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THE PREPARATION AND SPECTRAL CHARACTERIZATION OF A SERIES OF PERFLUOROALKYLENAMINES AND PERFLUOROALKYLENAMINOKETONES

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Abstract—A series of perfluoroalkylenamines of formula $R_FCF_2CH{=}CHNR_2$ has been obtained by the addition of secondary amines to perfluoroalkylethynes. Only the *E* isomer is formed. The dominant feature of their chemistry is the lability of the allylic C–F bonds, which is responsible for their instability and for the fact that acid hydrolysis yields mainly the enaminoketones $R_FCOCH{=}CHNR_2$, a reaction which provides a general route to this latter class of compounds. On the other hand, no alkylation, acylation or bromination was observed. The rotation around the C–N bond in the perfluoroalkylenaminoketones is strongly hindered ($\Delta G^{\neq} \simeq 17$–$18\,\mathrm{kcal.mole^{-1}}$). The spectroscopic characteristics of these two series of compounds are reported and discussed.

Enamines are important reagents in hydrocarbon chemistry, but their perfluoroalkylated analogues have received little attention as yet. Two methods for obtaining these compounds have been reported; they are based on the reaction of amines with 1 perfluoroalkenes and 2 perfluoroalkynes. However, method 1 gave in most cases a simple addition of the amine to the double bond, followed when the reaction conditions were more drastic by complex reactions involving the enamines as intermediates.[1] This route has only allowed the enamines to be isolated and characterized in two cases.[2,3] The second method has been employed less often, because there were few alkynes available.[2,4] The enamines which were obtained proved to be rather unstable, especially those derived from the 1-hydryl perfluoroalk-1-ynes, $R_FC{\equiv}CH$. Their reactivity and potential usefulness in synthesis have never been investigated.

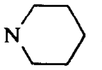
On the other hand, only one example of enaminoketone $C_3F_7COCH{=}CHNEt_2$ has previously been prepared in satisfactory yields. It was obtained in an unexpected reaction between triethylamine and perfluorobutyryl chloride. Its reactivity has not been investigated.

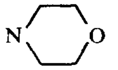
RESULTS AND DISCUSSION

The perfluoroalkylenamines 2 to 7 were obtained by the addition of secondary amines to hydryl-1-perfluoroalk-1-yne 1,[6] according to:[7]

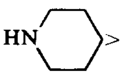
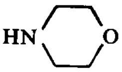
$$\underset{\mathbf{1}}{R_FCF_2C{\equiv}CH} + HNR_2 \longrightarrow \underset{\mathbf{2\text{–}7}}{R_FCF_2CH{=}CH\text{-}NR_2} \qquad (1)$$

$R_F = C_5F_{11}$ **1a**; C_7F_{15} **1b**.

$NR_2 = NEt_2$ **2**; $N(iBu)_2$ **3**; $N(CH_2Ph)_2$ **4**;  **5**:

 **6**:  **7**.

The reaction was performed in various solvents (CCl_4, $CHCl_3$, ether, dioxan, $CClF_2CFCl_2$). Its rate depends mainly on the basicity of the amine, and decreases in the following order:

$HNEt_2 \sim HN(iBu)_2 \sim$  >  >  ≫ $HN(CH_2Ph)_2$.

The stability of the enamines also depends on the amine, the most stable being 4 whose solutions can be stored for several days at 20°, and which decomposes rapidly only above 50°. They could all be preserved for several days when stored at 0° in solution, and were identified by IR and NMR (see Table 1).

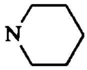
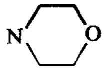
In CCl_4 solution they all show a very strong absorption band at $1650\,\mathrm{cm^{-1}}$ in the IR, which is assigned to the C=C stretching frequency. In the ^1H NMR spectra the value of the coupling constant between the vinylic protons (*ca.* 13 Hz) is characteristic of an *E* configuration of the double bond.[8] The presence of a *Z* isomer was never detected in the spectra, showing that reaction (1) is highly stereospecific. In the ^{19}F NMR spectra the most typical feature is the low value of the chemical shifts of the allytic fluorine atoms, which is *ca.* 5–15 ppm downfield from those found in general.[9]

The reactivity of the perfluoroalkylenamines differs profoundly from that of their hydrocarbon analogues: first, the nitrogen atom is far less basic and no *N*-alkylation was observed, for example with **3a** in the presence of a large excess of benzyl bromide, until decomposition occurred at *ca.* 50°. Similarly, no acylation could be performed on **2a** and **3a** in the usual conditions (at room temperature in dioxan in the presence of NEt_3).[10] Moreover, the double bond is less reactive with respect to electrophilic additions: no bromination was observed with compounds **2a** and **3a**, even at room temperature, whereas this reaction proceeds readily at −78° with the hydrocarbon analogues.[11]

The observed instability of the perfluoroalkylenamines seems only to arise from the mobility of the allylic fluorine atoms, as illustrated by their hydrolysis:

$$R_FCF_2CH{=}CHNR_2 \xrightarrow[35\text{–}40^\circ]{HCl\ 20\%} R_FCF{=}CH\text{-}CHO \quad \mathbf{8}$$
$$+\, R_FCOCH{=}CHNR_2 \quad \mathbf{9\text{–}14} \qquad (2)$$

