Journal of Fluorine Chemistry, 20 (1982) 53–63

Received: May 11, 1981

HALOGEN EXCHANGE OF FLUOROALKYL AMINES SYNTHESIS OF POLYCHLORO- AND BROMO-TRIALKYLAMINES

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SUMMARY

Fluoralkylamines $(CF_3)_{3-n}N(CHF_2)_n$, $n = 1$ to 3, and analogous C_2F_5 derivatives exhibit a selective reactivity of the CHF_2 group towards Lewis acids like BCl_3, $TiCl_4$ and BBr_3, $CHCl_2$ and $CHBr_2$ groups being formed in nearly quantitative yield. Halogenated trialkylamines of the general formulae $(CF_3)_{3-n}N(CHCl_2)_n$, $n = 1$ to 3, and $(CF_3)_{3-n}N(CHBr_2)_n$, $n = 1$ and 2, were obtained for the first time and characterized by nmr, ir, Raman and mass spectra. The halogen exchange reaction proceeds via an intermediate immonium cation, but the chloro and bromoalkyl amines are non-ionic. Both $(CF_3)_2NCHF_2$ and $(CF_3)_2NCHCl_2$ undergo photochlorination to yield $(CF_3)_2NCF_2Cl$ and $(CF_3)_2NCCl_3$.

INTRODUCTION

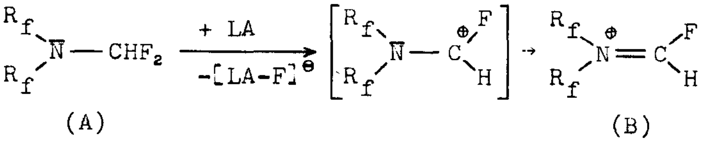
Perfluoroalkyl amines, $(R_f)_3N$, show little tendency to enter chemical reactions [1, 2] and in some cases, e.g. $(CF_3)_3N$, are even insoluble in common organic solvents. In contrast, incompletely fluorinated methylamines of the series $(CF_3)_{3-n}N(CHF_2)_n$, $n = 1$ to 3 (A) [3] dissolve in n-hexane, benzene, ether and carbon tetrachloride. This solubility encouraged us to examine the possibility of chemically reactive CN, CH or CF bonds in these derivatives.

0022-1139/82/0000-0000/$02.75

In this study we deal with replacement reactions of fluorine and hydrogen in A by chlorine and bromine, and we describe the first synthesis and the characterization of hitherto unknown poly-chloro- and bromomethyl-perfluoroalkylamines. For example, the chlorination of trimethylamine at low temperature, which is a common method for the preparation of chloroalkylamines, is restricted to monosubstitution [4]. Chlorotrialkylamines tend to form the tautomeric salts $[R_2N=CR'R'']^{\oplus}Cl^{\ominus}$. Polychlorination can be achieved at high temperature, and the amine $N(CHCl_2)_3$ (V) has been obtained by different routes [5, 6]. Partial and selective fluorination of such chloroalkyl-amines has however not yet been reported. The replacement of fluorine by other halogen atoms described in the following is the reverse of the common fluorination of halides with HF, CsF etc. to form CF bonds. Suitable hydrogen - containing precursors, A, and the analogous perfluoroethyl amines $C_2F_5N(CF_3)_n(CHF_2)_{2-n}$, n = 0 and 1, were obtained as volatile by-products in the electrochemical fluorination of $N(CH_3)_3$ and $C_2H_5N(CH_3)_2$ [7].

FLUORINE SUBSTITUTION

Fluoroalkyl compounds are well known to form carbonium ions with strong Lewis acids (LA). The reaction of fluoroalkyl amines A with suitable Lewis acids, e.g. $TiCl_4$ or BBr_3, certainly proceeds via the formation of cations which are stabilized under formation of immonium ions according to eqn. 1



(1)

Such fluoroalkylimmonium salts can be obtained if the fluoroalkyl amine contains CHF_2 groups; they are stable at room temperature and can be easily characterized by nmr spectroscopy [8].

