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THE SYNTHESIS OF PERFLUORO HIGHLY BRANCHED HETEROCYCLIC FLUORINE COMPOUNDS BY DIRECT FLUORINATION

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SUMMARY

The direct fluorination of hexamethyleneimine, heptamethyleneimine, 2,6-dimethylmorpholine, thiomorpholine, 1,4-dimethylpiperazine and piperazine produced the corresponding perfluorinated products. The ^{19}F NMR spectrum of perfluoro N,N'-difluoropiperazine was found to be temperature-dependent.

INTRODUCTION

Recently efforts have been extended to the investigation of fluorinating heterocyclic nitrogen compounds with elemental fluorine (see Fig. 1). Several new fluorocarbons with intact C-N bonds were prepared and are now reported. The syntheses of perfluoro N-fluoro-hexamethylene-imine, perfluoro N-fluorohepta-methyleneimine, perfluoro N-fluoro-2,6-dimethylmorpholine, N-fluorotetrafluorosulfide perfluorothiomorpholine, perfluoro N,N'-difluoropiperazine, and perfluoro N,N'-bis(trifluoromethyl)-piperazine by the very general direct fluorination techniques developed in our laboratory [1] were undertaken in order to produce perfluorinated heterocyclic compounds with correct volatility for oxygen-carriers and blood-substitutes studies. This work was done in collaboration between our laboratory and that of Professor Leland C. Clark, Jr. of Cincinnati's Children's Hospital Research Foundation. In some cases we synthesized monohydro compounds in order to determine if one proton strategically placed on such a molecule altered the physiological properties of such fluorocarbons. In the course of these preparations, we prepared several new compounds, provided higher yield syntheses for perfluoro N,N'-difluoro-

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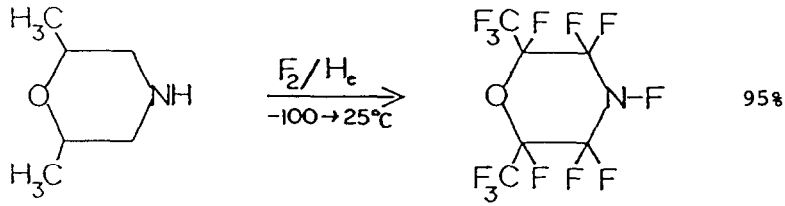
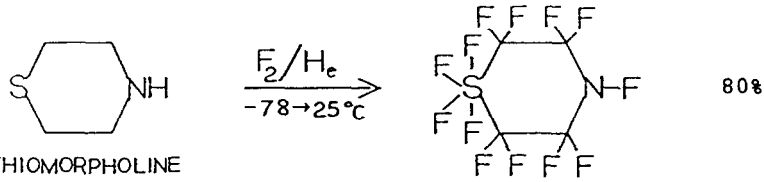
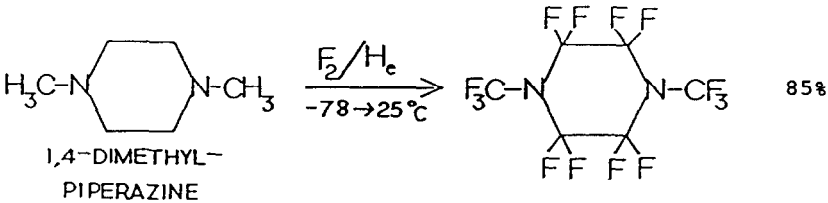


