PERFLUORINATED PARA-ELEMENT IMIDO DERIVATIVES

ALOIS HAAS and KEITH PETERMAN

Anorganische Chemie II, Ruhr-Universität Bochum,

D-4630 Bochum 1 (F.R.G.)

SUMMARY

The comparative reaction chemistry between first and second derivative paraelement analogs ($(CF_3)_2PH$, $(CF_3S)_2PH$, CF_3SH, CF_3SSH, CF_3SNH_2, $(CF_3S)_2NH$, $(CF_3S)_3N$) and F-N-isopropylacet-imidoyl chloride $[CF_3CCl=NCF(CF_3)_2$, I$]$ has been investigated. Reaction schemes are presented. The reactions of I with NH_3 and NaI are also reported. Analytical data is provided for previously unreported compounds along with more detailed analysis of known compounds.

INTRODUCTION

The recently advanced element displacement principle provides a means for classifying new element groups (para-elements) which are neither isoelectronic nor isosteric ligands as having been derived from base elements in the fourth to the seventh main groups [1, 2]. These new paraelements or radical groups may be expanded to include first, second, and higher order derivatives of the given base elements. For example, with -Cl as the reference element, $-SCF_3$ and $-P(CF_3)_2$ represent first order derivatives while $-SSCF_3$ and $-P(SCF_3)_2$ are the subsequent second order derivatives.

---

*York College of PA., York, PA. 17405 (U.S.A.).

In many instances, the available literature data supports this concept as a new periodic classification principle based on observed trends in physical properties and similarity of chemical properties. However, many data are lacking and, to date, no systematic study has been conducted which compares or contrasts the physical and chemical properties of a series of first and second derivative para-elements to the reference element under similar conditions.

The original intent of this study was to prepare a series of perfluorinated imido paraelement ester derivatives ($>$C=N-, G = paraelement radical) and investigate physical parameters as they relate to stereochemical isomerization about the imine bond. For such a study, F-N-isopropylacetimidoyl chloride, $\begin{smallmatrix} CF_3 \\ \\ Cl \end{smallmatrix}$>C=N-CF(CF_3)_2$ (I), was selected as the parent species from which first and second order imido paraelement ester derivatives could be synthesized since previous work had shown that the chloride ion was susceptible to direct nucleophilic displacement [3, 4]. In addition, the derivatives would be likely to undergo stereochemical isomerization at such a rate on the NMR time scale as to permit resolution of the syn- and anti-isomers at reduced temperatures thus affording the opportunity to obtain valuable thermodynamic and kinetic data. While this objective was in part achieved, the resulting chemistry proved to be of greater significance.

RESULTS AND DISCUSSION

The perfluorinated imido thio ester $CF_3(CF_3S)C=NCF(CF_3)_2$ (II) was previously prepared by the reaction of CF_3SH with I in the presence of Me_3N [3]. The infrared spectrum of II exhibits two distinct ν(C=N) at 1701 cm^{-1} and 1672 cm^{-1} demonstrating that

syn- and anti-stereochemical isomers are clearly observed on the infrared time scale. An accompanying low temperature NMR investigation showed that these isomers could also be resolved on the NMR time scale.

