Journal of Fluorine Chemistry, *34* (1986) 209–227

Received: November 19, 1985; accepted July 2, 1986

MASS SPECTRA OF HYDRAZIDES AND ALKYLHYDRAZIDES OF FLUORINATED ALKANECARBOXYLIC ACIDS

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SUMMARY

Main pathways in the electron-impact induced mass spectrometric fragmentation of hydrazides and alkylhydrazides of alkanecarboxylic acids have been studied. The effect of the structure of fluorinated acyl group and hydrocarbon radical on the dissociation mode has been established.

INTRODUCTION

Despite the wide application of hydrazides of fluorinated alkanecarboxylic acids in organic synthesis, no information concerning their behavior under electron impact is available at present.

RESULTS AND DISCUSSION

We have studied the mass spectra of $R_fC(O)NH\text{-}NHR_1$ with R_f = FCH_2, F_2CH, $F_3C(CF_2)_n$, n = 0-5 as well as those of CH_3; with R_1 = H, CH_3, C_2H_5, C_3H_7, $CH(CH_3)_2$, C_6H_5.

The mass spectra of these compounds with R_1 = H are given in Table 1. As seen from this Table, the intensity of the molecular ion of acetohydrazides is 16%. On increasing the number of fluorine atoms F(m) in the series $F_mH_{3-m}CC(O)NHNH_2$ the molecular ion becomes relatively more intense (23 - 74%). The unusually sharp increase in the molecular ion stability in the presence of

0022-1139/86/$3.50

TABLE 1

Mass Spectra of Compounds $R_fC(O)NHNH_2$ (I-VIII)

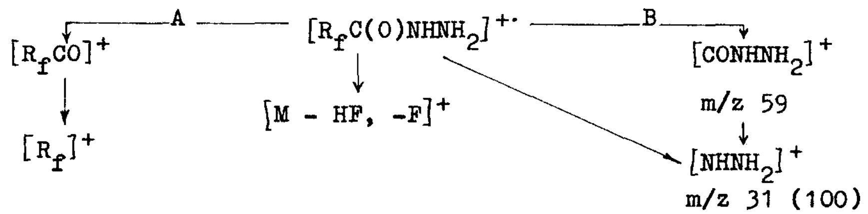
R_f	CH_3	FCH_2	F_2CH	CF_3	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}
Compound / Ion	I	II	III	IV	V	VI	VII	VIII
1	2	3	4	5	6	7	8	9
$[M]^{+\bullet}$	74(16)*	92(59)	110(74)	128(100)	178(60)	228(61)	278(41)	378(23)
$[M-HF_2]^+$	-	-	71(5)	31(100)	-	189(1)	239(2)	339(2)
$[C_4F_9]^+$ m/z 219	-	-	-	-	-	-	(2)	-
$[M-CHOF_2]^+$	-	-	-	-	111(5)	161(9)	211(5)	311(1)
$[C_3F_7]^+$ m/z 169	-	-	-	-	-	-	(8)	(4)
$[M-CO-F]^+$	-	-	-	81(5)	131(2)	181(8)	231(5)	331(2)
$[M-CO]^{+\cdot}$	-	64(1)	82(5)	-	150(3)	200(2)	250(1)	-
$[M-F]^+$	-	-	91(2)	109(3)	-	209(7)	259(3)	359(3)
$[C_2F_5]^+$ m/z 119	-	-	-	-	(22)	(23)	(12)	(9)
$[C_2F_4]^+$ m/z 100	-	-	-	-	(9)	(26)	(16)	(5)
$[C_2F_3]^+$ m/z 81	-	-	-	-	(5)	(9)	(4)	(2)
$[R_fCO]^+$	43(81)	61(19)	79(9)	-	-	-	-	-
$[M-HF]^{+\bullet}$	-	-	90(25)	108(54)	-	-	-	-

$[CF_3]^+$ m/z 69	-	-	-	(79)	(29)	(70)	(90)	(30)
$[CONHNH_2]^+$ m/z 59	-	(2)	(54)	(42)	(20)	(14)	(47)	(12)
$[NH_2NH_2]^{+\cdot}$ m/z 32	(100)	-	-	-	-	-	-	-
$[NHNH_2]^+$ m/z 31	-	(100)	(100)	(100)	(100)	(100)	(100)	(100)

* m/z Values and relative abundances, % (in parentheses).

extra electronegative fluorine atoms may be explained by variation of the site of localization of the positive charge. It may be assumed that in the molecular ion originating from $CH_3C(O)NHNH_2$ (I) with m = 0 the positive charge is mainly localized on the oxygen atom. In its fluoro substituted compounds with m = (1 - 3) the positive charge is localized at two neighbouring nitrogen atoms. The stability of the molecular ions enhances on increasing the electronegativity of the perfluoroacyl groups (I - IY). The stability of molecular ions of hydrazides of higher perfluorocarboxylic acids (n = 3,5; comp. VII, VIII) decreases which is related to lengthening of the acyl fragment. Similar trend is observed in the mass spectra of higher perfluoroalkanes [1].