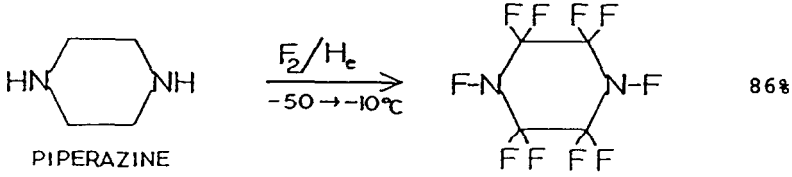
2,6-DIMETHYL-MORPHOLINE



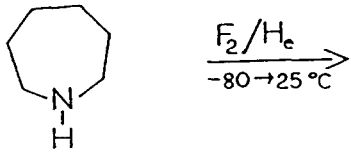
THIOMORPHOLINE



1,4-DIMETHYL-PIPERAZINE



PIPERAZINE

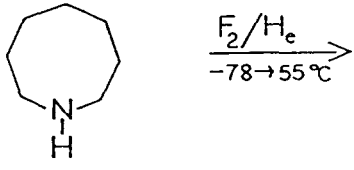


HEXAMETHYLENE IMINE

60%

$CF_3CF_2(CF_2)_4NF_2$ 5.3%

$CF_3CF_2(CF_2)_3CF_3$ 15.4%



HEPTAMETHYLENE IMINE

64%

$CF_3CF_2(CF_2)_5NF_2$ 3.8%

$CF_3CF_2(CF_2)_4CF_3$ 13.3%

Fig.1. Fluorination of Heterocyclic Hydrocarbons.

piperazine previously prepared by Banks and Haszeldine [2], and a synthesis for perfluoro N,N'bis(trifluoromethyl)piperazine previously prepared in low yield by Ogden at 3M [3]. Also presented are very detailed NMR studies on both the novel compounds and those previously synthesized by the Banks-Haszeldine team and by the 3M group.

EXPERIMENTAL

Hexamethyleneimine, heptamethyleneimine, 2,6-dimethylmorpholine, thiomorpholine, piperazine and 1,4-dimethylpiperazine were used as received from Aldrich Chemical without further purification. The fluorination of hexamethyleneimine, heptamethyleneimine, 2,6-dimethylmorpholine and thiomorpholine were conducted in the four-zone cryogenic reactor [1] while the fluorination of piperazine and 1,4-dimethylpiperazine were conducted in a one-zone reactor [1].

The ^{19}F NMR spectra were recorded on a Varian EM 390 spectrometer operating at 84.67 MHz. $CFCl_3$ was used as an external standard. The resonance at high field of the reference was designated negative. Mass spectra were measured in the gas phase on a Bell & Howell Model 21-490 mass spectrometer. The gas phase IR spectra were recorded on a Beckman Acculab 8 spectrometer. A Bendix 2500 gas chromatograph equipped with a fluorosilicone column or SE-30 column was used for final purification. Elemental analyses were done by E+R Microanalytical Laboratory, Inc., Corona, New York. The low-temperature ^{19}F NMR spectra were taken on a Bruker WH-90 instrument.

Fluorination of hexamethyleneimine

A mixture of 1.42 g of hexamethyleneimine and approximately 10 g of powdered sodium fluoride was loaded in a 5 in. x 1 in. brass tube and placed in the first zone. The rest of the zones were packed with fluorinated copper turnings. The fluorination was carried out under the procedures and conditions listed in Table 1. The major products were perfluoro N-fluoro-hexamethyleneimine (60%), azaperfluorohexane (5.3%) and 15.4% of the starting material was converted to perfluorohexane.

Perfluoro N-fluoro-hexamethyleneimine, bp. 81 °C. Anal. Calcd. for $C_6F_{13}N$: C, 21.64; F, 74.16. Found: C, 21.79; F, 73.84%. IR: 1350-1150 (vs,br), 1132 (s,sh), 1040 (m), 1000 (s,sh), 935 (s) cm^{-1}. MS, m/e (fragment ion): 333 ($C_6F_{13}N$), 295 ($C_6F_{11}N$), 276 ($C_6F_{10}N$), 264 ($C_5F_{10}N$),

181 (C_4F_7), 176 (C_4F_6N), 145 (C_3F_5N), 131 (C_3F_5, base peak), 119 (C_2F_5), 114 (C_2F_4N), 100 (C_2F_4), 69 (CF_3). The NMR data are reported in Table 5.

