

NITROGEN INVERSION IN α -FLUOROALKYL AZIRIDINES

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(Received in UK 15 January 1968; accepted for publication 28 March 1968)

The high rate of nitrogen inversion in the derivatives of aziridines without π -electrons or empty orbital substituents was observed for I-aziridinecarbinols (I) and I-(trifluoromethyl)-2,2-difluoroaziridine (2). However, in the first case, this fact is explained by the speedy reversible dissociation of the compounds in solutions (3), and in the second case it may be attributed to the influence of 2-position F-atoms, which is analogous to the influence of the π -electron system in 2-allenimine (4).

We have prepared I-(α -fluoroalkyl)aziridines, I-IV, by adding aziridines to perfluoroolefines (in CH_2Cl_2 and Et_2O , at $t -55^\circ$ to -45°C), (Table I).

In the same conditions more basic diethylamine gives a mixture of saturated (V) and unsaturated adducts with perfluoropropene, and exclusively unsaturated ones with perfluoroisobutene, as has been already reported (5).

TABLE I

Compounds	Yield(%)	B.p. $^\circ\text{C}$ (mm)	n_D^{20}
I $\text{CF}_3\text{CFHCF}_2\text{N}$ 	60	92 (750)	I. 3215
II $\text{CF}_3\text{CFHCF}_2\text{N}$  $(\text{Me})_2$	55	64 (120)	I. 3530
III $(\text{CF}_3)_2\text{CHCF}_2\text{N}$ 	37	48 (58)	I. 3250
IV $(\text{CF}_3)_2\text{CHCF}_2\text{N}$  $(\text{Me})_2$	45	35 (15)	I. 3418

In mass-spectra of I-IV the most intensive fragment is X^+ and as well as in spectra of $\text{CF}_3\text{CFHCF}_2\text{SC}_2\text{H}_5$ (VI)*, $(\text{CF}_3)_2\text{CHCF}_2\text{OC}_2\text{H}_5$ (VII)* and $(\text{C}_2\text{F}_5)_3\text{N}$ (VIII) there is no M-19 fragment, but there is visible $\text{X}^+ = \text{CF}_2$ fragment (relative abundance,%): I (17); II (3.5); III (16); IV (9.2); VI (43); VII (3); VIII (7.5), like spectra of $(\text{CF}_3)_2\text{NR}$ (6).

The NMR spectra of I-IV (Table II, Fig. I) indicate the high rate of nitrogen inversion in these compounds in contrast to I-alkylaziridines (I,4).

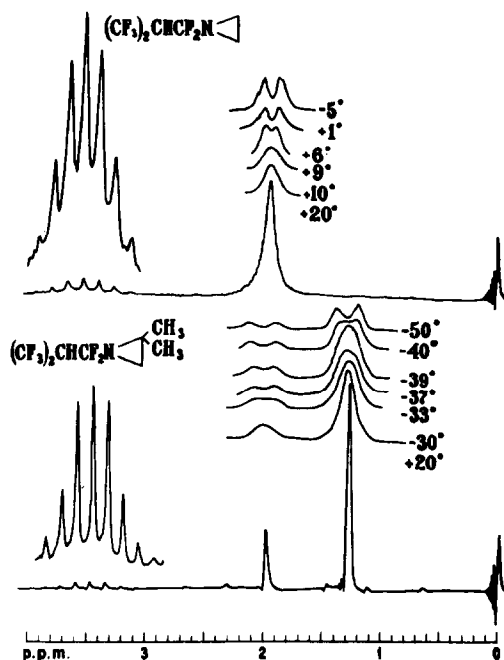


FIG. I

The acceleration of inversion in case of II and IV is probably attributable to steric effects which are especially significant in IV.

* The authors are grateful to Dr. B. Dyatkin and Dr. E. Rokhlin for samples of VI and VII.

The fact that the coalescence temperature is not the same for the methyl and methylene protons in the last case may be explained by considerations similar to those stated in (3).

TABLE II

Compounds	$(\text{CH}_2)_2\text{N}$	CH_3	δ ppm ^{a)} CH_2	CH	$J_{\text{F}19-\text{H}1}$ cps	T_c °C	E_a ^{c)} kcal/mole	ν_0 ^{b)} sec ⁻¹
I	I.92			4.75 ^{e)}	6.3 ^{e)}	+II	9.1	4.10 ⁹
II		I.28	I.95	4.64	6.3	-I3	6.9	2 10 ⁸
III	I.95			3.53 ^{d)}	7.8 ^{d)}	+ 9	6.8	7 10 ⁷
IV		I.26	I.99	3.49	7.7	$\left. \begin{array}{l} -39(\text{CH}_2) \\ -31(\text{CH}_2) \end{array} \right\}$	5.8	6 10 ⁷

a) On the JNM-3H-60 spectrometer, in CCl_4 , with $(\text{Me}_3\text{Si})_2\text{O}$ as a standard.

b) Calculated as in reference (7).

c) For V δ_{CH} 4.80 ppm; $J_{\text{F}19-\text{H}1}$ 6.0 cps.

For VI δ_{CH} 4.72 ppm; $J_{\text{F}19-\text{H}1}$ 6.3 cps.

d) For VII δ_{CH} 3.42 ppm; $J_{\text{F}19-\text{H}1}$ 7.6 cps.

It is likely that double bond - no bond resonance (8-10) is responsible for the high rate of nitrogen inversion in $\begin{array}{c} \text{>N-C-F} \\ | \\ \text{>N-C-F} \end{array}$ and it is consistent with the great mobility of fluorine in $\begin{array}{c} \text{>N-C-F} \\ | \\ \text{>N-C-F} \end{array}$ (II), notwithstanding that the C-F bond is covalent in the ground state of this system, with distinction from the pure ionic C-Hal bond in other α -haloalkylamines (12).

Thus, the data obtained together with (2) testify to analogy between CF_2 and CO (I) groups in the ground state as in excited (I3) one.

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