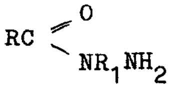
The general fragmentation pathway of compounds (I-VIII) is as follows:



In the mass spectrum of acetohydrazide (I)a fragmentation involving cleavage of the C-N bond (route A) is predominant. An increase in the number of fluorines in an acyl radical (compounds II-IV) enhances the portion of products due to the fragmentation at the C-C(O) bond (route B). In the series $F_3C-(CF_2)_nCONHNH_2$, starting with n = 1 (compounds V-VIII) no products resulting from cleavage of the C-N bond are observed in fact. For compounds (I-VIII) the $[NHNH_2]^+$ ion m/z 31, is the maximum ion (Table 1). This suggests this ion to originate not only from the fragment at m/z 59 (route B), but also from the molecular ion by cleavage of the C-N bond, involving both the formation of the rapidly disintegrating ion $[R_fCO]^+ \longrightarrow [R_f]^+ + CO$ and the route $[R_fCONHNH_2]^{+\cdot} \longrightarrow [R_fCO]^\cdot + [NHNH_2]^+$.

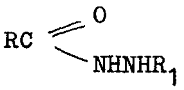
In the spectra of compounds (II-VIII), along with the above fragmentation routes, elimination of molecular HF and radical $F^\cdot$ from both the molecular ion and the fragment, does take place. No ions produced by cleavage of N-N bonds have been observed.

It is known that carboxylic alkylhydrazides can exist in two isomeric forms [2,3] :



$RC(=O)NR_1NH_2$ (I)

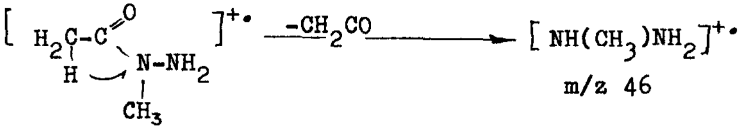
and



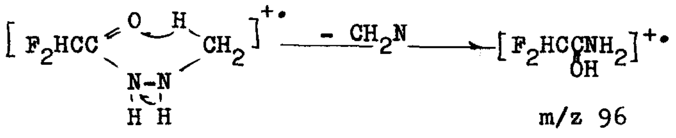
$RC(=O)NHNHR_1$ (II)

We have previously shown that acylation of methylhydrazine with trifluoroacetic derivatives leads to only isomer (II). Difluoroacetic derivatives give a mixture of the two isomers. The previous synthesis of 1-methyl-1-trifluoroacetylhydrazine [4] is erroneous[5]. The effect of structural isomerism on the fragmentation pathway has been investigated using 1-methyl-1-difluoroacetyl- (IX) and 1-methyl-2-difluoroacetylhydrazine (XI) and compound (X) (Table 2).

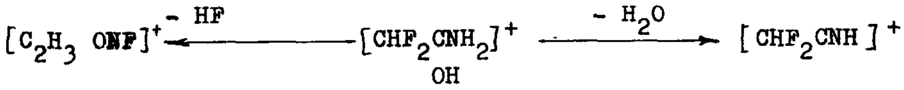
The fragmentation of IX, XI involves cleavage of C-C(O) bonds (route B) to produce ions $[C_2H_5ON_2]^+$ at m/z 73 and ions $[CH_5N_2]^+$ at m/z 45 which show the highest intensity. In contrast to mass spectra of fluorinated hydrazines (IX, XI) the mass spectrum of 1-acetyl-1-methylhydrazine shows the most intense peak at m/z 46 which appears to arise from hydrogen migration to a hydrazine fragment



The mass spectrum of compound (XII) contains a peak at m/z 96 whereas no similar peak is observed for (IX). This peak may originate from the rearrangement of the molecular ion with transfer of two hydrogen atoms by a six-center mechanism:



A similar rearrangement has been observed in the mass spectrum of 1,2-dibenzoyl-1,2-dimethylhydrazine [6]. Further fragmentation of the m/z 96 ion involves loss of the H_2O or HF molecules:



$$[C_2H_3ONF]^+ \xleftarrow{-HF} [CHF_2C(OH)NH_2]^+ \xrightarrow{-H_2O} [CHF_2CNH]^+$$