(anti)   (syn)
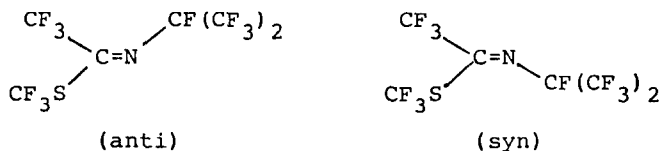
In the present study, kinetic measurements and lifetimes were obtained by classical NMR line-broadening techniques [5, 6] with the accompanying data presented on fig. 1. From the Arrhenius plot of ln $(1/\tau)$ versus $(1/T)$, an activation energy of approximately 49 KJ/mol was calculated for the stereochemical isomerization about the C=N bond. This value is significantly lower (ca. half) than that observed for comparable hydrogenated compounds.
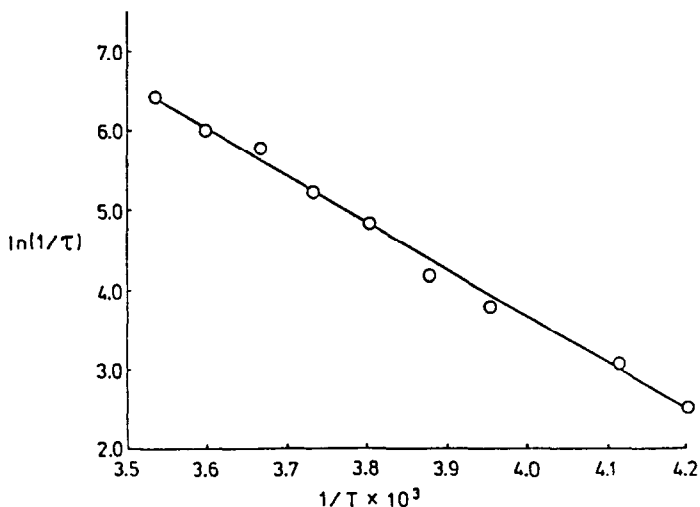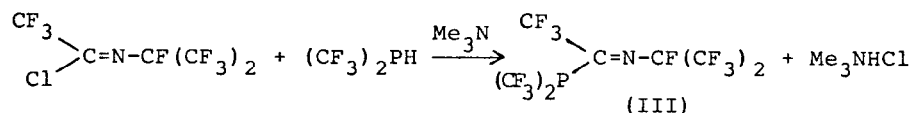

Fig. 1. Arrhenius plot for the activation energy of stereochemical isomerization in II. Lifetimes (τ) in sec., Temperature (T) in K.

Under similar reaction conditions, a new perfluorinated imido phospho ester (III) has been synthesized via substitution of the $(CF_3)_2P$ radical for Cl.

$$\begin{array}{c} CF_3 \\ \diagdown \\ Cl \end{array} C=N-CF(CF_3)_2 \;+\; (CF_3)_2PH \xrightarrow[]{\;Me_3N\;} \begin{array}{c} CF_3 \\ \diagdown \\ (CF_3)_2P \end{array} C=N-CF(CF_3)_2 \;+\; Me_3NHCl$$

$$(III)$$

As was observed with its CF_3S-paraelement analog II, this species (III) also exhibited two distinct ν(C=N) in the I.R. at 1691 cm^{-1} and 1666 cm^{-1} indicating that, here too, syn-, anti-isomerization was being observed although, it should be noted that, the higher wave-number peak, characteristic of the anti-isomer, was much stronger. The ^{19}F-NMR spectrum of III, like that of II, displayed only broad unresolved signals at ambient temperature supporting the probability that syn-, anti-isomerization was sufficiently slow to be observed on the NMR time scale also. However, at reduced temperatures, the more stable anti-isomer predominated to the exclusion of any observable syn-isomer such that no meaningful kinetic data could be collected. Nevertheless, due to the similarity of the ambient temperature spectra and comparable temperatures for resolved spectra of both II and III, it is not unreasonable to assume that the activation energy for stereochemical isomerization in III is also in the 50 KJ/mol region.

The iodide derivative of I, $CF_3CI=NCF(CF_3)_2$ (IV), was prepared by the direct nucleophilic displacement of Cl$^-$ by I$^-$ in acetone. Neither the chloride (I) nor the iodide (IV) derivatives showed any temperature dependance to temperatures of -90°C suggesting

that only one isomer predominated in each case even at ambient

temperatures. In view of the absence of a large $CF_3-C=N-C-F$

coupling constant (ca. 40 Hz), which is characteristic of the

anti-isomers (i.e. CF_3 is syn- to C-F) [3], a syn-structure was

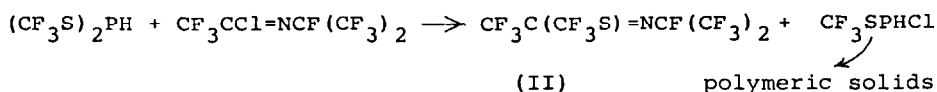assigned to each of the imidoyl halides.

$$\underset{I}{\overset{CF_3}{>}}C=N\underset{CF(CF_3)_2}{\diagdown} \qquad \underset{Cl}{\overset{CF_3}{>}}C=N\underset{CF(CF_3)_2}{\diagdown}$$

This high barrier to stereochemical isomerization is in keeping

with that observed for a close analog, $\overset{CF_3}{\underset{CF_3}{>}}C=N-CF(CF_3)_2$, which

exhibits a coalescence temperature above 32°C for the non-equiva-

lent CF_3 groups on the double bond [7].

