms, 1293 s, 1264 s, 1220 vs, 1193 ms, 1181 ms, 1161 ms, 1111 ms, 1071 m, 1004 ms, 960 w, 901 w, 867 m, 730 w, 701 m
$CF_3(C_2H_5S)C{=}NCH(CF_3)_2$	2985 vw, 2950 vw, 1642m,[a] 1368 m, 1298 ms, 1273 ms, 1221 s, 1197 m, 1184 m, 1164 m, 1114 m, 1078 w, 1003 m, 906 w, 871 w, 735 m, 706 w

[a] Unsymmetrical.

on the infrared or nmr time scale.

Experimental Section

Materials. Literature methods were used to prepare $CF_3CCl{=}NCF(CF_3)_2$[8] and CF_3SH.[16] The commercially available starting materials, $(CF_3)_3COH$, $(CF_3)_2CHOH$, and CF_3CH_2OH (PCR, Inc.) and CH_3SH and C_2H_5SH (Matheson), were used as received.

General Procedures. Most 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. Products of lower volatility were weighed. Volatile products were purified by trap-to-trap distillation or by gas chromatography. For gas chromatographic separations, the columns were constructed of 0.25-in. copper tubing packed with 25% Kel-F No. 3 oil on Chromosorb P, 37% FS-1265 on Chromosorb P, or 25% dimethyl sulfone on Chromosorb P. Helium was used as a carrier gas. Vapor pressure studies were made by using an isoteniscopic method.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer by using a 50-mm Pyrex glass cell equipped with KBr windows. ^{19}F and ^1H nmr spectra were obtained on a Varian HA-100 spectrometer with CCl_3F and tetramethylsilane as internal standards. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

General Synthetic Methods. The imido esters and imido thio esters were synthesized by condensing successively at −183° equimolar amounts of the alcohol (or thiol), $CF_3CCl{=}NCF(CF_3)_2$, and Me_3N into an evacuated flame-dried 8-ml Pyrex vessel equipped with a Teflon stopcock. After a given reaction time the imido esters were purified by trap-to-trap fractionation and the imido thio esters were separated by gas chromatography. Infrared spectra, ^{19}F and ^1H nmr spectra, elemental analyses, and thermodynamic data of the new compounds are summarized in Tables I–III, respectively. Mass spectral data have been tabulated and are available upon request.

Synthesis of $CF_3(R_fO)C{=}NCF(CF_3)_2$ ($R_f = (CF_3)_3C, (CF_3)_2CH, CF_3CH_2$). After condensing 2 mmol of the appropriate alcohol [$(CF_3)_3COH$, $(CF_3)_2CHOH$, or CF_3CH_2OH], $CF_3CCl{=}NCF(CF_3)_2$, and Me_3N into the vessel, it was allowed to warm to and remain at ambient temperature for 4–5 hr. Following trap-to-trap fractionation, each of the imido esters, $CF_3(R_fO)C{=}NCF(CF_3)_2$, was obtained pure in a trap at −55° after passing a trap at −20°. Based on the amount of unreacted imidoyl chloride recovered, the yields were 99% when $R_f = (CF_3)_2CH$ and CF_3CH_2 and 45% when $R_f = (CF_3)_3C$.

Synthesis of $CF_3(CF_3S)C{=}NCF(CF_3)_2$. The equimolar portions (5 mmol) of CF_3SH, $CF_3CCl{=}NCF(CF_3)_2$, and Me_3N were allowed to warm as above to ambient temperature for a given time period. Maximum yields of purified $CF_3(CF_3S)C{=}NCF(CF_3)_2$ (24–30%) were obtained after a reaction time of 6 hr. Purification was obtained by gas chromatography on a 6-ft. column of FS-1265. Other products included $CF_3CF{=}NCF(CF_3)_2$[10] (30%) and $(CF_3S)_2CS$[17] (yields vary). High yields of $(CF_3S)_2CS$ were obtained with a short reaction time (1.5 hr) but further purification of this compound by gas chromatography on a 6-ft column of Kel-F No. 3 oil was necessary before positive identification could be made.[18]