TABLE 2

Mass Spectra of Compounds $R_fC(O)NR_1NH_2$ and $R_fC(O)NHNHR_1$ (IX-XVI)
$R_1 = CH_3$, m/z, (%)

R_f	CHF_2	CH_3	CHF_2	CF_3	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}
Ion \ Compound	IX	X	XI	XII	XIII	XIV	XV	XVI
1	2	3	4	5	6	7	8	9
$[M]^{+\bullet}$	124(54)	88(44)	124(26)	142(9)	192(35)	242(6)	292(6)	392(4)
$[M-F]^+$	-	-	105(4)	123(1)	173(1)	223(1)	273(1)	373(2)
$[R_fCOHNH_2]^{+\bullet}$	-	-	96(41)	114(51)	164(64)	214(43)	264(20)	364(11)
$[R_fHCN]^+$	-	-	78(4)	96(4)	146(5)	196(2)	246(2)	346(2)
$[R_fHCN-HF]^+$	-	-	58(6)	-	126(2)	176(2)	226(1)	326(1)
$[R_fHCN-CF_2]^+$	-	-	-	-	96(1)	146(2)	-	-
$[C_3F_7]^+$ m/z 169	-	-	-	-	-	(4)	-	(2)
$[C_2F_5]^+$ m/z 119	-	-	-	-	(81)	(26)	(3)	(4)
$[C_2F_4]^+$ m/z 100	-	-	-	-	(34)	(20)	(3)	(3)
$[C_2F_3]^+$ m/z 81	-	-	-	-	(7)	(2)	-	(3)
$[C_2H_5N_2O]^+$ m/z 73	(4)	(4)	(4)	(7)	(7)	(1)	(1)	(1)
$[R_f]^+$	51(62)	-	51(39)	69(29)	119(81)	169(29)	219(1)	-

m/z 71	-	-	-	(6)	(4)	-	-	(5)
$[CF_3]^+$ m/z 69	-	-	-	(28)	(56)	(44)	(17)	(39)
m/z 66	-	-	-	-	(3)	(4)	-	-
m/z 46	-	(100)	-	-	-	-	-	-
m/z 44	(21)	(86)	(28)	(19)	(37)	(10)	(8)	(12)
$[CH_5N_2]^+$ m/z 45	(100)	(16)	(100)	(100)	(100)	(100)	(100)	(100)
m/z 43	(38)	(95)	(27)	(9)	(23)	(22)	(11)	(10)

TABLE 3

Metastable Peaks and the Corresponding Transitions in the Mass Spectra of Hydrazides and Alkylhydrazides of Fluorinated Alkanecarboxylic Acids (50 eV)

No	Compound	m^*	Transition
1	2	3	4
XII	$CF_3C(O)NHNHCH_3$	92.0	142 --- 114 + CH_2N
XIII	$C_2F_5C(O)NHNHCH_3$	140.1	192 --- 164 + CH_2N
		122.1	177 --- 147 + 30
		18.7	45 --- 29 + 16
		17.4	45 --- 28 + 17
		12,4	59 --- 27 + 32
XIV	$C_3F_7C(O)NHNHCH_3$	189.3	242 --- 214 + CH_2N
		175.9	214 --- 194 + HF
		128.8	214 --- 166 + 48
		128,4	166 --- 146 + HF
XVII	$CF_3C(O)NHNHC_2H_5$	107.3	141 --- 123 + H_2O
		83.3	156 --- 114 + 42
		77.5	114 --- 94 + HF
XVIII	$C_2F_5C(O)NHNHC_2H_5$	130.6	206 --- 164 + 42
		156.7	191 ---173 + H_2O
		16.3	59 --- 31 + 28
XIX	$C_3F_7C(O)NHNHC_2H_5$	189.3	242 --- 214 + CH_2N
		179.5	214 --- 196 + H_2O
XXI	$CF_3C(O)NHNHC_3H_7$	76.5	170 --- 114 + 56
		107.3	141 --- 123 + H_2O

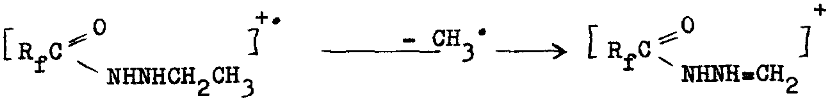
(continued)

TABLE 3 (cont.)