Azaperfluorohexane, bp. 88 °C. Anal. Calcd. for $C_6F_{15}N$: C, 19.42; F, 76.80. Found: C, 19.71; F, 76.43%. IR: 1400-1100 (vs,br), 1085 (w), 1010 (w), 940 (m), 750 (m,br) cm^{-1}. MS, m/e (fragment ion): 319 (C_6F_{13}), 231 (C_5F_9), 181 (C_4F_7), 169 (C_3F_7), 131 (C_3F_5), 119 (C_2F_5), 114 (C_2F_4N), 100 (C_2F_4), 69 (CF_3, base peak). The NMR chemical shifts are reported in Table 5.

Fluorination of heptamethyleneimine

The reaction was initiated with the first two zones cooled to -50 °C, and ended with the last two zones warmed to 50 °C as shown in Table 2. In the early steps, the last two zones were maintained at -78 °C to prevent the partly fluorinated products from leaving the reactor before the reaction was complete. After fluorination 1.38 g of heptamethyleneimine yielded 3.20 g of crude products. The products isolated were characterized as perfluoro N-fluoroheptamethyleneimine, azaperfluoroheptane and perfluoroheptane. The yields were 64%, 3.8% and 13.3%, respectively.

Perfluoro N-fluoroheptamethyleneimine, bp 105 °C. Anal. Calcd. for $C_7F_{15}N$: C, 21.95; F, 74.39. Found: C, 22.02; F, 74.69%. IR: 1350-1150 (vs,br), 1105 (w), 1062 (w), 1014 (m), 1002 (m), 940 (s), 894 (s), 725 (m) cm^{-1}. MS, m/e (fragment ion): 383 ($C_7F_{15}N$), 364 ($C_7F_{14}N$), 345 ($C_7F_{13}N$), 326 ($C_7F_{12}N$), 231 (C_5F_9), 181 (C_4F_7), 176 (C_4F_6N), 169 (C_3F_7), 145 (C_3F_5N), 131 (C_3F_5, base peak), 119 (C_2F_5), 114 (C_2F_4N), 100 (C_2F_4), 69 (CF_3). The NMR data are summarized in Table 5.

Azaperfluoroheptane, bp 110 °C. Anal. Calcd. for $C_7F_{17}N$: C, 19.97, F, 76.71. Found: C, 20.14; F, 76.52%. IR: 1330 (m), 1300-1200 (vs,br), 1150 (s), 980 (m), 940 (m), 725 (s), 700 (m) cm^{-1}. MS, m/e (fragment ion): 402 ($C_7F_{16}N$), 369 (C_7F_{15}), 281 (C_6F_{11}), 219 (C_4F_9), 181 (C_4F_7), 169 (C_3F_7, base peak), 131 (C_3F_5), 119 (C_2F_5), 100 (C_2F_4), 69 (CF_3), 500 (CF_2). The NMR data are reported in Table 5.

Fluorination of 2,6-dimethylmorpholine

2,6-Dimethylmorpholine (1.45 g) was fluorinated in the temperature range from -100 °C to room temperature. The reaction conditions are listed in Table 3. After reaction the highly volatile products were removed by

TABLE 1

Fluorination conditions for hexamethyleneimine

Time (day)	He (cc/min)	F_2 (cc/min)	Zones, Temp (°C) 1	2	3	4
1.0	50	1.0	-80	-80	-80	-80
0.5	30	1.0	-80	-80	-80	-80
0.5	30	2.0	-80	-80	-80	-80
0.5	15	2.0	-80	-80	-80	-80
0.5	15	3.0	-80	-80	-80	-80
0.5	0	2.0	-80	-80	-80	-80
0.5	0	2.0		-80	-80	-80
0.5	0	2.0			-80	-80
0.5	0	2.0				-80
0.5	0	2.0	25	25	25	25