Attempts to synthesize second derivative perfluorinated para-

element imido derivatives of the type

$$\overset{CF_3}{\underset{G}{>}}C=N-CF(CF_3)_2 \quad (G = CF_3SS, (CF_3S)_2P, (CF_3S)_2N)$$
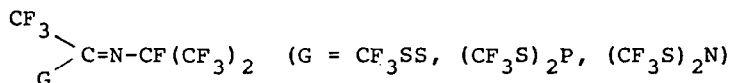
by reaction of (I) with the respective precursor G-H in Me_3N led

to products other than those expected from direct displacement

of the Cl.

In the reactions of both CF_3SSH and $(CF_3S)_2PH$ with I, the major

product was II. As a result of the weak P-S bond, $(CF_3S)_2PH$

readily fragments the CF_3S group forming II.

$$(CF_3S)_2PH + CF_3CCl=NCF(CF_3)_2 \longrightarrow CF_3C(CF_3S)=NCF(CF_3)_2 + CF_3SPHCl$$

$$(II) \qquad\qquad \text{polymeric solids}$$

Due to the dearth of published literature regarding $(CF_3S)_2PH$, no attempt is made to address the mechanistic path way.

With CF_3SSH, the product (II) most likely results from decomposition of the disulfane in Me_3N to CF_3SH which then reacts with I to form II. Burton and Shreeve had reported the synthesis of several trifluoromethyl disulfane esters via reaction of CF_3SSH with selected fluorinated acid halides in the presence of a metal fluoride at low temperature [8]. Attempts to parallel this work with the imidoyl chloride were unfruitful since the chloride was not sufficiently labile to undergo substitution under these conditions.
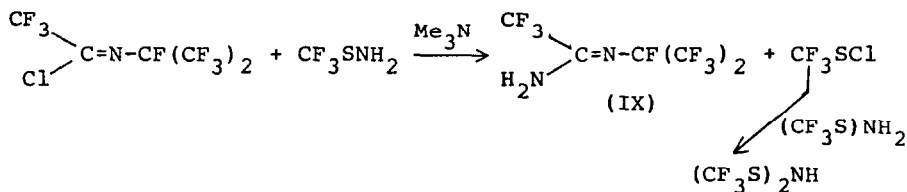
Reaction of I with $(CF_3S)_2NH$ led to a new N-trifluoromethylthio diimino species VII according to the following reaction scheme.
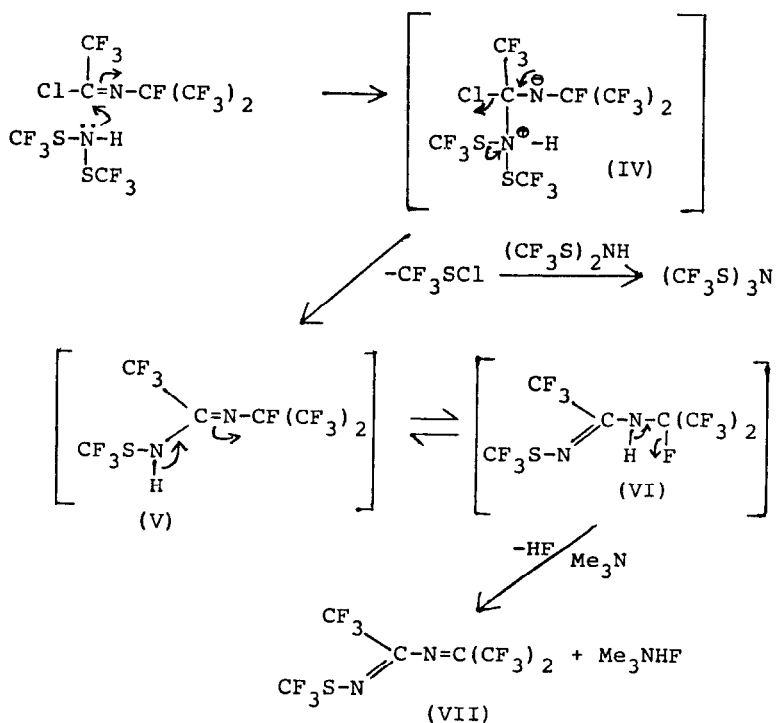
The $(CF_3S)_2NH$ attacks I with concomitant loss of CF_3SCl instead of HCl. This behavior had been observed previously in the reaction of $(CF_3S)_2NH$ with the functionally similar compound $C_6H_5C(O)Cl$ [9]. The scheme is in keeping with a study by Ta-Shma and Rappoport which determined that substitution on imidoyl chlorides by amines in polar solvents favors an addition-elimination process via a zwitterion intermediate like IV when the imidoyl chloride contains strong electron-withdrawing substituents [10]. The resulting imido amide (V) tautomerizes to VI which readily loses HF in the presence of Me_3N to provide the isolated product VII. No CF_3SCl was isolated since it reacted with excess $(CF_3S)_2NH$ to $(CF_3S)_3N$. Small amounts of CF_3SSCF_3 and $CF_3CF=NCF-(CF_3)_2$ were also observed from respectively the decomposition of $(CF_3S)_3N$ in Me_3N and the direct nucleophilic displacement of Cl^- by F^- from NH_4F. Attempts to synthesize the desired second order derivative VIII via a similar scheme from I and $(CF_3S)_3N$ were unsuccessful.

