SYNTHESIS OF NEW FLUORINATED AMPHIPHILES R_F-$CH_2CH_2CONH_2$ AND R_F-$(CH_2)_n$-CH-$(CH_2)_m$-R_H BY PHOTOAMIDATION OF THE CORRESPONDING OLEFINS
$\overset{|}{CONH_2}$

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SUMMARY

We describe the synthesis of new fluorinated amphiphiles R_F-$CH_2CH_2CONH_2$ and $R_F(CH_2)_n$-$CH(CONH_2)$-$(CH_2)_m$-R_H (R_F = C_4F_9, C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$; n = 0,1,2; m = 0,1; R_H = C_4H_9, C_8H_{17}, $C_{10}H_{21}$) by photoamidation of the corresponding olefins in tert-butanol. The different regioselectivities observed are discussed and interpreted.

INTRODUCTION

Considerable research, both fundamental and applied has been devoted to long chain fluorinated amphiphiles. We will only mention here a few of the many studies carried out to date.

- segregation phenomena between these derivatives and the corresponding hydrogenated ones [1,2]
- applications based on their surfactant properties, formation of emulsions, foams, etc. [3-5]
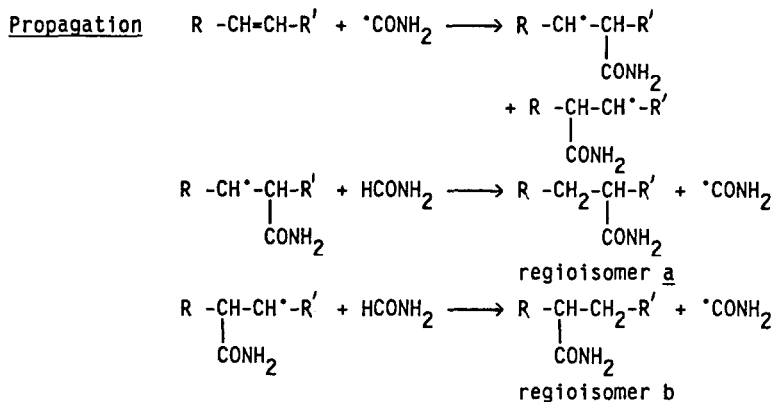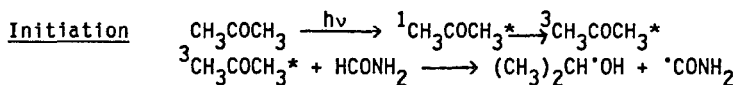
In this study we describe the synthesis of two new series of molecules with an amide group as polar head.

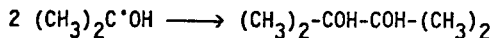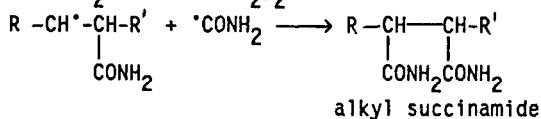1 - with a single fluorinated chain R_F-CH_2-CH_2-$CONH_2$
2 - with a fluorinated and a hydrogenated chain R_F-$(CH_2)_n$-$CH(CONH_2)$-$(CH_2)_m$-R_H; n = 0,1,2; m = 0,1.

They were synthesized by photoamidation of the corresponding olefins R_F-$CH=CH_2$ and R_F-$(CH_2)_m$-$CH=CH$-R_H in tert-butanol [6].
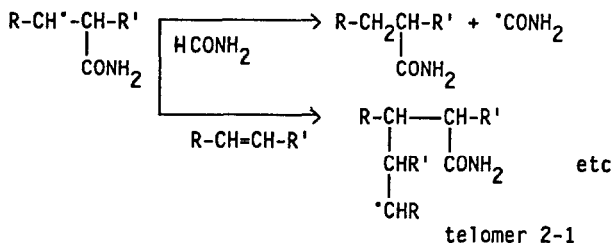
In the case of the hydrogenated olefins, this reaction has been extensively investigated by Elad and Rockach [7-9] and Ollivier and Leibovici [10]. It involves a radical chain reaction, initiated by the photoreduction by formamide of acetone excited to the triplet state.

