

N-Polyfluoroalkyl Aziridines

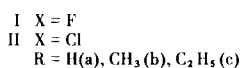
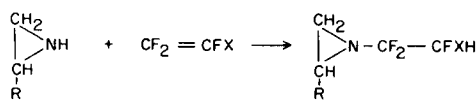
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Aziridines add almost quantitatively and without ring opening to tetrafluoroethylene and chlorotrifluoroethylene to yield *N*-polyfluoroalkyl aziridines. Physical properties, H^1 -NMR, F^{19} -NMR and IR spectra of these compounds are reported, along with their susceptibility to undergo rearrangements catalyzed by electrophiles.

Part I. Synthesis and Properties.

Reactions of aziridines with higher polyfluorinated olefins have recently been described (1), however reaction products of tetrafluoroethylene and chlorotrifluoroethylene have only been alluded to (2). The reactions of aziridines with tetrafluoroethylene and chlorotrifluoroethylene were investigated and found to proceed almost quantitatively to *N*-polyfluoroalkyl aziridines according to the equation:



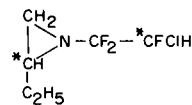
The structure indicated for these compounds is supported by elemental analysis, molecular weight determination, and is consistent with IR, H^1 -NMR and F^{19} -NMR spectra. These data are listed in Tables I and II together with boiling points, refractive indices and percent yields. The *N*-polyfluoroalkyl aziridines are colorless liquids, quite stable to boiling methanolic potassium hydroxide, but readily undergo ring opening upon addition of Lewis acids.

The H^1 -NMR spectra of both types I and II compounds are consistent with retention of the aziridine ring structure. For compounds of type I in all cases a triple-triplet is observed corresponding to the CF_2H group. The patterns of IIa and IIc consist of a simple double-triplet corresponding to the CFCIH group. However, in the case of IIb a double-double-doublet is observed because of coupling between two non-equivalent fluorine atoms.

The F^{19} -NMR spectrum of compound Ia consists of two double-triplets corresponding to the CF_2 - and CF_2H -

groups. Absorptions of the CF_2H group in Ib and Ic are also double-triplets while absorptions for the CF_2 - group are broadened so that fine coupling patterns are not observed. Compound Ib shows an overall AB-type pattern ($J_{\text{AB}} 198$ c/s) for the CF_2 resonance. This pattern is not present with compound Ic.

Compound IIa shows a double-doublet corresponding to the CF_2 group and a double-triplet corresponding to the CFCIH group. Similarly, for IIc a double-triplet is observed for the CFCIH group, further doubled because of the presence of two asymmetric centers.



IIc

The CF_2 absorptions are somewhat broadened but there is no evidence for an AB-type pattern. Compound IIb again shows an overall AB-type pattern ($J_{\text{AB}} 192$ c/s) indicating that the fluorine atoms of the CF_2 group are not equivalent.

The F^{19} -NMR spectra showed some unexpected patterns for the CF_2 resonance in those compounds having asymmetric centers. AB-type patterns, though not required, would normally be expected and, in fact, were observed for compounds Ib and IIb. Unexpectedly, such were not observed for compounds Ic, IIa and IIc.

In order to determine if there were either solvent influence or temperature dependence of the CF_2 resonance in each of these two classes of compounds, IIb and IIc were selected for further studies.

F^{19} -NMR spectra obtained for these compounds in a variety of solvents (benzene, pyridine, acetic acid, perfluorocyclobutane) and in a temperature range from -126° to $+100^\circ$ in CFCl_3 remained unchanged in the CF_2 resonance for either compound.