$$I + (CF_3S)_3N \not\rightarrow \underset{(CF_3S)_2N}{\overset{CF_3}{>}}C=N-CF(CF_3)_2 + CF_3SCl$$
$$(VIII)$$
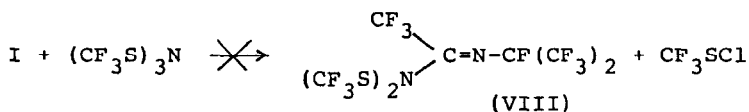
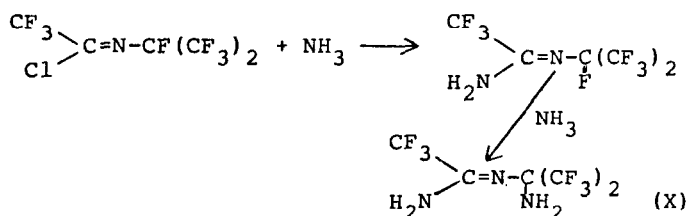Trifluoromethylthio amine, CF_3SNH_2, was reacted with I in order to compare its chemistry with that of bistrifluoromethylthio-amine. In this case, however, a product from the first step in the reaction, IX, was isolated.

$$\underset{Cl}{\overset{CF_3}{>}}C=N-CF(CF_3)_2 + CF_3SNH_2 \xrightarrow{Me_3N} \underset{H_2N}{\overset{CF_3}{>}}C=N-CF(CF_3)_2 + CF_3SCl$$
$$(IX)$$
$$\downarrow (CF_3S)NH_2$$
$$(CF_3S)_2NH$$

None of the expected dehydrofluorinated tautomer $HN=\overset{\overset{\displaystyle CF_3}{|}}{C}-N=C(CF_3)_2$ was found. However, in addition to IX, a very viscous, multi-component liquid was also produced but, due to the limited reaction scale, in a quantity too small to permit further isolation and identification.

Product IX was very difficult to isolate from $(CF_3S)_2NH$; therefore it seemed reasonable to synthesize IX via direct reaction of I with NH_3. Although some IX was obtained in this reaction, the major product (X) resulted from further reaction of NH_3 with the labile isopropyl fluorine.
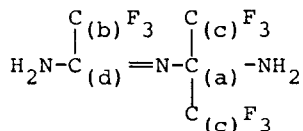
$$\underset{Cl}{\overset{CF_3}{\diagdown}}C=N-CF(CF_3)_2 \ + \ NH_3 \ \longrightarrow \ \underset{H_2N}{\overset{CF_3}{\diagdown}}C=N-\underset{F}{\overset{|}{C}}(CF_3)_2$$

$$\Bigg\downarrow NH_3$$

$$\underset{H_2N}{\overset{CF_3}{\diagdown}}C=N-\underset{NH_2}{\overset{|}{C}}(CF_3)_2 \qquad (X)$$

Only recently prepared by Kapran et al. via an alternate route, X is stabilized to loss of NH_3 by the CF_3 groups which reduce the basicity of the amino groups [11]. As a low molecular weight perfluorinated organo-nitrogen compound possessing three functionalities (two NH_2 functions and a C=N function), it should prove to be a valuable precursor for both heterocyclic and acyclic compounds in future synthetic work.