Initiation

$$CH_3COCH_3 \xrightarrow{h\nu} {}^1CH_3COCH_3* \xrightarrow{} {}^3CH_3COCH_3*$$

$${}^3CH_3COCH_3* + HCONH_2 \longrightarrow (CH_3)_2CH^{\cdot}OH + {}^{\cdot}CONH_2$$

Propagation

$$R-CH=CH-R' + {}^{\cdot}CONH_2 \longrightarrow R-CH^{\cdot}-CH-R'$$
$$\underset{CONH_2}{|}$$

$$+ R-CH-CH^{\cdot}-R'$$
$$\underset{CONH_2}{|}$$

$$R-CH^{\cdot}-CH-R' + HCONH_2 \longrightarrow R-CH_2-CH-R' + {}^{\cdot}CONH_2$$
$$\underset{CONH_2}{|} \qquad\qquad \underset{CONH_2}{|}$$
$$\text{regioisomer } \underline{a}$$

$$R-CH-CH^{\cdot}-R' + HCONH_2 \longrightarrow R-CH-CH_2-R' + {}^{\cdot}CONH_2$$
$$\underset{CONH_2}{|} \qquad\qquad \underset{CONH_2}{|}$$
$$\text{regioisomer } \underline{b}$$

Termination Radical recombination

$$2 {}^{\cdot}CONH_2 \longrightarrow (CONH_2)_2 \text{ ethane diamide or oxamide}$$

$$R-CH^{\cdot}-CH-R' + {}^{\cdot}CONH_2 \longrightarrow R-CH-\!\!-CH-R'$$
$$\underset{CONH_2}{|} \qquad\qquad\qquad \underset{CONH_2 \, CONH_2}{|\quad\;|}$$
$$\text{alkyl succinamide}$$

$$2 (CH_3)_2C^{\cdot}OH \longrightarrow (CH_3)_2\text{-COH-COH-}(CH_3)_2$$

Secondary products can be formed via telomerization of the olefin:

$$R-CH^{\cdot}-CH-R' \qquad \xrightarrow{} R-CH_2CH-R' + {}^{\cdot}CONH_2$$
$$\underset{CONH_2}{|} \quad [HCONH_2] \qquad \underset{CONH_2}{|}$$

$$\xrightarrow[R-CH=CH-R']{} R-CH-\!\!-CH-R'$$
$$\underset{CHR'\;\; CONH_2}{|\qquad|} \qquad etc$$
$$\underset{{}^{\cdot}CHR}{|}$$
$$\text{telomer 2-1}$$

RESULTS

Method of Elad and Rockach

For the synthesis of the derivatives with both a single fluorinated chain and those with a fluorinated and hydrogenated chain, the method described by Elad and Rockach was selected [8,9]. This consists of irradiating fraction containing a mixture of the olefin and formamide in the presence of acetone at 300 nm. The fractions of the mixture are introduced successively into the reaction mixture in order to limit the secondary reaction mentioned above. The mixture is made homogeneous by addition of tert-butanol.

At the end of the reaction, the tert-butanol, the acetone and the excess formamide are eliminated by evaporation under reduced pressure.

This method which works well with hydrogenated olefins could not be used for the olefins $R_F-CH=CH_2$ and $R_F-(CH_2)_n-CH=CH-R_H$. Only the olefin $C_4F_9-CH=CH_2$ led to the product with an amide terminal at a yield of 4%. The olefins $R_F-CH=CH_2$ with longer chains (R_F) are insoluble in the reaction mixture. With the mixed olefins $R_F-(CH_2)_n-CH=CH-R_H$, which are soluble in the reaction mixture, no reaction apart from some production of oxamide and secondary telomers took place.

Modification of the method for fluorinated olefins

The perfluorinated olefins $R_F-CH=CH_2$ can be dissolved to make a homogeneous solution in a large excess of tert-butanol (10-fold more dilute than normal). Radical chain reactions are not normally favored in such dilute media, although in the case of the derivatives $R_F-CH=CH_2$ and $R_F-(CH_2)_n-CH=CH-R_H$, amidation occurred. This was probably because the secondary reactions were relatively unfavored in such a dilute medium. In fact only small amounts of the oxamide were isolated under these conditions. In addition, the method could be simplified by mixing all the reactants together at once.

The results after 48 h irradiation (300 nm, 30°C) are listed in Table I. The yields given are for the products isolated. The regioisomers a and b were not separated. The regioselectivities were determined by GLC, ^{1}H NMR and mass spectroscopy (cf. experimental part).