TABLE 2

Fluorination conditions for heptamethyleneimine

Time (day)	He (cc/min)	F_2 (cc/min)	Zones, Temp (°C) 1	2	3	4
0.5	40	1.0	-50	-50	-78	-78
0.5	30	1.0	-50	-50	-78	-78
0.5	20	1.0	-50	-50	-78	-78
0.5	10	1.0	-50	-50	-78	-78
0.5	0	2.0		-78	-78	-78
0.5	0	2.0			-78	-78
0.5	0	2.0				-78
0.5	0	2.0	25	25	25	25
0.5	0	2.0			55	55

TABLE 3

Fluorination conditions for 2,6-dimethylmorpholine

Time (day)	He (cc/min)	F_2 (cc/min)	Zones, Temp (°C)			
			1	2	3	4
0.5	30	1.0	-100	-100	-100	-100
0.5	20	1.0	-100	-100	-100	-100
0.5	10	1.0	-80	-80	-80	-80
0.5	10	3.0	-80	-80	-80	-80
1.0	0	1.0		-80	-80	-80
0.5	0	2.0			-80	-80
0.5	0	2.0				-80
0.5	0	2.0	25	25	25	25

TABLE 4

Fluorination conditions for thiomorpholine

Time (day)	He (cc/min)	F_2 (cc/min)	Zones, Temp (°C)			
			1	2	3	4
1.0	40	1.0	-60	-60	-78	-78
0.5	40	1.5	-60	-60	-78	-78
0.5	40	2.0	-60	-60	-78	-78
0.5	40	2.0		-78	-78	-78
0.5	30	2.0		-78	-78	-78
0.5	15	2.0			-78	-78
1.0	0	1.0			-78	-78
0.5	0	1.0				-78
0.5	0	1.0	25	25	25	25
1.0	10	1.0	25	25	25	25

pumping through a -78 °C trap and 3.27 g of products were obtained. The GC assay gave 4.18 g of perfluoro N-fluoro-2,6-dimethylmorpholine, corresponding to a 95% yield.

Perfluoro N-fluoro-2,6-dimethylmorpholine, bp. 78 °C. Anal. Calcd. for $C_6F_{13}NO$: C, 20.65; F, 70.76. Found: C, 20.57; F, 70.55%. IR: 1320 (m), 1245 (vs), 1170 (m), 1135 (m), 1100 (m), 990 (w), 910 (m), 836 (w), 740 (w), 682 (w) cm^{-1}. MS, m/e (fragment ion): 330 ($C_6F_{12}NO$), 280 ($C_5F_{10}NO$), 214 (C_4F_9N), 195 (C_4F_7N), 169 (C_3F_7, base peak), 164 (C_3F_6N), 150 (C_3F_6), 145 (C_3F_5N), 131 (C_3F_5), 119 (C_2F_5), 114 (C_2F_4N), 100 (C_2F_4), 69 (CF_3). The ^{19}F NMR chemical shifts are reported in Table 5.

Fluorination of thiomorpholine

The reaction conditions (see Table 4) were similar to those used for the fluorination of heptamethyleneimine, except that the fluorination was initiated at -60 °C and raised to room temperature. Thiomorpholine (1.7 g) produced 5.0 g of crude products after fractionation. Final purification resulted in the isolation of 4.50 g of N-fluorotetrafluorosulfide perfluoro thiomorpholine. The yield was 80%. Unseparated products with shorter GC retention time were low molecular weight fragments.

N-Fluorotetrafluorosulfide perfluorothiomorpholine, bp. 98 °C. Anal. Calcd. for $C_4F_{13}NS$: C, 14.09; F, 72.41. Found: C, 14.40; F, 72.66%. IR: 1300-1175 (vs,br), 1154 (vs,br), 1112 (vs,br), 1008 (w), 958 (vs,br), 870 (vs,sh), 812 (vs,sh), 775 (vs,sh), 732 (m). MS, m/e (fragment ion): 202 (C_3F_8N), 164 (C_3F_6N), 150 (C_3F_6), 145 (C_3F_5N), 119 (C_2F_5, base peak), 114 (C_2F_4N), 101 (CF_3S), 100 (C_2F_4), 95 (C_2F_3N), 89 (SF_3), 76 (C_2F_2N), 70 (SF_2), 69 (CF_3), 51 (SF_2), 50 (CF_2). The ^{19}F NMR data are given in Table 5.