CF_3 and CHF_2 groups thus exhibit a pronounced difference in reactivity. While the former are not attacked, the CHF_2 groups are completely substituted by suitable chlorides and bromides (2).

$$\underset{(A)}{{>}\overline{N}-CHF_2} \xrightarrow{E(Hal)_n} \underset{(C)}{\{{>}\overline{N}-CHF(Hal)\}} \xrightarrow{E(Hal)_n} \underset{(D)}{{>}\overline{N}-CH(Hal)_2} \qquad (2)$$

Reaction (2) is reversible because compounds D can be fluorinated to amines A or the respective cations B. Thus the conversion of V to $N(CHF_2)_3$ by treatment with SbF_3 has been reported most recently [9]. The monosubstituted intermediate C could not be detected which indicates that it is more reactive towards $E(Hal)_n$ than the base A is. Preferential cation formation by the $CH(Hal)_2$ group rather than the CHF_2 group is proved by reaction (3) in which an excess of

$$\underset{(III)}{CF_3N(CHCl_2)_2} \xrightarrow{SbF_5} \underset{(E)}{[CF_3(CHF_2)N=CHCl]^{\oplus}}\, Sb_n(F,Cl)_m^{\ominus} \qquad (3)$$

III is reacted with SbF_5. While the cis and trans isomers of the cation E were observed, no formation of the $[CF_3(CHCl_2)N=CHF]^{\oplus}$ ion was detected. This is in agreement with the considerable stability of dichloromethylene ammonium salts [10].

$CF_3N(CHF_2)_2$ and $N(CHF_2)_3$ undergo multiple fluorine substitution when treated with BCl_3. The amines III and V were

$$\underset{III}{CF_3N(CHCl_2)_2} \qquad \underset{V}{N(CHCl_2)_3} \qquad \underset{VI}{C_2F_5(CF_3)NCHCl_2} \qquad \underset{VII}{C_2F_5N(CHCl_2)_2}$$

obtained in practically quantitative yields. Similarly, the perfluoroethyl derivatives VI and VII were synthesized from the appropriate fluoroalkyl amines and BCl_3.

The reactivity of the amines towards BCl_3 increases with the number of CHF_2 groups attached to nitrogen. BCl_3 is a convenient reactant because of its miscibility with the amines A and ready reactivity. The progress of reaction (2) can be monitored by the characteristic BF quartet in the ^{19}F nmr spectrum, and BF_3 is sufficiently volatile to facilitate its separation from the halomethyl amines formed.

$TiCl_4$ is similarly reactive, but the resulting TiF_4 precipitate is somewhat difficult to separate if the chloromethyl amine has a low volatility.

$AlCl_3$, $SiCl_4$ and $SnCl_4$ were found to be insufficiently reactive towards $(CF_3)_2NCHF_2$ to achieve fluorine substitution. On the other hand, formation of a strong fluoride acceptor like SbF_5, might enter into the undesired back reaction (3) and prevent complete conversion. With BBr_3 at room temperature, $(CF_3)_2NCHF_2$ and $CF_3N(CHF_2)_2$ undergo analogous exchange reactions, $(CF_3)_2NCHBr_2$ (II) and $CF_3N(CHBr_2)_2$ (IV) being formed quantitatively. $TiBr_4$ is similarly reactive, but less convenient.

Attempts to react $(CF_3)_2NCHF_2$ with BI_3 at room temperature afforded only the decomposition product HCI_3.

HYDROGEN SUBSTITUTION

Octafluorotrimethylamine, $(CF_3)_2NCHF_2$, and the chloro derivative I undergo photochlorination according to eqn. 4

$$(CF_3)_2\overline{N} - CHX_2 \xrightarrow[RT]{Cl_2,\ h\nu} HCl + (CF_3)_2\overline{N} - CClX_2 \quad (X = F, Cl) \tag{4}$$

I is more reactive than $(CF_3)_2NCHF_2$, while the photochlorination of III could not be achieved at room temperature even upon irradiation with a mercury lamp for a period of several days. Again yields of VIII and IX were essentially quantitative, and no substantial CN cleavage was observed.

$(CF_3)_2NCF_2Cl$	$(CF_3)_2NCCl_3$
VIII	IX

PROPERTIES

Compounds I to IX were isolated and characterized by their nmr, mass, ir and Raman spectra. The temperature dependence of the vapour pressure of sufficiently volatile compounds was determined (Table 1).

TABLE 1

Physical properties of the amines I to IX

	mp [°C]	bp_{760} [°C]	log p [Torr] = A	-A/T + B B
I	-72	57	1677	7.960
II	-58	90	1817	7.885
III	-26			
IV	33			
V	170[a]			
VI	-64			
VII	4			
VIII	-110	18	1450	7.861
IX	-51	83	1814	7.974

[a] Ref. [5] 171 - 173 °C.

IV and V form colorless crystals; all other compounds are liquids at room temperature.

All halomethyl amines are non-basic; e.g., they do not react with HCl or boron halides in excess. They are not miscible with water and are stable to mineral acids and P_4O_{10}. They react with strong alkali, their reactivity increasing with their chlorine and bromine content.