TABLE 1

Amides synthesized in tert-butanol, at high dilution

| Initial olefin	Derivatives obtained	No	Yield (%)	ratio a/b
$C_4F_9-CH=CH_2$	$C_4F_9C_2H_4CONH_2$ (a)	1	57	100% a
$C_6F_{13}-CH=CH_2$	$C_6F_{13}C_2H_4CONH_2$ (a)	2	50	"
$C_8F_{17}-CH=CH_2$	$C_8F_{17}C_2H_4CONH_2$ (a)	3	82	"
$C_{10}F_{21}-CH=CH_2$	$C_{10}F_{21}C_2H_4CONH_2$ (a)	4	73	"
$C_4F_9-CH_2-CH=CH-C_8H_{17}$	$C_4F_9C_2H_4-CH-C_8H_{17} + C_4F_9-CH_2-CH-C_9H_{19}$ (a) $\quad$ CONH$_2$ $\quad$ (b) $\quad$ CONH$_2$	5	68	2.89
$C_6F_{13}-CH_2-CH=CH-C_4H_9$	$C_6F_{13}C_2H_4-CH-C_4H_9 + C_6F_{13}-CH_2-CH-C_5H_{11}$ (a) $\quad$ CONH$_2$ $\quad$ (b) $\quad$ CONH$_2$	6	63	1.39
$C_8F_{17}-CH_2-CH=CH-C_4H_9$	$C_8F_{17}C_2H_4-CH-C_4H_9 + C_8F_{17}-CH_2-CH-C_5H_{11}$ (a) $\quad$ CONH$_2$ $\quad$ (b) $\quad$ CONH$_2$	7	87	1.22
$C_8F_{17}-CH=CH-C_{10}H_{21}$	$C_8F_{17}-CH_2-CH-C_{10}H_{21} + C_8F_{17}-CH-C_{11}H_{23}$ (a) $\quad$ CONH$_2$ $\quad$ (b) $\quad$ CONH$_2$	8	64	7.71

The yields were satisfactory in view of the low reactivity of the corresponding olefins, especially that of the $R_F-CH=CH_2$ derivatives [11].

Regioselectivity of amidation of olefins $R_F-CH=CH_2$

In general, the radical addition reactions are governed by a complex set of factors which include polar and steric effects as well as the relative stabilities of the radicals involved in the reaction.

i) Polar effects

The carbamoyl radical $^\bullet CONH_2$ is markedly electrophilic. Writing its structure in the resonance forms (keeping the free electron on the attacking carbon atom):

$$^\bullet C\diagup^{O}_{\diagdown NH_2} \longleftrightarrow ^\bullet C^+\diagup^{O^-}_{\diagdown NH_2} \longleftrightarrow ^\bullet C\diagup^{O^-}_{\diagdown^+NH_2}$$
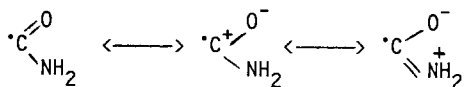
It can be seen that the carbon atom retains a partial positive charge. If polar effects predominate, the addition reaction would take place on the α

carbon to the fluorinated chain $R_F + \underset{\alpha}{CH} = \underset{\beta}{CH_2}$. This was not, however, observed.

ii) Steric effects

On the other hand, approach of the carbamoyl radical is favored on the β carbon which is less hindered than the α atom.

Addition $R_F-CH=CH_2 + {}^{\bullet}CONH_2 \longrightarrow R_F-{}^{\bullet}CH-CH_2CONH_2$

iii) Stability of the radicals

Moreover, the radical formed $R_F-{}^{\bullet}CHCH_2CONH_2$ is more stable than the radical $R_F-CH(CONH_2)-{}^{\bullet}CH_2$ which would be formed by attack on the α carbon.

Thus steric effects and radical stability act in concert outweighing polar effects.

However, we have neglected the transfer reaction in the above arguments.

Transfer $R_F-{}^{\bullet}CH-CH_2CONH_2 + HCONH_2 \longrightarrow R_FCH_2CH_2CONH_2 + {}^{\bullet}CONH_2$
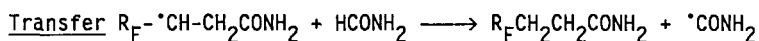
In fact the presence of large amounts of formamide would argue in favor of a fast transfer reaction and a predominance of the addition reaction.
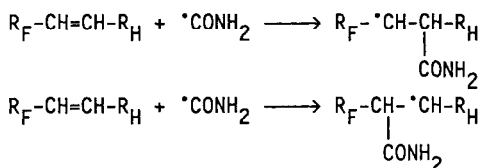
Regioselectivity of amidation of olefins $R_F-(CH_2)_m-CH=CH-R_H$

1 - Case of olefin $C_8F_{17}-CH=CH-C_{10}H_{21}$

Compared to the terminal olefins $R_F-CH=CH_2$, the donor effect of the R_H alkyl chain of the mixed olefin $C_8F_{17}-\underset{\alpha}{CH}=\underset{\beta}{CH}-C_{10}H_{21}$ will tend to favor attack on the β carbon, whereas considerations of charge would tend to favor amidation on the α carbon, which was not in fact observed.