TABLE I

N-Polyfluoroalkyl Aziridines
Selected Properties and Analytical Data

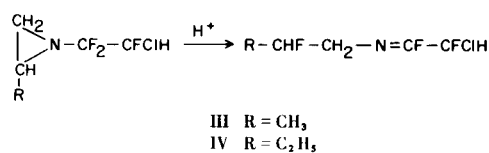
Compound	Yield	B.p. C° 760° mm	n_D^{23}	Elemental Analysis					Molecular Weight						
				Calculated					Found						
				C	H	N	Cl	F	C	H	N	Cl	F	Calcd.	Found (a)
Ia C ₄ H ₅ NF ₄	91%	79-80°	1.3315	33.6	3.5	9.8		53.1	34.0	3.6	9.8		52.8	143	147
Ib C ₅ H ₇ NF ₄	92%	90°	1.3415	38.1	4.5	8.9		48.4	37.9	4.6	8.9		48.1	157	158
Ic C ₆ H ₉ NF ₄	95%	116°	1.3590	42.1	5.3	8.2		44.4	42.3	5.4	7.9		44.0	171	166
IIa C ₄ H ₅ NF ₃ Cl	95%	109-110°	1.3871	30.1	3.1	8.7	22.2	35.7	30.4	3.2	8.6	21.9	35.7	160	164
IIb C ₅ H ₇ NF ₃ Cl	92%	120°	1.3827	34.6	4.1	8.1	20.4	32.8	34.9	4.1	8.0	20.2	32.8	173	173
IIc C ₆ H ₉ NF ₃ Cl	93%	139-140°	1.3947	38.4	4.9	7.4	18.9	30.4	38.6	5.0	7.3	18.6	30.2	188	196

(a) Molecular weight by effusion, supported by mass spectrometry.

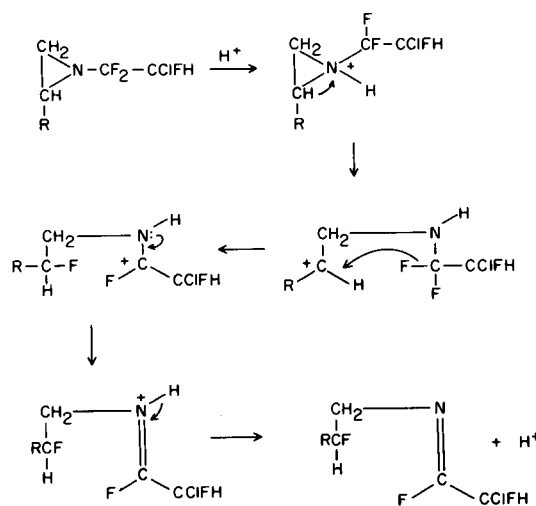
Part II. Rearrangements.

Previous studies (3) have shown that activated aziridines undergo rearrangements involving ring opening catalyzed by both electrophiles and nucleophiles and yielding different products. The term activated is applied to those derivatives having electron withdrawing groups adjacent to the aziridinyl nitrogen.

We have observed rearrangements of *N*-polyfluoroalkyl activated aziridines catalyzed by protons. This rearrangement catalyzed by traces of trifluoroacetic acid at room temperature was followed by H¹-NMR and found to proceed according to the equation:



The structure of the aza-alkene products (III and IV) has been established by H¹-NMR and F¹⁹-NMR (Table III), which show that the ring opening has taken place between the ring nitrogen and the alkylated carbon atom of the ring. A possible mechanism (4) is expressed by the following scheme:



Apparently, initial ring-opening gives the most stable carbonium ion, the electron rich fluorine migrates and the new carbonium ion is stabilized by the lone pair on the adjacent nitrogen atom. The mode of ring opening is in agreement with the proton catalyzed rearrangement of *N*-aroyl aziridines to oxazolines as shown below:

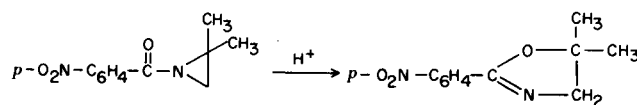


TABLE II
Spectral Data *N*-Polyfluoroalkyl Aziridines

Compound	F^{19} -NMR ϕ Values		H^1 -NMR τ Values	IR Microns (b)		
	$-CF_2-$	$-CF_2H$	$-CF_2H$			
Ia	110.7	136.1	4.19	3.3 (w)	7.5 (s)	7.6 (s)
				8.0 (m)	8.5 (s)	8.7 (s)
				9.0 (vs)	10.6 (m)	11.0 (m)
				11.6 (w)	12.1 (m)	12.5 (m)
				14.0 (m)	14.4 (w)	
Ib	107.1 (a) 110.3 (a) $J_{AB} = 198$ c/s	136.3	4.19	3.4 (w)	6.8 (w)	7.1 (m)
				7.3 (w)	7.6 (s)	7.8 (s)
				8.1 (s)	8.3 (s)	8.7 (s)
				9.0 (vs)	9.6 (m)	10.0 (w)
				10.2 (m)	10.3 (m)	11.3 (m)
				11.6 (m)	12.3 (s)	14.5 (m)
Ic	108.5	136.9	4.19	3.4 (m)	6.8 (m)	7.1 (m)
				7.6 (s)	7.8 (s)	8.1 (s)
				8.3 (s)	9.0 (vs)	9.4 (s)
				9.5 (s)	9.8 (m)	10.6 (m)
				10.9 (m)	11.3 (w)	11.6 (w)
				12.3 (s)	12.9 (w)	14.5 (m)
IIa	$-CF_2-$ 106.0	$-CFCIH$ 151.6	$-CFCIH$ 3.80	3.3 (w)	7.4 (m)	7.5 (s)
				7.6 (s)	7.9 (m)	8.1 (m)
				8.2 (m)	8.5 (m)	8.8 (s)
				9.3 (vs)	10.7 (m)	10.9 (m)
				11.9 (s)	12.6 (m)	12.9 (m)
				14.9 (w)		
IIb	101.7 (a) 106.5 (a) $J_{AB} = 192$ c/s	152.0	3.82	3.4 (m)	6.8 (m)	7.1 (s)
				7.2 (m)	7.4 (m)	7.6 (s)
				7.8 (s)	8.3 (s)	8.7 (s)
				9.3 (vs)	9.7 (m)	10.2 (m)
				11.3 (s)	12.0 (s)	12.8 (s)
IIc	103.7	151.5	3.81	3.4 (m)	6.8 (m)	7.1 (m)
				7.4 (m)	7.7 (s)	8.0 (s)
				8.4 (s)	8.8 (s)	9.3 (vs)
				9.8 (m)l	10.7 (m)	11.4 (m)
				11.9 (s)	12.7 (m)	

(a) Calculated ϕ Values. (b) w = weak; m = medium; s = strong; vs = very strong.

A rearrangement of *N*-polyfluoroalkyl aziridines catalyzed by the nucleophile iodide ion was not observed. This is in contrast to the reported rearrangement of *N*-aroyl aziridines catalyzed by nucleophiles (5,6), but is consistent with the assumed mechanism where the aziridinyl nitrogen is attacked by electrophiles and the carbonyl group adjacent to the ring nitrogen is attacked by the nucleophile.

EXPERIMENTAL

F^{19} -NMR spectra were measured on a Varian V-4300-2 instrument operating at 40.0 Mc, using trichlorofluoromethane as

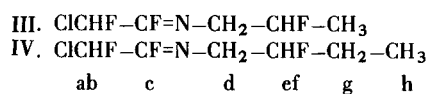
an internal standard. H^1 -NMR spectra were obtained on a Varian A-60 instrument using tetramethylsilane as the reference. IR spectra were obtained on a Perkin-Elmer Model 21 double beam instrument using sodium chloride-cell windows.

Preparation.

A one-liter stainless steel autoclave was flushed with nitrogen and charged with two moles of the aziridine compound and 4 ml. of limonene. The vessel was closed, cooled in dry ice, evacuated and charged with 3.3 moles of the fluoro-olefin ($CF_2 = CF_2$ or $CF_2 = CFCl$). After the reaction vessel and contents had warmed to room temperature the mixture was heated from 50-70° for eight hours. After bleeding off excess gases the product was removed from the autoclave and distilled at atmospheric or

TABLE III

Spectral Data Aza-alkene Products



Compound	Group	ν *	τ	Jc/s	
III	ClCHF	144.4	3.60	J _{ab}	48.4
				J _{ac}	10.0
				J _{bc}	26.1
	CF=CH ₂	51.4	6.40	J _{de}	6.0
				J _{df}	21.0
	CFH	178.3	5.23	J _{ef}	47.7
J _{eg}				6.0	
J _{fg}				22.8	
IV	ClCHF	144.4	3.58	J _{ab}	48.3
				J _{ac}	10.4
				J _{bc}	26.5
	CF=CH ₂	51.5	6.38	J _{de}	6.0
				J _{df}	21.0
	CFH	186.1	5.48	J _{ef}	48.0
				J _{eg}	6.0
				J _{fg}	21.0
	CH ₂		8.4	J _{gh}	7.2
CH ₃		8.99 ~			

reduced pressure. Yields: 90 to 95%.

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