Fluorination of piperazine

Approximately 1.0 g of piperazine and 2.5 g of sodium fluoride were ground to fine powder and mixed well. The mixture was placed in the nickel boat in the one-zone reactor for fluorination, using the following conditions: 10 cc/min of He and 2.0 cc/min of F_2 at -50 °C for 12 hours; 5 cc/min of He and 2.0 cc/min of F_2 at -50 °C for 12 hours; 5 cc/min of He and 2.0 cc/min of F_2 at -30 °C for 12 hours; 1.0 cc/min of F_2 at -30 °C for 12 hours; 1.0 cc/min of F_2 at -10 °C for 24 hours. The reaction provided perfluoro N,N'-difluoropiperazine in a 86% yield as well as two straight-chain by-products:

$CF_3CF_2N(F)CF_2CF_2NF_2$ (2.7%) and $CHF_2CF_2N(F)CF_2CF_2NF_2$ (2.3%). These products were characterized by NMR, mass and infrared spectra.

The ^{19}F NMR spectrum of perfluoro N,N'-difluoropiperazine consisted of two peaks at -107.5 ppm (-CF_2-) and -110.6 ppm (-NF-). The reported peaks were -109.7 ppm and -113.2 ppm [2]. Low-temperature NMR spectra were monitored in the temperature range from 0 °C to -85 °C. The $CFCl_3$ solution containing 33% (v/v) of sample was sealed in a 3 mm evacuated glass tube which was then placed in the 5 mm NMR tube containing acetone-d^6. $CFCl_3$ and acetone-d^6 were used as an internal standard and a locking solvent, respectively. The temperature-dependent spectra are shown in Fig. 2. The variation of chemical shifts with temperatures was reported in Table 6. The mass spectrum of perfluoro N,N'-difluoropiperazine gave a parent peak at m/e 266 ($C_4F_{10}N_2$). Other important peaks were as follows: 247 ($C_4F_9N_2$), 209 ($C_4F_7N_2$), 197 ($C_3F_7N_2$), 164 (C_3F_6N), 159 ($C_3F_5N_2$), 145 (C_3F_5N), 119 (C_2F_5), 114 (C_2F_4N, base peak), 100 (C_2F_4), 95 (C_2F_3N), 76 (C_2F_2N), 69 (CF_3), 64 (CF_2N), 50 (CF_2). IR: 1320 (vs), 1280 (s,sh), 1225 (vs), 1184 (vs), 1140 (vs,sh), 960 (vs), 730 (m,br) cm^{-1}.

$CF_3CF_2N(F)CF_2CF_2NF_2$
a b c d e f

^{19}F NMR: a(-85.5, doublet, 3F), b(-119.0, triplet, 2F), c(-93.7, unresolved multiplet, 1F), d(-110.0, unresolved multiplet, 2F), e(-108.0, doublet, 2F), f(+14.3, unresolved multiplet, 2F).

IR: 1250 (vs,br), 1195 (vs), 1100 (s), 1030 (m,sh), 970 (m,sh), 935 (s,sh), 800-690 (m, multiple bands) cm^{-1}.

MS, m/e (fragment ion): 235 ($C_3F_9N_2$, P-CF_3), 214 (C_4F_8N), 202 (C_3F_8N), 164 (C_3F_6N), 145 (C_3F_5N), 119 (C_2F_5, base peak), 114 (C_2F_4N), 100 (C_2F_4), 95 (C_2F_3N), 69 (CF_3), 50 (CF_2).