1	2	3	4
XXII	$C_2F_5C(O)NHNHC_3H_7$	122.3 156.7 56.2 56.2	220 --- 164 + 56 191 --- 173 + H_2O 178 --- 100 + 78 164 --- 96 + 68
XXIII	$C_3F_7C(O)NHNHC_3H_7$	206.3 56.1	241 --- 223 + H_2O 204 --- 107 + 97
XXXII	$CF_3C(O)NHNHC_6H_5$	33.7 59.6	77 --- 51 + 26 142 --- 92 + 50
XXXIII	$C_2F_5C(O)NHNHC_6H_5$	45.1 33.7 59.6	254 --- 107 + 147 77 --- 51 + 26 142 --- 92 + 50

This is indicated by the presence of peaks of the corresponding ions in the mass spectra (Table 2). The above fragmentation pathway is confirmed by metastable transition peaks (Table 3).

The mass spectra of 1-ethyl-2-perfluoroacylhydrazines contain the same ions as those mentioned above and in addition $[M-CH_3]^+$ ions (compounds XVII-XX) (Table 4).



$$[R_fC(=O)NHNHCH_2CH_3]^{+\bullet} \xrightarrow{-\,CH_3^{\bullet}} [R_fC(=O)NHNH{=}CH_2]^+$$

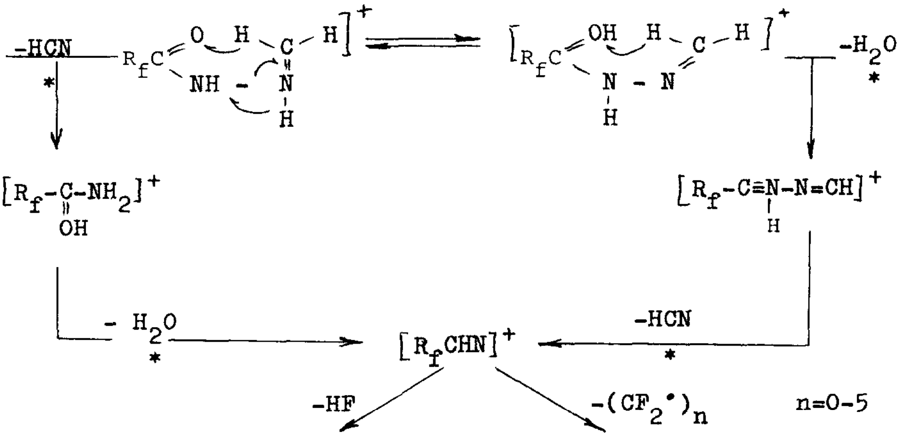
1-Propyl-2-perfluoroacylhydrazines (XXI-XXV) dissociate to give similar ions of the same structure, but their peaks in the spectra are most abundant (Table 4). Further fragmentation follows the scheme on p. 220.

TABLE 4

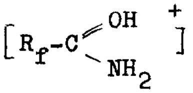
Mass Spectra of Compounds $R_fC(O)NHNHR_1$ with $R_1 = C_2H_5$ (XVII-XX), C_3H_7 (XXI-XXV), C_9H_{19} (XXVI,XXVII)

R_f	CF_3	C_2F_5	C_3F_7	C_4F_9	CF_3	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}	CF_3	C_2F_5
Ion / Compound	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	XXVI	XXVII
1	2	3	4	5	6	7	8	9	10	11	12
$[M]^{+\bullet}$	156 (1)	206 (25)	256 (15)	306 (3)	170 (20)	220 (19)	270 (14)	320 (7)	420 (11)	254 (3)	304 (2)
$[R_fCONHNHCH_2]^+$	141 (10)	191 (50)	241 (36)	291 (8)	141 (100)	191 (100)	241 (100)	291 (100)	391 (100)	141 (68)	191 (38)
$[R_fCH_3N_2O]^{+\bullet}$	-	178 (2)	-	-	128 (3)	178 (6)	-	-	-	128 (9)	178 (53)
$[R_fC(=OH)NH_2]^+$	114 (21)	164 (97)	214 (73)	364 (33)	114 (23)	164 (48)	214 (53)	264 (52)	364 (62)	114 (3)	164 (3)
$[R_fCONHNHCH_2\text{-}H_2O]^+$	123 (1)	173 (14)	223 (1)	-	123 (11)	173 (23)	223 (5)	273 (13)	373 (2)	123 (5)	173 (11)
$[C_4F_9]^+$ m/z 219	-	-	-	(3)	-	-	-	(9)	(6)	-	-
$[C_3F_7]^+$ m/z 169	-	-	(19)	(2)	-	-	(27)	(6)	(11)	-	-
$[R_fC(OH)NH_2\text{-}HF]^+$	94 (1)	144 (6)	194 (7)	244 (3)	94 (4)	144 (8)	194 (10)	244 (4)	- -	94 (1)	- -