Synthesis of $CF_3(RS)C{=}NCF(CF_3)_2$ and $CF_3(RS)C{=}NCH(CF_3)_2$ ($R = CH_3, C_2H_5$). Equimolar portions (5 mmol) of the thiol (CH_3SH or C_2H_5SH), $CFCCl{=}NCF(CF_3)_2$, and Me_3N were allowed to warm as above to ambient temperature for a given time period. Maximum yields of $CF_3(RS)C{=}NCF(CF_3)_2$ ($R = CH_3$, 68%; C_2H_5, 40%) were obtained after a reaction time of 4–6 hr. After a reaction time of 24 hr., increased yields of $CF_3(RS)C{=}NCH(CF_3)_2$ ($R = CH_3$, 14%; C_2H_5, 15%) were obtained with a concomitant lowering in the yields of $CF_3(RS)C{=}NCF(CF_3)_2$. Other products obtained after gas chromatographic separations included $CF_3CF{=}NCF(CF_3)_2$ (2–8%) and $(RS)_2$. $CF_3(CH_3S)C{=}NCF(CF_3)_2$ and $CF_3(CH_3S)C{=}NCH(CF_3)_2$ were purified by gas chromatography with a 2-ft column of dimethyl sulfone. Initial purification of $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$ and $CF_3(C_2H_5S)C{=}NCH(CF_3)_2$ was obtained by passing the reaction mixture through a 6-ft column of FS-1265 followed by final purification by using a 2-ft column of dimethyl sulfone.

Results

Earlier we found that catalytic chlorofluorination of $CF_3CCl_2N{=}C(CF_3)_2$ led to $CF_3CF_2NClCF(CF_3)_2$ *via* a series of ClF addition and subsequent dechlorination steps.[8] Our mechanism postulated $CF_3CCl{=}NCF(CF_3)_2$ as an intermediate in the reaction. This intermediate was isolated as a stable compound by an alternate route after reaction of $CF_3C(O)NClCF(CF_3)_2$ with PCl_5. This same study showed that in the presence of CsF, the imidoyl chlorine of $CF_3CCl{=}NCF(CF_3)_2$ is readily displaced by fluorine, thus accounting for the fact that it was not isolated in the presence of CsF. This reaction indicated the compound was susceptible to nucleophilic attack and in the present study the reactions conducted verify this initial assumption. Initial reactions conducted with *F* alcohols ($(CF_3)_3COH$, $(CF_3)_2CHOH$, and CF_3CH_2OH) in the presence of trimethylamine showed that a nucleophilic displacement by the *F*-alkoxy group does occur

$$CF_3CCl{=}NCF(CF_3)_2 + R_fOH + Me_3N \rightarrow CF_3(R_fO)C{=}NCF(CF_3)_2 + Me_3NH^+Cl^-$$

The resulting imido esters were all stable and were easily purified by trap-to-trap fractionation.

Reaction of an *F* thiol, CF_3SH, with the imidoyl chloride led to a more complex mixture of volatile products with a concomitant reduction in the yield of the imido thio ester. As in the case of the *F* alcohols, a nucleophilic displacement led to $CF_3(CF_3S)C{=}NCF(CF_3)_2$. However, in a competing reaction, the base reacted with CF_3SH to produce $(CF_3S)_2CS$ *via* the intermediate formation of thiocarbonyl fluoride and *F*-methyldithioformate[17] (see eq 1–3). Trimethylamine is also