SPECTROSCOPIC DATA

As stated earlier, III showed two distinct ν(C=N) in the infrared spectrum resulting from observable syn- and anti-isomers.

The ambient temperature ^{19}F-NMR spectrum consists of broad, un-resolved peaks. At reduced temperature (ca. -40°C), the spectrum is clearly resolved.

(a. Ø in ppm, b. J in Hz)

The anti-structure can be readily assigned, based on the large long-range $F_3C-C=N-C-F$ coupling (J = 39.0 Hz). All fluorine resonances are in the expected regions. A large coupling is observed for the CF_3 groups directly attached to the P$[J((CF_3)_2P)$ = 75.6 Hz$]$ while the CF_3 group on the C=N, being further removed, shows a much smaller coupling $[J(CF_3-P)$ = 31.6 Hz$]$.

The infrared spectrum of VII displayed stretching vibrations at 1730 cm^{-1} and 1642 cm^{-1} for the two respective C=N functions in the mole-cule. The ^{19}F-NMR was rather elementary with singlet resonances occuring in the expected regions.

IX displayed asymmetrical and symmetrical stretching vibrations, character-istic of the -NH$_2$ function, at 3575 cm^{-1} and 3462 cm^{-1} respec-tively and a ν(C=N) at 1738 cm^{-1}. The ^{19}F-NMR data consisted of first order spectra as presented in the experimental section.

The sublimable solid X showed characteristic, albeit poorly defined, N-H, C=N, and C-F stretching vibrations in the infrared spectrum determined from a KBr pellet. Even with the elemental analysis, ^{1}H and ^{19}F NMR data, and available literature data [11], various cyclic and acyclic structures remained a possibility. The structure for X, therefore, could be unequivocally assigned only with a ^{13}C NMR analysis as follows.

$$
\begin{array}{ccc}
\underset{(b)}{C}{}^{F}{}_{3} & \underset{(c)}{C}{}^{F}{}_{3} & \\
| & | & \\
H_2N-\underset{(d)}{C}=N-\underset{(a)}{C}-NH_2 \\
& | & \\
& \underset{(c)}{C}{}^{F}{}_{3} &
\end{array}
$$

The spectrum provided a septet $[J(C_{(a)}-F) = 28.61\ Hz]$ at $\emptyset\ 76.9$ for $C_{(a)}$ which is coupled with the fluorine atoms of the two adjacent $C_{(c)}F_3$ groups. The small coupling constant is expected since $C_{(a)}$ is not directly attached to the fluorine atoms. Quartets appeared at $\emptyset\ 118.9$ and $\emptyset\ 124.4$ for $C_{(b)}$ and $C_{(c)}$ respectively with each showing very large coupling constants $[J(C_{(b)}-F) = 278.4\ Hz,\ J(C_{(c)}-F) = 289.9\ Hz]$ resulting from the three directly attached fluorine atoms on each carbon. $C_{(b)}$ is further split into a triplet $[J(C_{(b)}-H) = 6.7\ Hz]$ by the two protons on the neighboring $-NH_2$ group. The sp^2 hybridized $C_{(d)}$ ($>C=N$) resonance occured as expected far downfield at $\emptyset\ 152.2$ as a quartet $[J(C_{(d)}-F) = 34.9\ Hz]$. This coupling is induced by the neighboring fluorines on the $C_{(b)}F_3$ group. Both the ^{19}F- and ^{1}H-NMR spectra displayed elementary singlet resonances in the expected regions based on the structure elucidated from the ^{13}C-NMR spectrum.

Mass spectra verify and support the assigned structures for each of the new compounds.

EXPERIMENTAL

General Procedures:

Most gases and liquids were handled in a conventional Pyrex vacuum apparatus equipped with a mercury manometer. Volatile starting materials and products were measured quantitatively by PVT techniques or weighed. Solids and products of lower volatility were weighed. Volatile products were purified by trap-to-trap distillation, gas chromatography, or sublimation. For preparative gas chromatographic separations, the column was constructed of 10 % OU 101 on Chromosorb P AW.