On the other hand, the perfluorinated chain has a greater steric hindrance than the hydrogenated chain due to the large size of the fluorine atoms and the greater conformational mobility of these substituents. Steric effects will thus favor addition to the β carbon atom.

Addition

$R_F-CH=CH-R_H + {}^{\bullet}CONH_2 \longrightarrow R_F-{}^{\bullet}CH-\underset{|}{CH}-R_H$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CONH_2$$

$R_F-CH=CH-R_H + {}^{\bullet}CONH_2 \longrightarrow R_F-\underset{|}{CH}-{}^{\bullet}CH-R_H$
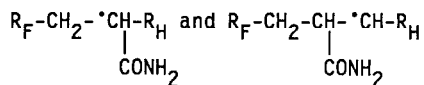$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CONH_2$$

In this case, the relative stability of the radicals formed is not readily estimated.

In summary, the results obtained for photoamidation of $C_8F_{17}-CH=CH-C_{10}H_{21}$ in tert-butanol indicate a predominant role for steric effects, accounting for the preponderance of the isomer with the amide group next to the R_H chain (regioselectivity = 7.71).

2 – <u>Case of olefins R_F-CH_2-CH=CH-R_H</u>

i) Although the attractive effect of the fluoroalkylated chain is attenuated by the CH_2 group in the α position to the double bond, attack at this position would still be favored on polar considerations. This was not, however, observed.

ii) The relative stabilities of the radicals formed are similar:

$$R_F\text{-}CH_2\text{-}^\bullet CH\text{-}R_H \quad \text{and} \quad R_F\text{-}CH_2\text{-}CH\text{-}^\bullet CH\text{-}R_H$$
$$\overset{|}{CONH_2} \qquad\qquad \overset{|}{CONH_2}$$

iii) Steric effects will also tend to favor addition at the β position. They are, however, attenuated by the CH_2 group between the double bond and the perfluorinated chain. Attack on the β carbon will be less favored, which is born out by the lower regioselectivities (1.22-2.89 versus 7.71 for C_8F_{17}-CH=CH-$C_{10}H_{21}$).

CONCLUSION

We describe a method for photoamidation of highly fluorinated olefins R_F-CH=CH_2 and R_F-$(CH_2)_m$-CH=CH-R_H. The corresponding fluorinated amides with a single fluorinated chain, or with a fluorinated and a hydrogenated chain were thus obtained.

The amidation by formamide in dilute condition in tert-butanol led to attack by the carbamoyl radical on the carbon terminal for the olefins R_F-CH=CH_2, and on the carbon bearing the alkyl group for the mixed olefins (hydrogenated and fluorinated chains). This regioselectivity was due to a predominance of steric over polar effects.

The amides synthesized are being evaluated as fire extinguishing foams in collaboration with Atochem [12]. These amides are readily hydrolyzed, producing the corresponding carboxylic acids and carboxylates. The surfactant properties of these compounds are also under investigation [13].

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 683 apparatus. The frequencies of the characteristic bands are expressed in cm^{-1}.

The proton and fluorine NMR spectra were recorded on Bruker AM-300-WB machine at 300 MHz using TMS as internal reference for the ^1H and CF_3COOH as external reference for the ^{19}F measurements. The chemical shifts are expressed in ppm with respect to the reference, and the signals characterized by s (singlet), d (doublet), t (triplet) and m (multiplet).

Melting points were measured on a Koffler block.

Elemental analyses of the synthesized products were carried out in the CNRS facilities (Lyon, France) and expressed as percentages of required (r) and experimental (f) values (Tables II and III).

An Intersmat IGC 120 FL was used for the GLC analyses, with the following operating conditions:

- SE 30 column with 10% silicone on chromosorb PAW 80/100 mesh (1.5 m long)
- input pressure nitrogen vector : 1.3 at
- detector temp. (FID) : 290°C
- temperature program : 30-300°C at 10°C/min.

The mass spectra of the compounds, separated by GLC (as above), were recorded on a Nermag R10-10A apparatus using desorption and chemical ionization.

Compounds

The fluorinated olefins (99% pure) were kindly supplied by Atochem. Acetone and formamide, and tert-butanol (Aldrich) were also 99% pure.