$CHF_2CF_2N(F)CF_2CF_2NF_2$
a b c d e f

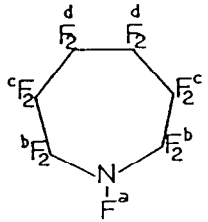
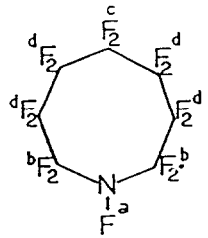
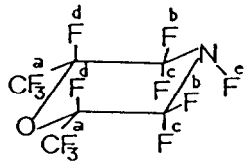
^{19}F NMR: a(-140.0, doublet of doublet, 2F), b(-128.9, triplet, 2F), c(-97.8, unresolved multiplet, 1F), d(-112.7, unresolved multiplet, 2F), e(-108.8, doublet, 2F), f(+15.0, unresolved multiplet, 2F).

^1H NMR: 5.48 (triplet of multiplet), J_{H-F} = 52.5 Hz.

IR: 3015 (w), 1340 (m), 1300 (s), 1250-1100 (vs,br), 1015 (m,sh), 970 (m,sh), 800 (m,sh), 730 (s,br) cm^{-1}.

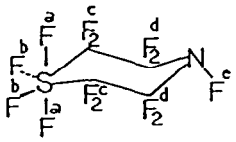
TABLE 5

Fluorine nmr chemical shifts of new organonitrogen fluorocarbons

Compound	Shift (ppm)	Splitting*	Rel.Int.
	a -98.5	m	1
	b -101.0	m	4
	c -123.0	m	4
	d -126.0	m	4
	a -94.3	m	1
	b -102.4	m	4
	c -119.3	m	2
	d -121.6	m	8
	a -80.6	multiplet	6
	b -104.0	AB quartet	4
	c -107.8		
	d -128.3	m	2
	3 -115.4	m	1

* m: broad unresolved multiplet

TABLE 5 (Cont.)

Compound	Shift (ppm)	Splitting*	Rel.Int.
	a +48.5	triplet of pentet	2
	b +21.1	triplet	2
	c -94.6	triplet	4
	d -100.4	broad singlet	4
	e -104.7	singlet	1
$CF_3CF_2CF_2CF_2CF_2CF_2NF_2$ a d c c c b e	a -81.3	triplet	3
	b -115.3	triplet	2
	c -122.0	m	6
	d -126.0	triplet	2
	e +17.0	m	2
$CF_3CF_2CF_2CF_2CF_2CF_2CF_2NF_2$ a c d d c c b f	a -81.0	triplet	3
	b -115.0	triplet	2
	c -121.5	m	4
	d -122.3	m	4
	e -126.0	triplet	2
	f +16.7	m	2