NMR SPECTRA

All compounds were investigated by ^{19}F and ^1H nmr spectroscopy. The chemical shifts and coupling parameters are summarized in Table 2. The ^{19}F spectra of I and II are temperature dependent, the CF_3 groups becoming non-equivalent at or below room temperature. Fig. 1 illustrates the temperature dependence of the ^{19}F nmr spectrum of I. At low temperature (-50°C), the two CF_3 groups are magnetically non-equivalent and appear as quartets. The behaviour of II is almost identical. The coalescence temperatures are -1 and +35° for I and II, determined at 56.4 and 84.7 MHz respectively on

TABLE 2

^{1}H and ^{19}F nmr spectra of I to IX

	I	II	III	IV	V	VI	VII	VIII	IX
δ (H) [ppm] [a]	7.05	7.15	7.15	7.30	7.28 [b]	7.00	7.20		
δ (F) [ppm] [c]									
δ CF_3N	-52.9 -59.8	-53.0 -60.4	-57.7	-58.0		-50.5		-55.5	-52.7
δ CF_3C						-86.4	-85.2		
δ CF_2N						-103.1	-99.6	-34.7	
^{4}J (FF) [Hz]	8.3	8.7				12.9		13.85	
^{5}J (FF) [Hz]						3.3			

[a] From internal TMS. [b] Ref. [5] 7.27 ppm. [c] From internal $CFCl_3$, positive sign = high frequency.

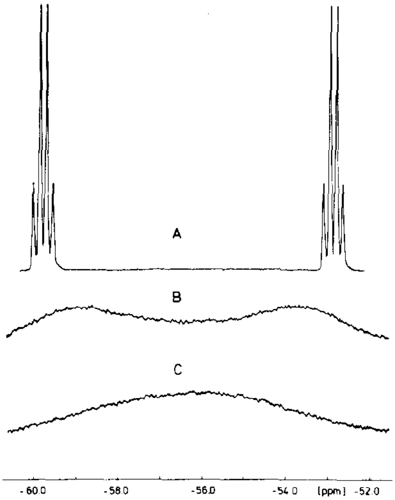


Fig. 1. ^{19}F nmr spectrum of $(CF_3)_2N\dot{C}HCl_2$ A, -50 °C. B, -3 °C. C, 1 °C.

neat liquids with 10 % $CFCl_3$ added. The ^{19}F NMR spectrum of VI shows a similar temperature dependence, the quartets of the CF_2 group displayed at low temperature collapsing between + 5 and + 10°. A detailed study of the observed phenomena which accounts for nitrogen inversion and hindered rotation of the CHX_2 group is in progress.

INFRARED AND RAMAN SPECTRA

The infrared and Raman spectra of the compounds I to V, VIII and IX have been recorded. Diagnostic group frequencies and skeleton modes are listed in Table 3. A complete list of frequencies can be obtained from the third author upon request. Beyond the CH and CF stretching and CH bending modes, most vibrations are strongly coupled, the coupling increasing with the mass of the peripheral atoms. The Raman spectrum of a single crystal of V depends on the orientation of the crystal. The solid state vibrational spectra of this compound will be discussed in context with the results of an X-ray diffraction investigation which is in progress. The observed spectrum of V is in agreement with that previously reported [6].

TABLE 3

Characteristic vibrations of the compounds I to V, VIII and IX, intensities (IR/Ra) and their assignments

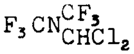
I	III	V	II	IV	VIII	IX	Assignment
180 m/mp	150 /w	134 /s	106 /w	100 /wp	130 /wp	150 /w	δ CNC
246 m/m 278 w/m	227 /m 243 /m	200 /m 242 /m	125 /m 150 /mp	150 /m 158 /m	273 m/mp	200 w/m 240 w/m	δ CCl, CBr
362 w/vsp	345 /vsp	342 /vs	264 w/vsp	235 /vsp	443 w/sp	416 w/vsp	ν CCl, ν CBr
					648 w/mp		δ CF_2
641 m/mp 710 s/sp	608 m/sp		637 m/m 741 m/sp	585 m/sp	705 s/ 768 s/sp	697 s/sp 715 s/sp	δ_s CF_3
777 s/sp	736 m/sp 775 s/wp	696 w/s 770 s/m 798 m/w	685 m/sp	633 /sp 692 s/mp		782 s/m	ν CCl, CBr
1136 m/wp	1142 s/wp 1165 vs/w	1158 s/w 1196 w/w	1134 m/mp	1140 vs/wp 1150 vs/w			γ CH
1207 vs/w 1215 /w 1274 vs/w	1248 vs/wp 1287 vs/w		1207 vs/w 1240 /w 1264 vs/w	1222 vs/wp 1270 vs/w	1222 vs/w 1325 vs/w 1353 vs/w	1225 vs/ 1277 vs/ 1336 vs/	ν CF
1355 vs/vw 1407 m/wp	1370 s/wp 1411 s/w	1328 w/w 1381 s/w	1353 vs/vw 1396 m/wp	1350 s/wp 1388 s/w			δ CH
3058 w/wp	3034 w/wp 3055 w/wp	3015 m/m	3050 w/wp	3009 m/wp 3031 m/wp			ν CH