Photoamidation reaction

After degassing with argon, the following mixture was irradiated at 300 nm in a Rayonet RP 600 for two days: 0.012 mole olefin, 35.3 ml of formamide (0.89 mole), 5 ml of acetone (0.068 mole) and 95 ml of tert-butanol (1.01 mole) [150 ml for $C_{10}F_{21}CH=CH_2$ and 105 ml for $C_8F_{17}CH=CHC_{10}H_{21}$].

The oxamide produced during the reaction was filtered off, and the filtrate evaporated to dryness under vacuum. The residue was taken up in 5 ml of water and recrystallized in water. The product was dried over P_2O_5. The following amides were obtained as white powders.

1,1,1,2,2,3,3,4,4-Nonafluorohexane-1-carboxamide $C_4F_9C_2H_4CONH_2$ 1

MW = 291; MP = 115°C; GLC = 1 peak at 140°C
IR = 3400 (N-H free); 3220 (N-H coupled); 1690 (C=O); 1230 (C-F)
NMR ^{1}H, CD_3COCD_3: 2.66(4p, m, $CH_2\alpha$ and β CO); 6.54-7.12(2p, m, N-H)
NMR ^{19}F, CD_3COCD_3 = -5.75(3f, t, CF_3); -39.05(2f, m, $CF_2\alpha CH_2$);
-49.94(2f, m, $CF_2\beta CH_2$); -50.55(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorooctane-1-carboxamide $C_6F_{13}C_2H_4CONH_2$ 2

MW = 391; MP = 120°C; GLC = 1 peak at 150°C
IR = 3460 (N-H free); 3200 (N-H coupled); 1670 (C=O); 1260 (C-F)
NMR ^{1}H, CD_3COCD_3: 2.66(4p, m, $CH_2\alpha$ and β CO); 6.54-7.11(2p, m, N-H)
NMR ^{19}F, CD_3COCD_3 = -5.46(3f, t, CF_3); -38.76(2f, m, $CF_2\alpha CH_2$);
-46.31(2f, m, $CF_2\beta CH_2$; -47.28(2f, m, $CF_2\gamma CH_2$); -47.97(2f, m, $CF_2\beta CF_3$);
-50.60(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluorodecane 1-carboxamide $C_8F_{17}C_2H_4CONH_2$ 3

MW = 491; MP = 140°C; GLC = 1 peak at 160°C
IR = 3400 (N-H free); 3200 (N-H coupled); 1670 (C=O); 1210 (C-F)
NMR ^{1}H, CD_3COCD_3: 2.53(4p, m, $CH_2\alpha$ and β CO); 6.64-7.00(2p, m, N-H)
NMR ^{19}F, CD_3COCD_3 = -5.23(3f, t, CF_3); -38.50(2f, m, $CF_2\alpha CH_2$);
-46.00(6f, m, CF_2); -46.83(2f, m, $CF_2\gamma CF_3$); -47.68(2f, m, $CF_2\beta CF_3$);
-50.32(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Uneicofluorododecane 1-carboxamide $C_{10}F_{21}C_2H_4CONH_2$ 4

MW = 591; MP = 142°C; GLC = 1 peak at 180°C
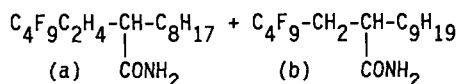IR = 3400 (N-H free); 3220 (N-H coupled); 1680 (C=O); 1210 (C-F)
NMR ^{1}H, CD_3COCD_3: 2.55(4p, m, $CH_2\alpha$ and β CO); 6.49-7.50(2p, m, N-H)
NMR ^{19}F, CD_3COCD_3 = -5.31(3f, t, CF_3); -38.57(2f, m, $CF_2\alpha CH_2$);
-45.94(10f, m, CF_2); -46.92(2f, m, $CF_2\gamma CF_3$); -47.77(2f, m, $CF_2\beta CF_3$);
-50.43(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4-Nonafluoropentadecane 6 and 7-carboxamides 5

$C_4F_9C_2H_4$-CH-C_8H_{17} + C_4F_9-CH_2-CH-C_9H_{19}

   (a) $\overset{|}{CONH_2}$ (b) $\overset{|}{CONH_2}$

MW = 417; MP = 80°C; GLC = double peak at 220°C

IR = 3400 (N-H free); 3200 (N-H coupled); 1660 (C=O); 1220 (C-F)

MR ^{1}H, CD_3COCD_3: 0.99(3p, t, CH_3); 1.40(14p, m, CH_2); 2.34(1p, m, CH);
2.85(4p, m, $CH_2\alpha$ and β CF_2); 6.51-7.07(2p, m, N-H)