* m: broad unresolved multiplet

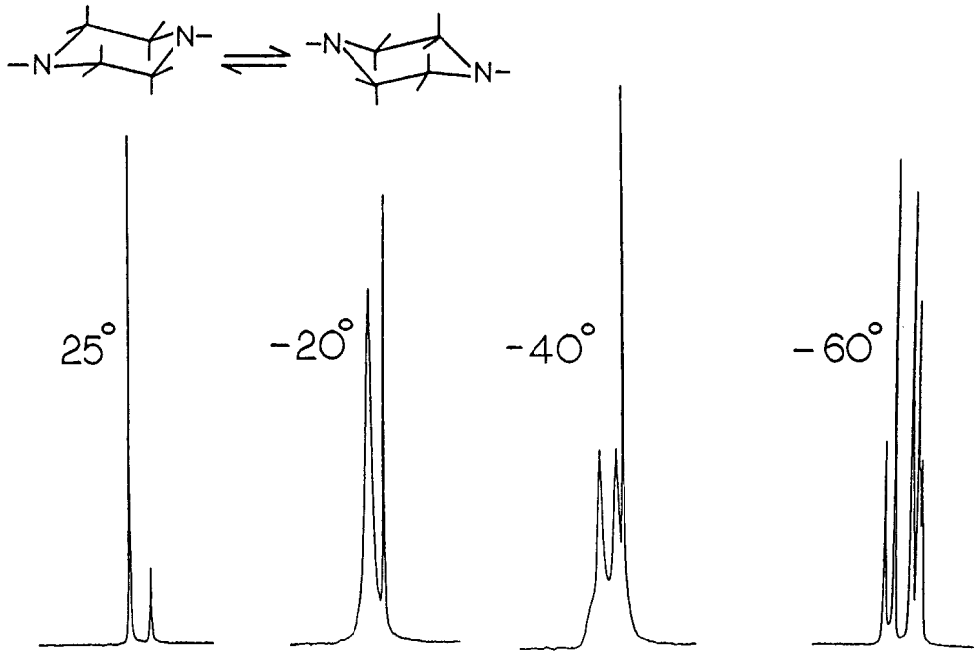


Fig. 2. Temperature-dependent F nmr spectra of perfluoro N,N'-difluoropiperazine.

TABLE 6

Temperature-dependent fluorine chemical shifts of perfluoro N,N'-difluoropiperazine

Temp (°C)	δN-F (ppm)	δ-CF_2CF_2- (ppm)
+25	-110.6	-107.5
-40	-110.6	-105.7 -109.1
-60	-110.5	-103.5 -105.6 -109.3 -111.3

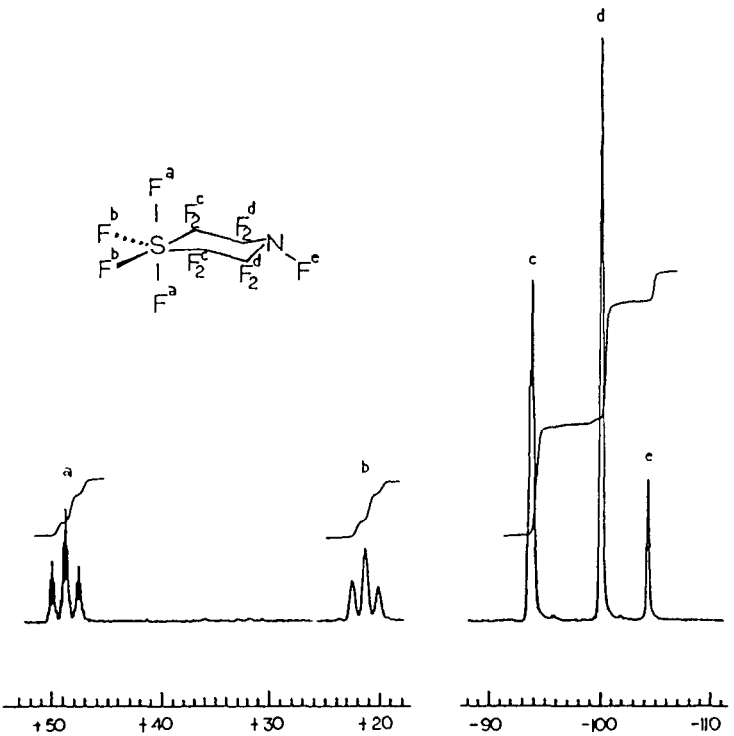


Fig. 3. F nmr spectrum of N-fluoro-tetrafluorosulfide perfluoro thiomorpholine.

MS, m/e (fragment ion): 235 ($C_3F_9N_2$), 196 (C_4F_9NH), 184 (C_3F_7NH), 177 (C_4F_6NH), 164 (C_3F_6N), 146 (C_3F_5NH), 145 (C_3F_5N), 119 (C_2F_5), 114 (C_2F_4N), 101 (C_2F_4H, base peak), 100 (C_2F_4), 96 (C_2F_3NH), 95 (C_2F_3N), 82 (C_2F_3H), 69 (CF_3), 51 (CF_2H), 50 (CF_2).