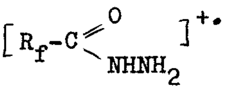
$[R_fCONHNHCH_2\text{-}HF]^+$	121 (2)	171 (5)	221 (1)	271 (2)	121 (16)	171 (7)	221 (2)	271 (3)	371 (3)	-	-
$[R_fCHN - CF_2]^+$	-	96 (2)	146 (6)	-	-	96 (6)	146 (15)	196 (5)	-	-	-
m/z 166	-	-	(8)	(1)	-	-	(22)	(5)	-	-	-
$[C_2F_5]^+$ m/z 119	-	(28)	(10)	(3)	-	(36)	(22)	(8)	(20)	-	(2)
m/z 116	-	(1)	-	-	-	(8)	(2)	-	-	-	-
$[C_2F_5]^+$ m/z 131	-	-	-	(7)	-	-	-	(16)	(13)	-	-
$[C_2F_4]^+$ m/z 100	-	(7)	(10)	(4)	-	(8)	(14)	(8)	(6)	-	-
$[CONHNHR_1]^+$	-	-	-	-	-	-	-	-	-	185 (1)	185 (1)
$[M\text{-}CH_3]^+$	141 (10)	191 (50)	241 (36)	291 (8)	-	205 (2)	-	305 (1)	-	-	-
m/z 92	(1)	(1)	-	(1)	-	(5)	(4)	-	-	-	-
m/z 71	(6)	(4)	(3)	-	(10)	(13)	(10)	(7)	(8)	(4)	(5)
$[CF_3]^+$ m/z 69	(25)	(22)	(37)	(27)	(25)	(35)	(54)	(68)	(78)	(8)	(33)
m/z 57	-	-	-	(4)	(11)	(35)	(40)	(56)	(72)	(9)	(11)
m/z 56	-	-	-	-	(10)	(37)	(47)	(76)	(89)	(19)	(19)
m/z 44	(19)	(29)	(27)	(21)	(6)	(49)	(49)	(37)	(42)	(6)	-
m/z 43	(41)	(30)	(26)	(42)	(2)	(54)	(68)	(72)	(78)	(100)	(100)
m/z 42	(16)	(17)	(22)	(24)	(1)	(15)	(17)	(12)	(12)	(10)	(64)



For compounds (XVIII, XXI, XXII) as well as for 1-nonyl-2-trifluoroacetyl--(XXVI) and 1-nonyl-2-pentafluoropionylhydrazine (XXVII) the ions


$[R_f-C(=OH)NH_2]^+$

and


$[R_f-C(=O)NHNH_2]^{+\bullet}$

are shown by metastable peaks to originate directly from the molecular ion (Table 3).

An increase in the perfluoroacyl group length does not affect much the fragmentation of compounds with $R_1 = CH_3$(XII-XVI), C_2H_5 (XVII-XX) and C_3H_7(XXI-XXV) and their mass spectra are dependent only on the alkyl substituent size.

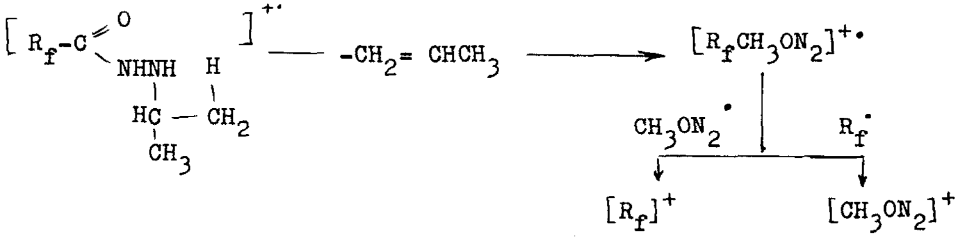
Similarly lengthening of the alkyl substituent R_1 to C_9H_{19} (compounds XXVI, XXVII) does not change the fragmentation route. In the mass spectra of these compounds the main contribution to the ion current is from ions resulting from cleavage of hydrocarbon chains.

Branching of a hydrocarbon radical induces some changes in the fragmentation of fluorocarboxylic alkylhydrazides. In the case of 1-isopropyl-2-perfluoroacylhydrazines (XXVIII-XXXI) the molecular ion fragmentation involves elimination of a propylene molecule to form a cation-radical with m/z of the unsubstituted hydrazide of the corresponding acid (Table 5).