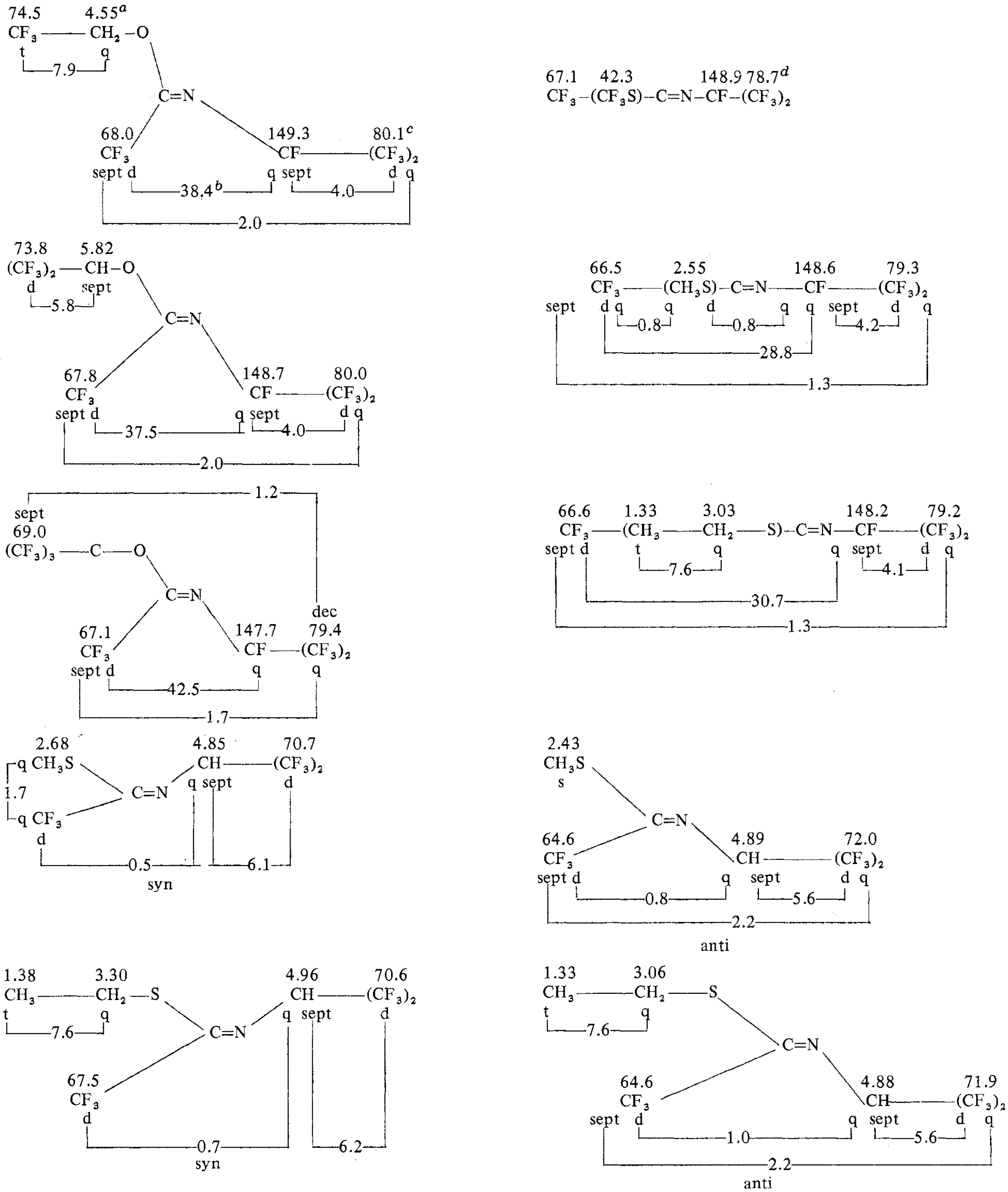
$$CF_3SH \xrightarrow{Me_3N} CSF_2 + HF \tag{1}$$

$$CF_3SH + CSF_2 \xrightarrow{Me_3N} CF_3SC(S)F + HF \tag{2}$$

$$CF_3SC(S)F + CF_3SH \xrightarrow{Me_3N} (CF_3S)_2CS + HF \tag{3}$$

an acceptor for HF, yielding trimethylammonium fluoride

Table II. ^{19}F and ^{1}H Nmr Spectra

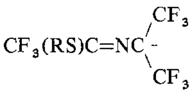


[a] ϕ in ppm; internal CCl_3F and $(CH_3)_4Si$. [b] J in Hz. [c] Key: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; dec, dectet. [d] At 30° the peaks are broad and unresolved; however, a low-temperature nmr study showing well-resolved syn and anti conformers is presented in the text.