NMR ^{19}F, CD_3COCD_3 = -5.75(3f, t, CF_3); -39.00(2f, m, $CF_2\alpha CH_2$);
-48.82(2f, m, $CF_2\beta CF_3$); -50.53(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorotridecane 8 and 9-carboxamides 6

$C_6F_{13}C_2H_4$-CH-C_4H_9 + C_6F_{13}-CH_2-CH-C_5H_{11}

    (a) $\overset{|}{CONH_2}$ (b) $\overset{|}{CONH_2}$
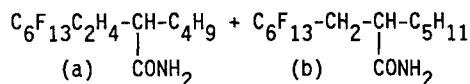
MW = 461; MP = 78°C; GLC = double peak at 170°C

IR = 3390 (N-H free); 3200 (N-H coupled); 1670 (C=O); 1210 (C-F)

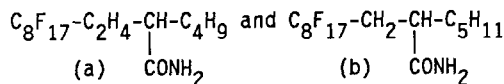NMR ^{1}H, CD_3COCD_3: 0.98(3p, t, CH_3); 1.41(6p, m, CH_2); 2.4(1p, m, CH);
2.9(4p, m, $CH_2\alpha$ and β CF_2); 6.65-7.44(2p, m, N-H)

NMR ^{19}F, CD_3COCD_3 = -5.09(3f, t, CF_3); -37.25(2f, m, $CF_2\alpha CH_2$);
-45.99(2f, m, $CF_2\beta CH_2$); -47.06(2f, m, $CF_2\gamma CH_2$); -47.89(2f, m, $CF_2\beta CF_3$);
-50.38(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoropentadecane
10 and 11-carboxamides 7

C_8F_{17}-C_2H_4-CH-C_4H_9 and C_8F_{17}-CH_2-CH-C_5H_{11}

    (a) $\overset{|}{CONH_2}$ (b) $\overset{|}{CONH_2}$

MW = 591   MP = 88°C; GLC = double peak at 190°C

IR = 3420 (N-H free); 3200 (N-H coupled); 1670 (C=O); 1200 (C-F)

NMR ^{1}H, CD_3COCD_3: 1.00(3p, t, CH_3); 1.43(6p, m, CH_2); 2.3(1p, m, CH);
3.00(4p, m, $CH_2\alpha$ and βCF_2); 6.55-7.24(2p, m, N-H)

NMR ^{19}F, CD_3COCD_3 = -5.33(3f, t, CF_3); -38.54(2f, m, $CF_2\alpha CH_2$);
-46.11(6f, m, CF_2); -46.94(2f, m, $CF_2\gamma CF_3$); -47.69(2f, m, $CF_2\beta CF_3$);
-50.41(2f, m, $CF_2\alpha CF_3$).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoroeicosane
9 and 10-carboxamides 8

$C_8F_{17}-CH_2-\overset{|}{C}H-C_{10}H_{21}$ and $C_8F_{17}-\overset{|}{C}H-C_{11}H_{23}$

    (a) $CONH_2$ (b) $CONH_2$
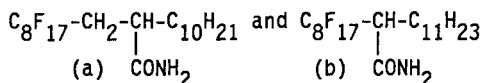
MW = 631   MP = 92°C; GLC = 2 peaks at 220°C and 245°C

IR = 3420 (N-H free); 3200 (N-H coupled); 1670 (C=O); 1200 (C-F)

NMR ^{1}H, CD_3COCD_3: 0.99 (3p, t, CH_3); 1.40(18p, m, CH_2); 2.40(1p, m, CH);
2.96(2p, m, $CH_2\alpha CF_2$); 6.50-7.19(2p, m, N-H)

NMR ^{19}F, CD_3COCD_3 = -5.31(3f, t, CF_3); -37.32(2f, m, $CF_2\alpha CH_2$);
-46.11(6f, m, CF_2); -46.94(2f, m, $CF_2\gamma CF_3$); -47.82(2f, m, $CF_2\beta CF_3$);
-50.43(2f, m, $CF_2\alpha CF_3$).

Determination of the regioselectivity

-For amides $C_8F_{17}-CH_2-\overset{|}{C}H-C_{10}H_{21}$ and $C_8F_{17}-\overset{|}{C}H-CH_2-C_{10}H_{21}$ (8) derived from the

                      $CONH_2$ (a) $CONH_2$ (b)

olefin $C_8F_{17}-CH=CH-C_{10}H_{21}$

   GLC of the mixture of the two amides gave two closely separated peaks (a
minor one at 220°C and a major one at 245°C). The ratio of the areas of the
two = 7.7:1.