TABLE 5

Mass Spectra of Compounds $R_fC(O)NHNHCH(CH_3)_2$ (XXVIII-XXXI)

R_f	CF_3	C_2F_5	C_3F_7	C_4F_9
	Compound			
Ion	XXVIII	XXIX	XXX	XXXI
$M^{+\bullet}$	170(9)	220(7)	270(3)	320(3)
$[M-CH_3]^+$	155(100)	205(100)	255(35)	305(3)
$[(M-CH_3)-H_2O]^+$	137(3)	187(1)	237(1)	287(1)
$[R_fCONHNH_2]^{+\bullet}$	128(22)	178(26)	228(8)	278(5)
$[M-C_3H_6N]^+$	114(9)	164(18)	214(11)	264(12)
$[C_4F_9]^+$ m/z 219	-	-	-	(4)
$[C_3F_7]^+$ m/z 169	-	-	(5)	(8)
$[C_2F_5]^+$ m/z 119	-	(16)	(3)	(3)
$[C_2F_4]^+$ m/z 100	-	-	(4)	(4)
$[C_3H_9N_2]$ m/z 73	(9)	(17)	(18)	(21)
$[CF_3]^+$ m/z 69	(73)	(12)	(18)	(25)
$[CONHNH_2]^+$ m/z 59	(84)	(3)	(5)	(8)
$[C_3H_7N]^+$ m/z 57	(16)	(32)	(56)	(55)
$[C_3H_6N]^+$ m/z 56	(15)	(12)	(13)	(20)
m/z 43	(73)	(79)	(100)	(100)
m/z 42	(98)	(84)	(32)	(72)



A similar transfer of hydrogen was also observed with 1-methyl-1-acetylhydrazine.

An alternative fragmentation route for the molecular ion of hydrazides with $R_1 = CH(CH_3)$ (XXVIII-XXXI) leads to $[M-CH_3]^+$ and $[(M-CH_3)-H_2O]^+$ ions. These same ions were also produced from 2-isopropylhydrazides of benzoic and isonicotinic acids [7]. In the mass spectra of (XXVIII) and (XXIX) peak ion $[M-CH_3]^+$ is the base peak and its intensity decreases with further increase in the perfluoroacyl group length.

As in (XII-XXVII), the dissociation of molecular ions of compounds with $R_1 = CH(CH_3)_2$ (XXVIII-XXXI) is characterized by rearranged ions at m/z 114, 164, 214 and 264, corresponding to breakage of the N-N bond. However, peaks ions $[R_fCHN]^+$ at m/z 96, 146, 196 and 246 are absent in mass spectra (XXVIII-XXXI). This points to a difference in the $[M-CH_2N]^+$ structure compounds (XII-XXVII) and (XXVIII-XXXI).

For 1-phenyl-2-perfluoroacylhydrazines (XXXII-XXXVI) (Table 6) the molecular ion peak is the most intense one. Its intensity is higher than that for 1-acetyl-2-phenylhydrazine [8]. Increasing in size of the perfluoroacyl radical (compounds XXXV, XXXVI) decreases the $[M]^+$ stability as in the case of compounds with $R_1 = H$. The possibility of delocalization of the positive charge between two nitrogens and the phenyl group decreases the stability of the $[C_6H_7N_2]^+$ fragment at m/z 107. In the mass spectra of (XXXII-XXXVI) the greatest contribution to the ion current is from the m/z 107 ions and the products of their further dissociation. The appearance of peaks at m/z 142 and 134 is somewhat unexpected. The high resolution measurements show the following structures:

$[C_7H_6NF_2]^+$	$[C_7H_6ON_2]^{+\cdot}$
m/z 142	m/z 134

TABLE 6

Mass Spectra of Compounds $R_fC(O)NHNHC_6H_5$ (XXXII-XXXVI)

R_f	CF_3	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}
	Compound				
Ion	XXXII	XXXIII	XXXIV	XXXV	XXXVI
$[M]^{+\bullet}$	204(83)	254(72)	304(67)	354(17)	454(29)
$[M-62]^+$	142(11)	192(3)	242(5)	292(1)	392(1)
$[C_7H_6ON_2]^{+\bullet}$ m/z 134	(4)	(5)	(9)	(2)	(2)
$[C_3F_7]^+$ m/z 169	-	-	(12)	-	(3)
$[C_7H_6NF_2]^+$ m/z 142	(4)	(3)	(8)	(7)	(6)
$[R_fCONHNH_2]^{+\cdot}$	128(2)	-	-	278(2)	-
$[C_2F_5]^+$ m/z 119	-	(15)	(2)	(1)	(3)
$[C_2F_4]^+$ m/z 100	-	(3)	(2)	-	(1)
$[C_6H_8N_2]^+$ m/z 108	(12)	(22)	(24)	(8)	(8)
$[C_6H_7N_2]^+$ m/z 107	(100)	(100)	(100)	(100)	(100)
$[R_f]^+$	69(24)	119(15)	169(12)	219(1)	-
m/z 105	(11)	(11)	(16)	(6)	(7)
$[C_6H_7N]^+$ m/z 93	(13)	(12)	(8)	(5)	(3)
$[C_6H_6N]^+$ m/z 92	(21)	(28)	(52)	(17)	(19)
$[C_6H_5N]^+$ m/z 91	(27)	(22)	(38)	(10)	(6)
$[C_6H_6]^+$ m/z 78	(21)	(20)	(32)	(6)	(4)
$[CF_3]^+$ m/z 69	(24)	(18)	(19)	(12)	(8)
$[C_6H_5]^+$ m/z 77	(57)	(50)	(62)	(46)	(44)
$[C_5H_5]^+$ m/z 65	(29)	(26)	(51)	(16)	(9)
$[C_4H_3]^+$ m/z 51	(29)	(13)	(41)	(19)	(8)