which in turn attacks the imidoyl chloride to produce the imidoyl fluoride

$$CF_3CCl{=}NCF(CF_3)_2 + Me_3NH^+F^- \rightarrow CF_3CF{=}NCF(CF_3)_2 + Me_3NH^+Cl^-$$

Two similar imido thio esters $CF_3(RS)C{=}NCF(CF_3)_2$ and $CF_3(RS)C{=}NCH(CF_3)_2$ ($R = CH_3, C_2H_5$) are produced upon reaction of hydrogenated thiols (CH_3SH or C_2H_5SH) with $CF_3CCl{=}NCF(CF_3)_2$ in the presence of Me_3N. While it is apparent that $CF_3(RS)C{=}NCF(CF_3)_2$ results from a straightforward nucleophilic displacement, $CF_3(RS)C{=}NCH(CF_3)_2$ must result *via* a complex mechanism in which the stable carbanion



$$CF_3(RS)C{=}NC^-(CF_3)_2$$

may be a probable intermediate.

Preliminary evidence for the formation of the imido esters is the shift in the infrared spectrum of the $\nu_{C=N}$ band to higher

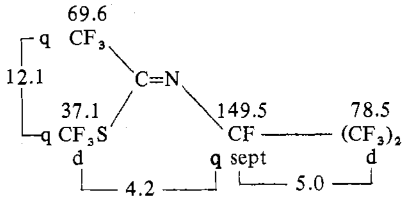
Table III. Elemental Analyses and Thermodynamic Data

Compd	Elemental anal., % C	N	F	H	S	Bp, °C	ΔH_{vap}, kcal/mol	ΔS_{vap}, eu	$\log P_{Torr} = A - BT$ A	B
$CF_3(CF_3CH_2O)C{=}NCF(CF_3)_2$	23.25	3.94	68.0	0.51		95.8	8.54	23.2	7.94	1867
	(23.14)[a]	(3.86)	(68.0)	(0.55)						
$CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$	22.12	3.39	70.3	0.25		90.8	8.60	23.6	8.04	1879
	(22.27)	(3.25)	(70.5)	(0.23)						
$CF_3[(CF_3)_3CO]C{=}NCF(CF_3)_2$	21.81	2.91	72.3			112.4	8.99	23.3	7.98	1965
	(21.64)	(2.81)	(72.3)							
$CF_3(CF_3S)C{=}NCF(CF_3)_2$	19.48	3.87	67.7		8.79	86.6	8.43	23.4	8.00	1841
	(19.72)	(3.83)	(67.7)		(8.76)					
$CF_3(CH_3S)C{=}NCF(CF_3)_2$	23.24	4.30	62.0	1.00	9.80	109.5	7.55	19.7	7.20	1651
	(23.15)	(4.50)	(61.1)	(0.96)	(10.28)					
$CF_3(C_2H_5S)C{=}NCF(CF_3)_2$	25.82	4.33	58.5	1.74	9.89	121.5	8.14	20.6	7.39	1778
	(25.85)	(4.31)	(58.5)	(1.54)	(9.85)					
$CF_3(CH_3S)C{=}NCH(CF_3)_2$	24.59	4.78	58.0	1.45	10.83	b				
	(24.57)	(4.78)	(58.4)	(1.37)	(10.92)					
$CF_3(C_2H_5S)C{=}NCH(CF_3)_2$	27.51	4.53	55.6	2.04	10.50	b				
	(27.36)	(4.56)	(55.7)	(1.95)	(10.42)					