Fluorination of 1,4-dimethylpiperazine

1,4-Dimethylpiperazine (0.79 g) was fluorinated under the following conditions: 20 cc/min of He and 2.0 cc/min of F_2 at -80 °C for 12 hours; 10 cc/min of He and 2.0 cc/min of F_2 at -80 °C for 12 hours; 10 cc/min of He and 2.0 cc/min of F_2 at -60 °C for 12 hours; 5 cc/min of He and 2.0 cc/min of F_2 at -50 °C for 12 hours; 5 cc/min of He and 2.0 cc/min of F_2 at -40 °C for 12 hours; 2.0 cc/min of F_2 at -40 °C and 25 °C for 12 hours, respectively. Approximately 2.16 g of perfluoro N,N'-bis(trifluoromethyl)-piperazine was produced. The yield was 85%. Perfluoro N,N'-bis(trifluoro-methyl)piperazine has a boiling point of 84 °C. The ^{19}F NMR spectrum consists of a quintet at -54.4 ppm ($-CF_3$) and a quartet at -93.8 ppm ($-CF_2-$) (reported: -52.8 ppm and -92.3 ppm) [3]. The coupling constant J_{F-F} is 13.8 Hz (reported: 12.6 Hz). The mass spectrum contained the parent peak at 366 ($C_6F_{14}N_2$) and other prominent peaks at 347 ($C_6F_{13}N_2$, P-F), 297 ($C_5F_{11}N_2$, P-CF_3), 259 ($C_5F_9N_2$), 209 ($C_4F_7N_2$), 171 (C_2F_7N), 164 (C_3F_6N), 119 (C_2F_5), 114 (C_2F_4N), 100 (C_2F_4, base peak), 69 (CF_3). IR: 1355 (vs,br), 1310 (vs,br), 1278 (vs,br), 1225 (vs,br), 1160 (vs,br), 1090 (s,sh), 960 (s,sh), 875 (s,sh), 725 (s,sh) cm^{-1}.

DISCUSSION

Perfluoro N-fluoro cyclic amines are of interest. The unusual properties associated with the N-F bond have been well-established [4].

The direct fluorination of hexamethyleneimine was accomplished from -80 °C to room temperature. Under similar conditions heptamethyleneimine gave a complex mixture of partially fluorinated species.

High yield synthesis of perfluoro N-fluoro-2,6-dimethylmorpholine was consistent with the previous results on the fluorination of morpholine [5]. The ^{19}F NMR spectrum of perfluoro N,N'-difluoropiperazine was found to be temperature-dependent. The NMR study has shown that the chair-to-chair interconversion of perfluoro N,N'-difluoropiperazine ceased at about -50 °C. On lowering the temperature, the CF_2 resonance first became broad, then appeared as two separate bands, and finally as a well-resolved AB type

quartet. The coupling constant between the geminal fluorine nuclei is 178.7 Hz. The N-F resonance, however, remained unchanged. The rapid ring inversion of perfluoro N,N'-bis(trifluoromethyl)piperazine was found to continue even at -100 °C [3]. It appears that the energy barrier associated with ring inversion is reduced by the attachment of bulky CF_3 groups to the nitrogen. No details on the synthesis of perfluoro N,N'-bis(trifluoromethyl)piperazine have been reported in the literature.

In the fluorination of high-melting point and low-vapor pressure materials such as thiomorpholine and heptamethyleneimine, the temperature control was more critical. By starting the fluorination at -100 °C instead of -60 °C, the yield of the corresponding perfluorinated thiomorpholine was decreased to 4.3%. It was thought that the initial lower temperature facilitated the build-up of partly fluorinated intermediates in the first zone, thus promoting the polymerization reaction as the temperature was gradually raised up in the following steps. The conditions described in the experimental section maximized the production of the desired products.

Under the experimental conditions the sulfur atom of thiomorpholine was oxidized to its highest valency state as expected. Two pairs of fluorine nuclei are located at axial and equatorial positions of an octahedral structure centered at the sulfur atom. Therefore, a triplet of quintets was observed for the axial fluorines. The quintet arises from spin-spin coupling with the nearest four methylene fluorines in the ring, and triplet (J = 105 Hz) arising from spin coupling with equatorial fluorines. The resonance of equatorial fluorines appeared as a triplet as shown in Fig.3. The use of milder conditions reduced the fragmentation reaction, but increased the number of partly fluorinated products. The resultant complex mixture proved difficult to separate.

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