TABLE 7
High Resolution EI Mass Spectra of Some Ions of Hydrazides and Alkylhydrazides of Fluorinated Alkanecarboxylic Acids

Compound 1	Peak observed 2	Formula 3	Deviation* 10^{-5} 4	Assignment 5
III	82.03429	$CH_4N_2F_2$	+ 3.0	M - CO
V	150.021657	$C_2H_3N_2F_5$	+ 1.4	M - CO
XI	96. 026114	$C_2H_4ONF_2$	+ 1.5	$CHF_2C(OH)NH_2$
XII	114.016977	$C_2H_3ONF_3$	+ 2.5	$CF_3C(OH)NH_2$
XII	96.006135	C_2HNF_3	+ 2.1	CF_3HCN
XIII	146.002939	C_3HNF_5	+ 1.5	C_2F_5HCN
XIV	195. 99973	C_4HNF_7	- 0.4	C_3F_7HCN
XIV	214.010307	$C_4H_3ONF_7$	+ 1.3	$C_3F_7C(OH)NH_2$
XVI	364.000703	$C_7H_3ONF_{13}$	+ 1.9	$C_6F_{13}C(OH)NH_2$
XVII	141.027583	$C_3H_4ON_2F_3$	+ 0.5	$CF_3CONHNHCH_2$
XVII	114.016985	$C_2H_3ONF_3$	+ 2.5	$CF_3C(OH)NH_2$
XVIII	173.013832	$C_4H_2N_2F_5$	+ 0.9	$C_2F_5CONHNHCH_2$-H_2O
XVIII	191.024411	$C_4H_4ON_2F_5$	+ 2.8	$C_2F_5CONHNHCH_2$
XIX	214.010311	$C_4H_4ONF_7$	+ 1.7	$C_3F_7C(OH)NH_2$
XX	291.017890	$C_6H_4ON_2F_9$	+ 1.7	$C_4F_9CONHNHCH_2$
XXI	128.019774	$C_2H_3ON_2F_3$	+ 2.1	$CF_3CH_3ON_2$
XXI	141.027598	$C_3H_4ON_2F_3$	+ 2.0	$CF_3CONHNHCH_2$
XXII	164.013474	$C_3H_3ONF_5$	- 1.0	$C_2F_5C(OH)NH_2$
XXII	178.016580	$C_3H_3ON_2F_5$	+ 1.7	$C_2F_5CH_3ON_2$
XXII	191.024399	$C_4H_4ON_2F_5$	+ 1.6	$C_2F_5CONHNHCH_2$
XXIII	214.010304	$C_4H_4ONF_7$	+ 1.0	$C_3F_7C(OH)NH_2$
XXIII	223.010650	$C_5H_2N_2F_7$	+ 1.7	$C_3F_7CONHNHCH_2$-H_2O
XXIV	273.013832	$C_6H_2N_2F_9$	+ 0.9	$C_4F_9CONHNHCH_2$-H_2O
XXIV	291.017890	$C_6H_4ON_2F_9$	+ 1.7	$C_4F_9CONHNHCH_2$
XXVI	114.016977	$C_2H_3ONF_3$	+ 1.7	$CF_3C(OH)NH_2$

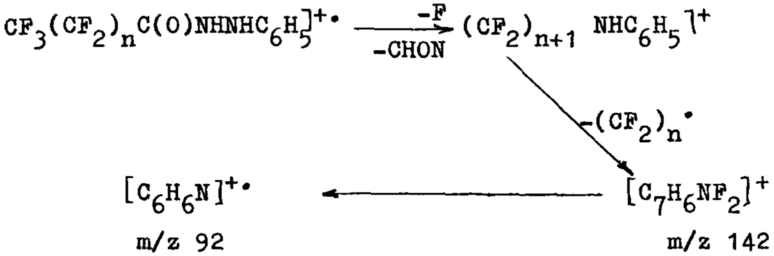
(continued)

TABLE 7 (cont.)