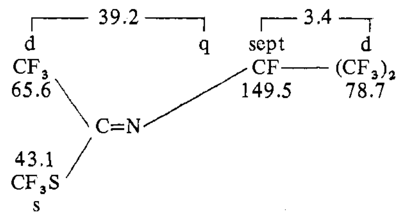
[a] Calculated values in parentheses. [b] This is a mixture of syn and anti isomers; therefore, thermodynamic data representative of a pure substance could not be obtained.

energy than that of the reacting imidoyl halide. Likewise, the imido thio esters are accompanied by a lowering in energy of the $\nu_{C{=}N}$ band relative to its precursor. The infrared spectrum of *F*-methyl-*N*-isopropylthiolacetimidate, $CF_3(CF_3S)C{=}NCF(CF_3)_2$, contains two C=N stretching frequencies in the infrared spectrum (1701 and 1672 cm^{-1}) which suggests a mixture of both the syn and anti conformers.[19] The remaining imido thio esters, $CF_3(RS)C{=}NCX(CF_3)_2$ (R = CH_3, C_2H_5; X = F, H), each have an unresolved, very unsymmetrical $\nu_{C{=}N}$ band in the infrared spectrum suggesting that the syn and anti isomeric forms are being observed on the infrared time scale also.

The nmr spectral studies provide the best evidence for apparent syn and anti conformers for each compound. Although both the syn and anti isomeric forms of $CF_3(CF_3S)C{=}NCF(CF_3)_2$ are observed on the infrared time scale, the ^{19}F nmr spectrum shows only broad unresolved peaks at 30°. A low-temperature nmr study of this molecule showed that the temperature of coalescence is about −10 to −20° with a well-resolved hyperfine splitting pattern being observed at −80°. By comparison of the long-range coupling (F_3—C—C=N—C—F) with other unsaturated systems,[20] we can readily assign the conformer with the large coupling constant (J = 39.2 Hz) as the anti form. Previous evidence has shown that when two fluorine atoms are in close proximity in a molecule, a large coupling results, even though the atoms are separated by several bonds.[21] Similarly, when the isopropyl group is cis to the CF_3S group, an F_3—C—S—C=N—C—F coupling pattern develops ($J_{CF_3S\text{-}CF}$ = 4.2 Hz) with concomitant loss of $J_{CF\text{-}CF_3}$. For steric reasons, the CF_3S group is nearer the CF_3 group in the syn conformer; therefore coupling between CF_3 and CF_3S occurs (J = 12.1 Hz). This is absent in the anti form. The anti conformer is the major isomer with a syn to anti ratio of 1:8.



syn (minor)

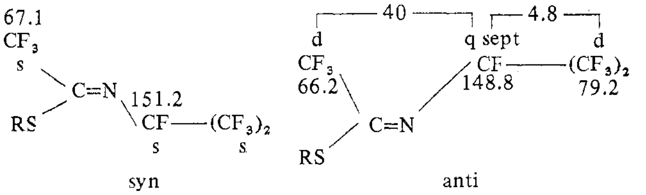


anti (major)

The partially fluorinated imido thio esters with hydrogenated thioalkoxy substituents offer an interesting example of the significant effect of substitution of a single H for F. For example, in the compounds $CF_3(RS)C{=}NCF(CF_3)_2$ (R = CH_3, C_2H_5), the barrier to inversion or rotation is sufficiently lowered to preclude observation of individual isomers in the nmr spectra at 30°. However, upon substitution of hydrogen for the isopropyl fluorine, the syn–anti mixture is clearly resolved at ambient temperature in the nmr. The peaks for each isomer of $CF_3(RS)C{=}NCH(CF_3)_2$ (R = CH_3, C_2H_5) were assigned on the basis of integrated intensities in both the ^{19}F and ^1H nmr spectra and on the expected chemical shifts. Considering the anti isomer of $CF_3(CH_3S)C{=}NCH(CF_3)_2$ (Table II), it can be seen readily that long-range coupling is present between the CF_3 groups (F_3—C—C=N—C—$(CF_3)_2$) with $J_{CF_3\text{-}(CF_3)_2}$ = 2.2 Hz. In the syn form, this coupling is absent; however, the CH_3S substituent couples with the CF_3 substituent with $J_{CF_3\text{-}CH_3}$ = 1.7 Hz. The other coupling constants for both the syn and anti conformers are similar in each case.