MASS SPECTRA

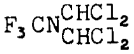
Compounds I to V, VIII and IX were investigated by EI mass spectroscopy. The observed m/e values and isotopic patterns of the fragment ions confirm the composition of the compounds investigated. The (M-Halogen$^+$) peak is always intense and in several cases the basis peak. The molecular ion M^+ was observed in the fragmentation pattern of V. Table 4 gives a list of the strongest peaks due to the lightest isotopomers (^{35}Cl and ^{79}Br) in the order of decreasing intensity.

TABLE 4
Observed fragments (lightest isotopomer) in the order of decreasing intensity at 70 eV

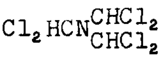
	m / e
I	200 (M-Cl$^+$), 69 ($CF_3{}^+$), 83 (CCl_2H^+), 96 (CF_3NCH^+), 112 (CF_2ClNCH^+), 130 (CF_3NCCl^+)
II	244 (M-Br$^+$), 69 ($CF_3{}^+$), 96 (CF_3NCH^+), 171 (CBr_2H^+), 156 (CF_2BrNCH^+), 174 (CF_3NCBr^+)
III	83 (CCl_2H^+), 214 (M-Cl$^+$), 69 ($CF_3{}^+$), 110 ($CHCl_2NCH^+$), 96 (CF_3NCH^+)
IV	171 (CBr_2H^+), 96 (CF_3NCH^+), 69 ($CF_3{}^+$), 396 (M-Br$^+$), 198 ($CHBr_2NCH^+$)
V	110 ($CHClNCHCl^+$), 83 (CCl_2H^+), 228 (M-Cl$^+$), 263 (M^+)
VIII	69 ($CF_3{}^+$), 85 ($CClF_2{}^+$), 202 (M-Cl$^+$), 114 (CF_3NCF^+), 130 (CF_3NCCl^+), 218 (M-F$^+$)
IX	69 ($CF_3{}^+$), 243 (M-Cl$^+$), 146 ($CF_2ClNCCl^+$), 85 (CF_2Cl^+), 117 ($CCl_3{}^+$), 130 (CF_3NCCl^+)

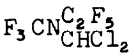

$F_3CN^{CF_3}_{CHCl_2}$ I

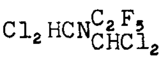

$F_3CN^{CF_3}_{CHBr_2}$ II

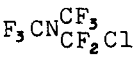

$F_3CN^{CHCl_2}_{CHCl_2}$ III

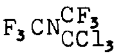

$F_3CN^{CHBr_2}_{CHBr_2}$ IV


$Cl_2HCN^{CHCl_2}_{CHCl_2}$ V


$F_3CN^{C_2F_5}_{CHCl_2}$ VI


$Cl_2HCN^{C_2F_5}_{CHCl_2}$ VII


$F_3CN^{CF_3}_{CF_2Cl}$ VIII


$F_3CN^{CF_3}_{CCl_3}$ IX

List of Compounds

EXPERIMENTAL

The synthesis of polyfluorotrialkylamines has been reported previously [3, 7].

Halogen exchange

$(CF_3)_2NCHF_2$ and excess BCl_3 are condensed into a glass tube and sealed off. After reacting 3 days at room temperature the volatile products are separated by fractional condensation in vacuo using standard techniques. Traces of BCl_3 may be removed by treatment with H_2O. I is obtained in quantitative yield. II to VII are obtained similarly, the time required for complete reaction being considerably shorter. The use of CCl_4 as solvent is recommended for the preparation of IV and V to moderate the vigorous reaction.

Photochlorination

$(CF_3)_2NCHF_2$ (or I) and 2 atm. Cl_2, sealed in a Pyrex tube, are irradiated with a NORMAG TNN 15/32 low pressure mercury lamp for 3 days. Excess of Cl_2 is removed with Hg. HCl and the reaction products VIII and IX are separated by fractional condensation in vacuo.

Physical measurements see Ref. [7].

ACKNOWLEDGEMENTS

We wish to thank the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Bayer AG and the Fonds der Chemie for generous support.

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