   ^{1}H NMR of the mixture of the two isomers a and b showed the almost
exclusive presence of a (α CH_2 to the CF_2). The major peak (245°C) was thus
attributed to isomer a and the minor peak to isomer b.

-For amides $R_F-C_2H_4-\overset{|}{C}H-R_H$ and $R_F-CH_2-\overset{|}{C}H-R_H$ (5 - 7)

                $CONH_2$ (a) $CONH_2$ (b)

   GLC of the mixture of the two isomers produced two closely separated
peaks with similar intensities, except for olefin $C_4F_9-CH_2-CH=CH-C_8H_{17}$ for
which the ratio of areas was 2.89:1 (5)

   For these amides, proton and fluorine NMR was unable to identify or
determine the relative proportions of the two isomers.

   In the case where the ratio of the two GLC peaks was more selective
(2.89:1 for $C_4F_9-CH_2CH=CH-C_8H_{17}$) mass spectrometry was used to analyze the
mixture of the two amides after separation by GLC:

$C_4F_9-CH_2CH_2-\overset{|}{C}H-C_8H_{17}$ and $C_4F_9-CH_2-\overset{|}{C}H-C_9H_{19}$ (5)

    (a) $CONH_2$ (b) $CONH_2$
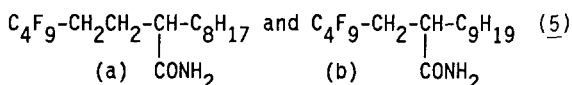
   The parent peak for the two isomers is M^+ = 417. The peak $(M+1)^+$ = 418 is
also observed. The breakages are essentially the same for both isomers with
successive losses of CH_3 and nCH_2.
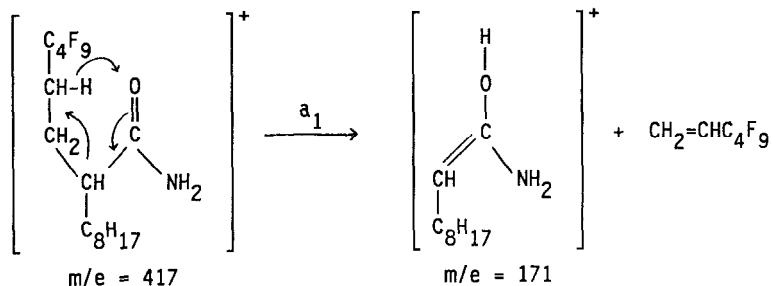
TABLE II

Elemental analyses of the fluorinated amides

No.	Empirical formula		C	H	N	F
1	$C_7H_6NF_9O$	r	28.87	2.06	4.81	56.76
		f	28.87	2.49	7.20	50.89
2	$C_9H_6NF_{13}O$	r	27.62	1.53	3.58	63.17
		f	27.72	1.46	3.45	63.02
3	$C_{11}H_6NF_{17}O$	r	26.88	1.22	2.85	65.78
		f	25.95	1.28	2.98	60.47
4	$C_{13}H_6NF_{21}O$	r	26.40	1.02	2.37	67.51
		f	28.52	1.69	3.58	61.74

TABLE III

Elemental analyses of the mixed amides

No.	Empirical formula		C	H	N	F
5	$C_{16}H_{24}NF_9O$	r	46.04	5.76	3.36	41.01
		f	46.36	5.88	3.56	40.09
6	$C_{14}H_{16}NF_{13}O$	r	36.44	3.47	3.04	53.58
		f	37.20	3.67	3.89	53.08
7	$C_{16}H_{16}NF_{17}O$	r	34.22	2.85	2.50	57.57
		f	34.28	2.75	3.45	55.19
8	$C_{21}H_{26}NF_{21}O$	r	39.07	4.03	2.17	50.08
		f	39.89	4.07	2.55	49.72

The two derivatives can also be differentiated by consideration of the various MacLafferty rearrangements:

Isomer a, product 5

$$\left[\begin{array}{c} C_4F_9 \\ CH-H \quad O \\ CH_2 \quad C \\ CH \quad NH_2 \\ C_8H_{17} \end{array} \right]^{+} \xrightarrow{a_1} \left[\begin{array}{c} H \\ O \\ C \\ CH \quad NH_2 \\ C_8H_{17} \end{array} \right]^{+} + \; CH_2=CHC_4F_9$$

m/e = 417   m/e = 171

Isomer a, product 5

$$\left[\begin{array}{c} C_6H_{13} \\ CH-H \quad O \\ CH_2 \quad C \\ CH \quad NH_2 \\ C_2H_4 \\ C_4F_9 \end{array} \right]^{+} \xrightarrow{a_2} \left[\begin{array}{c} H \\ O \\ C \\ CH \quad NH_2 \\ C_2H_4 \\ C_4F_9 \end{array} \right]^{+} + \; CH_2=CHC_6F_{13}$$