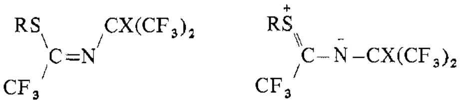
Analogous to the CH_3S analog, $CF_3(C_2H_5S)C{=}NCH(CF_3)_2$ exists as a syn–anti mixture with the peaks being easily assigned on the basis of chemical shifts and both the ^1H and ^{19}F nmr spectra integrated area ratios. The pattern is slightly different in this instance since the RS—CF_3 coupling is absent even in the syn form where these groups are in closer proximity. However, the long-range coupling of F_3—C—C=N—C—$(CF_3)_2$ (J = 2.2 Hz) readily distinguishes the anti conformer. The integrated intensities from the ^{19}F and ^1H nmr spectra show that the syn:anti ratio is 1.0:1.5 for both of the imido thio esters.

As stated above, $CF_3(RS)C{=}NCF(CF_3)_2$ (R = CH_3, C_2H_5) compounds are not observed as individual conformers at ambient temperature in the nmr spectra which is attributed to rapid stereoisomerization about the C=N bond. A low temperature ^{19}F nmr spectral study of one of the compounds, $CF_3(C_2H_5S)C{=}NCF(CF_3)_2$, did in fact resolve the two conformers below the coalescence temperature of −35°. At −60° the syn isomer shows only slightly broadened singlets for each of the three ^{19}F nmr peaks. The anti isomer is characterized by the expected long-range F_3—C—C=N—C—F coupling (J = 40 Hz). The anti isomer is more favorable



sterically as indicated by the syn:anti ratio of 1:4.3.

The foregoing discussion has shown that all of the imido thio esters in this work either exist as syn–anti mixtures at ambient temperature or exhibit temperature-dependent nmr spectra with the syn–anti conformers being resolved at low temperatures. Conversely, the imido esters exist in the anti form at ambient temperature so that no temperature dependence was observed in the ^{19}F nmr spectrum of $CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$. Comparison of the ^{19}F and ^1H nmr hyperfine coupling schemes of the imido esters in Table II with those of the imido thio esters shows a clear similarity to the anti conformers. The strongest argument for the anti conformer of the imido esters is the large long-range F_3—C—C═N—C—F coupling constants. Preference for the anti configuration has been attributed to interorbital electron repulsion in the syn form between the nonbonding electrons upon the oxygen atom and the lone pair on the nitrogen localized in an sp^2 orbital.[22] Substitution of sulfur for oxygen in the imido thio esters reduces the effect of this lone pair–lone pair interaction due to the greater length of the sulfur–carbon bond relative to the oxygen–carbon bond, reduced electronegativity of sulfur relative to oxygen, and a favorable contribution of resonance structure A toward delocalizing the lone pairs on the sulfur. Therefore, although the imido esters require the anti configuration, the imido thio esters have a relatively more stable syn configuration such that the syn–anti mixture can be observed in the nmr spectra.



A

The mass spectra obtained at an ionization voltage of 70 eV confirmed all of the compounds.[23] A molecular ion was observed for all of the imido thio esters and an M − F peak was the heaviest fragment observed for the imido esters. The numerous intense ion fragments in the mass spectra verify and support the structures proposed for each new compound.

Acknowledgment. Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Dr. N. R. Zack for mass spectra and Mr. C. Srivanavit for high-resolution nmr spectra.