1	2	3	4	5
XXVI	123.017037	$C_3H_2N_2F_3$	+ 2.4	$CF_3CONHNHCH_2-H_2O$
XXVI	141.027595	$C_3H_4ON_2F_3$	+ 1.7	$CF_3CONHNHCH_2$
XXVII	164.013497	$C_3H_3ONF_5$	+ 1.3	$C_2F_5C(OH)NH_2$
XXVII	191.024398	$C_4H_4ON_2F_5$	+ 1.5	$C_2F_5CONHNHCH_2$
XXIX	178.016577	$C_3H_3ON_2F_5$	+ 1.4	$C_3H_3ON_2F_5$
XXX	214.010303	$C_4H_4ONF_7$	+ 0.9	$M - C_3H_6N$
XXXI	278.010193	$C_5H_3ON_2F_9$	+ 1.0	$C_5H_3ON_2F_9$
XXXII	134.048018	$C_7H_6ON_2$	+ 0.5	$C_7H_6ON_2$
XXXII	142.046849	$C_7H_6NF_2$	+ 1.5	M - 62
XXXIII	134.048023	$C_7H_6ON_2$	+ 1.0	$C_7H_6ON_2$
XXXIII	142.046844	$C_7H_6NF_2$	+ 1.0	$C_7H_6NF_2$
XXXV	134.048025	$C_7H_6ON_2$	+ 1.2	$C_7H_6ON_2$

* The deviation represents the difference between observed and calculated values.

These ions possibly arise from a skeletal rearrangement the mechanism of which needs further investigation.



The occurence of the ion at m/z 92 is a feature of the mass spectra of (XXXII-XXXVI). This indicates a weakness of N-N bonds in compounds with $R_1 = C_6H_5$ as compared with their analogs with R_1 = Alk.

EXPERIMENTAL

The synthesis of compounds (IV-XVII, XIX, XXVI) was described in [2,5, 10-15]. Compounds (XVIII,XX, XXII-XXIV, XXVII) were obtained as follows. To a solution of 0.02 moles of methyl ester of perfluoroalkanecarboxylic acid in 30 ml of dry methanol, a solution of the corresponding alkylhydrazine in 10 ml of dry methanol was added upon stirring. The reaction mixture was allowed to stand at room temperature for 4 hours. After removal of the solvent at reduced pressure the reaction products were purified by sublimation in vacuum.

1-Ethyl-2-pentafluoropropionylhydrazine (XVIII). Yield 81%, m.p. 57-58°. Found, %: C 29.16, H 3.48, F 45.95, N 13.77, $C_5H_7F_5N_2O$. Calculated, %: C 29.14, H 3.42, F 46.09, N 13.59.

1-Ethyl-2-nonafluoropentanoylhydrazine (XX). Yield 77%, m.p. 68-69°. Found, %: C 27.58, H 2.37, F 55,65, N 9.14, $C_7H_7F_9N_2O$. Calculated, %; C 27.46, H 2.3, F 55.85, N 9.15.

1-Propyl-2-heptafluorobutyrylhydrazine (XXIII). Yield 55%, m.p. 79-80°. Found, %: C 30.94, H 3.36, F 49.27, N 10.34. $C_7H_9F_7N_2O$. Calculated, %; C 31.12, H 3.36, F 49.23, N 10.37.

1-Propyl-2-pentafluoropropionylhydrazine (XXII). Yield 69%, m.p. 84°. Found, %: C 32.54, H 4.32, F 43.15, H 12.66. $C_6H_9F_5N_2O$. Calculated, %: C 32.74, H 4.12, F 43.15, N 12.66.

1-Propyl-2-nonafluoropentanoylhydrazine (XXIV). Yield 72%, m.p. 73-74°. Found, %: C 29.92, H 2.80, F 53.33, N 8.74. $C_2H_9F_9N_2O$. Calculated, %; C 30.18, H 2.83, F 53.28, N 8.75.

1-Nonyl-2-pentafluoropropionylhydrazine (XXVII). Yield 67%, m.p. 71° (from hexane). Found, %: C 47.15, H 7.12, F 30.92, N 9.32. $C_{12}H_{21}F_5N_2O$. Calculated, %: C 47.36, H 6.96, F 31.22, N 9.21.

The mass spectra were recorded on Varian MAT 212 (70 eV) and MX-1303 (50 eV) mass spectrometers. Source temperature 200° C. The substances were introduced directly into the ion source. The temperature varied within a 25-300° range depending on the sample volatility. High resolution spectra were taken at 10^4 resolution for the assignment of some ions.

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