Infrared spectra were recorded on either a Perkin-Elmer 398 spectrophotometer or a Bruker IFS-85 FT-IR spectrometer. Gas phase spectra were obtained at 4 to 6 torr in a 10 cm Pyrex cell equipped with NaCl windows. Solid samples were prepared by grinding the sample with spectral quality KBr and preparing a pellet. ^{1}H-, ^{19}F- and ^{13}C-NMR spectra were obtained on a Bruker WM 250 spectrometer with chemical shifts reported relative to TMS (^{1}H and ^{13}C) or CFCl$_3$ (^{19}F). Mass spectra were obtained with CH-7 and CH-5 Varian-Mat-spectrometers.

Elemental analyses were performed by the microanalytical section of our laboratories.

Literature methods were used to prepare CF$_3$SH [12], CF$_3$SSH [13], (CF$_3$S)$_3$N, (CF$_3$S)$_2$NH, CF$_3$SNH$_2$, (CF$_3$S)$_2$PH [14], and CF$_3$CCl=NCF-(CF$_3$)$_2$ [15]. (CF$_3$)$_2$PH was provided by Prof. Grobe, Münster.

The commercially available starting materials Me$_3$N, NH$_3$, acetone, and NaI were used as received or, where appropriate, purified before use.

Preparation of $CF_3[(CF_3)_2P]C=NCF(CF_3)_2$ (III).

Equimolar amounts (3.7 mmol) of $(CF_3)_2PH$, $CF_3CCl=NCF(CF_3)_2$, and $(CH_3)_3N$ were successively condensed at $-196°C$ into an evacuated, flame-dried Pyrex vessel equipped with a Teflon stopcock. The vessel was immersed in a $-78°C$ bath for 2 h after which it was allowed to warm to ambient temperature. Following trap-to-trap fractionation, 1.0 mmol (28 % yield) of III was obtained pure in a trap at $-65°C$ after passing a trap at $-30°C$.

IR: 1690 m, 1666 w, 1317 ms, 1266 vs, 1246 s, 1212 s, 1194 s, 1171 vs, 1144 s, 1121 s, 1096 ms, 996 ms, 962 w, 944 m, 765 w, 750 w, 736 m, 696 w, 682 w, 632 w, 558 w, 540 w.

NMR (in $CDCl_3$): $\emptyset$ -50.2 (d, $(CF_3)_2P$), $\emptyset$ -63.3 (br, CF_3), $\emptyset$ -78.1 (s, $(CF_3)_2C$), $\emptyset$ -149.4 (br, C-F).

Anal. Found (Calc.): C, 19.0 (19.4), N, 3.4 (3.2).

Preparation of $CF_3CI=NCF(CF_3)_2$ (IV).

Into a Pyrex vessel containing 1.0 g NaI in 1.0 ml acetone was condensed 3.0 mmol I. The imidoyl chloride (I) was quantitatively consumed as the reaction mixture warmed to ambient temperature. IV was isolated as a yellow liquid in a $-60°C$ trap after passing a trap at $-20°C$. It slowly decomposed at ambient temperature as evidenced by the appearance of a purple color, presumably from free I_2.

NMR (in d^6-acetone): $\emptyset$ -72.5 (d, CF_3), $\emptyset$ -78.8 (d, $(CF_3)_2$), $\emptyset$ -169.7 (mult., C-F); $J(CF_3-CF) = 0.61$ Hz, $J((CF_3)_2-CF) = 5.07$ Hz.

Preparation of $CF_3SN=C(CF_3)N=C(CF_3)_2$ (VII).

Into a Pyrex vessel equipped with a Teflon stopcock were success-sively condensed $(CF_3S)_2NH$ (7.15 mmol), I(5.3 mmol) and Me_3N

(6.2 mmol) at -196°C after which the reaction vessel warmed slowly to ambient temperature. A mixture of $(CF_3S)_3N$ (45 %) and VII (54 %) as determined by analytical GC, was isolated in a -78°C trap after passing a trap at -55°C. Preparative G.C. provided 3.2 mmol (61 %) VII.

I.R.: 1730 w, 1642 w, 1338 m, 1321 ms, 1270 vs, 1245 s, 1229 s, 1216 s, 1195 vs, 1130 vs, 1097 m, 989 ms, 859 w, 764 w (br), 734 w, 721 w, 700 w.

NMR (in d-acetone): $\emptyset$ -50.0 (s, CF_3S), $\emptyset$ -69.0 (s, $(CF_3)_2$), $\emptyset$ -69.2 (s, CF_3).

Anal. Found (Calc.): C, 19.6 (20.0), N, 7.9 (7.8).