Registry No. *anti*-$CF_3[(CF_3)_3CO]C{=}NCF(CF_3)_2$, 54120-06-8; *anti*-$CF_3[(CF_3)_2CHO]C{=}NCF(CF_3)_2$, 54181-87-2; *anti*-$CF_3(CF_3CH_2O)C{=}NCF(CF_3)_2$, 54181-88-3; *anti*-$CF_3(CF_3S)C{=}NCF(CF_3)_2$, 54181-89-4; *syn*-$CF_3(CF_3S)C{=}NCF(CF_3)_2$, 54120-07-9; $CF_3(CH_3S)C{=}NCF(CF_3)_2$, 54120-08-0; *anti*-$CF_3(C_2H_5S)C{=}NCF(CF_3)_2$, 54120-09-1; *syn*-$CF_3(C_2H_5S)C{=}NCF(CF_3)_2$, 54120-10-4; *anti*-$CF_3(CH_3S)C{=}NCH(CF_3)_2$, 54120-11-5; *syn*-$CF_3(CH_3S)C{=}NCH(CF_3)_2$, 54120-12-6; *anti*-$CF_3(C_2H_5S)C{=}NCH(CF_3)_2$, 54181-90-7; *syn*-$CF_3(C_2H_5S)C{=}NCH(CF_3)_2$, 54120-13-7; $CF_3CCl{=}NCF(CF_3)_2$, 54120-14-8; $(CF_3)_3COH$, 2378-02-1; $(CF_3)_2CHOH$, 920-66-1; CF_3CH_2OH, 75-89-8; CF_3SH, 1493-15-8; CH_3SH, 74-93-1; C_2H_5SH, 75-08-1; $(CF_3S)_2CS$, 461-08-5.

References and Notes

(1) The nomenclature in this paper follows the approved rules for naming highly fluorinated molecules as set forth by the American Chemical Society Division of Fluorine Chemistry. The main principle of these rules is the transfer of the usually assumed prevalence from hydrogen to fluorine, by use of the symbol "*F*."
(2) R. Roger and D. S. Neilson, *Chem. Rev.*, **61**, 179 (1961).
(3) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N.Y., 1968.
(4) R. Bonnett in "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N.Y., 1970, Chapter 13.
(5) P. A. S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, New York, N.Y., 1965, p 172.
(6) H. Ulrich, E. Kober, H. Schroeder, R. Ratz, and C. Grundmann, *J. Org. Chem.*, **27**, 2585 (1962).
(7) B. L. Dyatkin, A. A. Gevorkyam, and I. L. Knunyants, *Zh. Obshch. Khim.*, **36**, 1326 (1966); *J. Gen. Chem. USSR*, **36**, 1340 (1966).
(8) K. E. Peterman and J. M. Shreeve, *Inorg. Chem.*, in press.
(9) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).
(10) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).
(11) P. H. Ogden and G. V. D. Tiers, *Chem. Commun.*, **11**, 527 (1967).
(12) P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, **89**, 3868 (1967).
(13) P. H. Ogden, *J. Org. Chem.*, **33**, 2518 (1968).
(14) D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Commun.*, **7**, 395 (1970).
(15) R. F. Swindell, D. P. Babb, T. J. Oullette, and J. M. Shreeve, *Inorg. Chem.*, **11**, 242 (1972).
(16) N. R. Zack and J. M. Shreeve, *Syn. Commun.*, **4**, 233 (1974).
(17) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).
(18) *F*-Dimethyl trithiocarbonate is a high-boiling red liquid which was identified by comparison of infrared and ^{19}F nmr spectra with reported literature data.[17] A molecular ion was also observed in the mass spectrum.
(19) E. Melendez and V. Sanchez del Olmo, *An. Quim.*, **66**, 217 (1970); *Chem. Abstr.*, **73**, 50344 (1970).
(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N.Y., 1966.
(21) R. E. Banks and M. G. Barlow, *Fluorocarbon Relat. Chem.*, **1**, 280 (1971).
(22) E. Yeh, R. M. Moriarty, and C. Yeh, *Tetrahedron Lett.*, **26**, 2655 (1972).
(23) Mass spectral data have been tabulated and are available upon request.