m/e = 417   m/e = 305

Isomer b, product 5

$$\left[\begin{array}{c} C_3F_7 \\ CF-F \quad O \\ CH_2 \quad C \\ CH \quad NH_2 \\ CH_2 \\ C_8H_{17} \end{array} \right]^{+} \xrightarrow[X]{b_1} \left[\begin{array}{c} F \\ O \\ C \\ CH \quad NH_2 \\ CH_2 \\ C_8H_{17} \end{array} \right]^{+} + \; CH_2=CFC_3F_7$$

m/e = 417   m/e = 329

Isomer b, product 5

$$\left[\begin{array}{c} C_7H_{15} \\ CH\text{-}H \quad O \\ CH_2 \quad C \\ CH \quad NH_2 \\ CH_2 \\ C_4F_9 \end{array}\right]^+ \quad \xrightarrow{b_2} \quad \left[\begin{array}{c} H \\ O \\ C \\ CH \quad NH_2 \\ CH_2 \\ C_4F_9 \end{array}\right]^+ \quad + \quad CH_2\!=\!CHC_7H_{15}$$

m/e = 417   m/e = 291
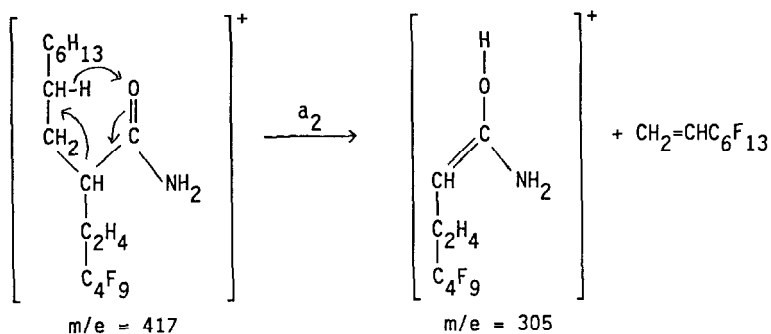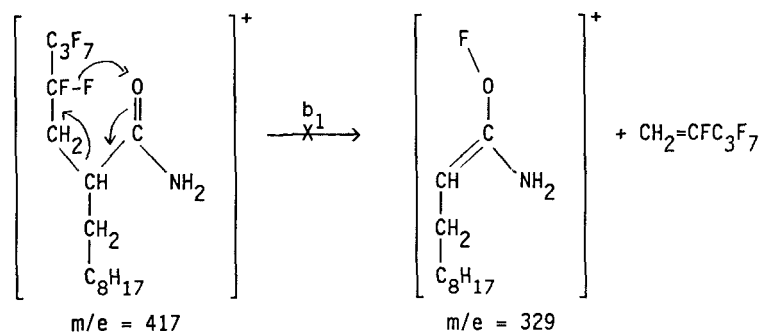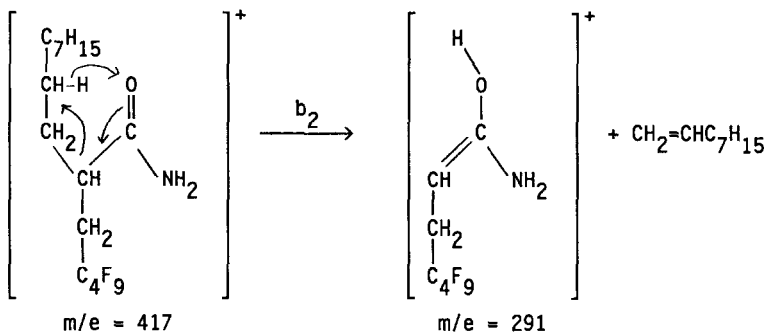
These rearrangements were supported by the spectral data:

GLC	Isomer		m/e	Intensity
Peak at 222°C	(a)	a_1	171	2.2
		a_2	305	20
Peak at 218°C	(b)	b_1	329	0.02
		b_2	291	18

The following comments can be made on these results:
i) the rearrangement b_1 is much less favored than b_2
ii) rearrangement a_2 is more favored than a_1
iii) the major isomer (a) leads to the peak at the higher temperature.

For the other derivatives of the mixed olefins $R_F\text{-}CH_2\text{-}CH\!=\!CH\text{-}R_H$ we assumed that the isomers (a) had the higher retention times.

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