Preparation of $CF_3(NH_2)C=NCF(CF_3)_2$ (IX).

In a typical reaction, equimolar amounts (5.5 mmol) of CF_3SNH_2, I, and Me_3N were condensed at -196°C into a Pyrex reaction vessel equipped with a Teflon stopcock. The vessel was allowed to warm slowly to ambient temperature after which the products were separated by fractional distillation. For analytical purposes, IX was isolated in a -50°C trap after passing a trap at -25°C; however, some IX passed through the -50°C trap to a colder trap. A cool bath below -50°C condenses $(CF_3S)_2NH$. Maximum isolated yield of IX was 17 %.

I.R.: 3575 m, 3462 m, 1738 s, 1608 w, 1425 w, 1335 m, 1310 m, 1290 m, 1260 vs, 1243 s, 1228 s, 1185 ms, 1175 ms, 1060 w, 1039 m, 998 ms, 842 w, 825 w, 650 w.

NMR (in C_6D_6): $\int$ 4.78 (br, NH_2), -74.2 (s, CF_3), -79.5 (d, $(CF_3)_2$), -155 (sept, C-F); $J((CF_3)_2-CF) = 4.88$ Hz.

Anal. Found (Calc.): C, 20.5 (21.4), N, 9.9 (10.0), H, 1.0 (0.7).

Preparation of $CF_3(NH_2)C=NC(CF_3)_2NH_2$ (X).

Into a Pyrex vessel equipped with a Teflon stopcock were success-
sively condensed 12 mmol NH_3 and 6.0 mmol I at $-196°C$. The
reaction vessel was allowed to warm slowly to ambient temperature.
Following fractional distillation, 3.2 mmol (53 %) of crystalline
X was isolated in a $-30°C$ trap. Small amounts of IX were also
detected in the reaction. Final purification of X was carried out by subli-
mation under a static vacuum onto a water cooled cold finger.
I.R. (KBr pellet): 3438 m, 3420 (sh), 3345 m, 3320 m, 3165 w,
1690 ms, 1670 ms, 1605 (sh), 1592 w, 1448 w, 1280 ms, 1255 s,
1220 s, 1200 (sh), 1165 s, 1148 s, 1120 ms, 990 s, 950 s, 832 s,
760 w, 738 w, 710 ms, 642 w, 570 w, 537 w, 470 w, 430 w.
NMR (in d-acetone): δ 7.16 (br, s, $H_2N-C=N$), δ 3.18 (s, H_2N-C-N),
$\emptyset$ -73.0 (s, CF_3), $\emptyset$ -78.4 (s, $(CF_3)_2$). C-13 NMR presented in text.
Anal. Found (Calc.): C, 21,6 (21.7), H, 1.5 (1.5), N, 15.2 (15.2).

REFERENCES

1 A. Haas, Chemiker Zeitung, 106 (1982) 239.

2 A. Haas, Advances in Inorganic Chemistry and Radiochemistry,
   28 (1984) 167.

3 K. E. Peterman and J. M. Shreeve, Inorg. Chem., 14 (1975) 1106.

4 K. E. Peterman and J. M. Shreeve, J. Fluorine Chem., 6 (1975) 83.

5 R. S. Drago, 'Physical Methods In Chemistry', Saunders , Phila-
   delphia, 1977, Chapter 8.

6   H. S. Gutowsky and C. H. Halm, J. Chem. Phys., 25 (1956) 1228.

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

8   C. A. Burton and J. M. Shreeve, J. Am. Chem. Soc., 98 (1976) 6545.

9   A. Haas and R. Lorenz, Z. Anorg. Allg. Chem., 385 (1971) 33.

10 R. Ta-Shma and Z. Rappoport, J. Am. Chem. Soc., 98 (1976) 8460.

11 N. A. Kapran, Y. L. Yagupol'skii, and V. M. Cherkasov,
    Zh. Org. Khim., 19 (1983) 1192. English Translation, J. Org.
    Chem. USSR, 19 (1983) 1063.

12 R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., (1953) 3219.

13 W. Gombler and F. Seel, Z. Naturforsch., 30b (1975) 169.

14 H. J. Eméleus and S. N. Nabi, J. Chem. Soc. [London], (1960) 1103.

15 K. E. Peterman and J. M. Shreeve, Inorg. Chem., 14 (1975) 1223.