Table 1. Spectroscopic data for the enamines **2** to **7**

	^{19}F and ^{1}H NMR δ (ppm)^a CF_3 —	CF_2—	$(CF_2)_n$—	CF_2 —	CH =	CH —	NR_2	J_{H-H} (Hz)	IR^b ν(C=C) (mc^{-1})
2a	80.0	124.9	121.0	102.4	4.01	6.76	NEt_2	12.5	1650
2b	80.0	123.5	119.6	101.7	4.08	6.65		13	1650
3a	80.0	124.8	120.8	102.4	3.97	6.76	$N(iBu)_2$	12.5	1650
3b	80.0	123.8	119.6	101.7	4.06	6.66		12	1650
4a	80.0	125.2	121.1	102.1	d	d	$N(CH_2Ph)_2$	d	1650
4b	80.4	124.6	120.4	102.9	4.43	c		12	1650
5a	80.0	124.9	121.1	102.0	d	6.73		13.5	1650
5b	80.0	123.8	120.0	102.1	4.18	6.60		13.5	1650
6a	80.0	124.8	120.8	102.2	3.95	6.90		13	1650
6b	79.6	123.8	120.4	101.3	d	6.90		13	1650
7a	80.0	125.2	121.0	102.4	4.26	6.60		13.5	1650
7b	80.0	123.8	120.4	102.9	d	d		d	1650

[a] In ppm from CCl_3F or TMS (CCl_4 solution).

[b] In CCl_4 solution.

[c] Masked by the resonances of the aromatic protons.

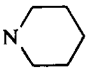
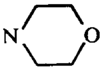
[d] Not detected owing to the low solubility of the compound.

In the crude reaction mixture the most abundant products (55–95%) are the enaminoketones **9** to **14**. The amounts of the aldehydes **8** are always less than 15%. This behaviour of the perfluoroalkylenamines can be rationalised on the basis of an anchimeric assistance by the nitrogen lone pair, as suggested in the case of 3-trifluoromethylindoles.[12] Similar behaviour was also observed in the case of some perfluorocycloalkenyl amines.[13] This hydrolysis reaction thus provides a general method of preparation of perfluoroalkylenaminoketones, which is specific to fluorocarbon chemistry.

The enaminoketones **9** to **14** were isolated in 15–46% yields. They are very stable crystalline compounds which are readily soluble in the usual organic solvents. As in the case of the perfluoroalkylenamines, their chemistry differs substantially from that of their hydrocarbon analogues. They do not readily react with electrophilic agents: for example, we observed no reactions between **10b** and benzyl bromide or benzoyl chloride after refluxing for 2 h in benzene or dioxan, neither did bromine add to **10b** at room temperature in the absence of light.

The NMR and IR spectroscopic data for **9** to **14** are given in Table 2. These compounds exhibit in the IR two strong bands, at 1670 and 1580 cm^{-1}, which are characteristic of enaminoketones in the s-*cis* conformation.[14] The *E* configuration of the C=C band is confirmed by the values of the coupling constants (J ≃ 11–12 Hz) between vinylic protons.[15]

Table 2. Spectroscopic data for the enaminoketones **9** to **14**

Compound	^{19}F and ^{1}H NMR δ (ppm)^a CF_3 —	CF_2 —	$(CF_2)_n$—	CF_2-CO—	CH =	CH —	NR_2	J_{H-H} (Hz)	IR^b (cm^{-1}) ν(C=O)	ν(C=C)
9a	81.6	126.6	123.4	119.9	5.15	7.84	NEt_2	12	1675 m	1580 S
9b	81.6	127.1	123.7	121.6	5.40	7.99		11	1675 m	1580 S
10a	81.6	127.4	123.4	120.9	5.16	7.76	$N(iBu)_2$	12	1675 m	1575 S
10b	81.2	127.1	123.4	120.9	5.51	8.05		11	1675 m	1575 S
11a	82.6	127.8	124.2	121.7	5.55	8.33	$N(CH_2Ph)_2$	12	1680 m	1570 S
11b	81.6	127.1	123.7	120.9	5.60	8.45		11	1680 m	1570 S
12a	81.6	127.1	123.4	120.9	5.26	7.82		12	1675 m	1580 S
12b	82.1	127.1	123.7	120.9	5.30	7.75		11	1675 m	1580 S
13a	82.1	127.1	123.4	120.9	5.12	7.90		12	1680 m	1580 S
13b	81.6	127.1	123.2	121.6	5.39	7.87		11	1695 m	1580 S
14a	82.1	127.4	123.7	121.2	5.30	7.90		12	1675 m	1580 S
14b	82.6	127.1	122.9	120.9	5.38	7.87		11	1680 m	1580 S

[a] In ppm from CCl_3F or TMS (CCl_4 solution).

[b] In CCl_4 solution.

Table 3. Mass spectra of the enaminoketones **9** to **14**

Compound	M^+	$(M\text{-}F)^+$	$(M\text{-}F\text{-}CO)^+$	$(M\text{-}R_F{}^a)^+$	$(M\text{-}R_FCO)^+$
9a	395	376	348	$\underline{126}$	98
9b	495	476	448	$\underline{126}$	98
10a[b]	451	432	404	182	154
10b[b]	551	532	504	182	154
11a[c]	519	500			222
11b[c]	619	600	572	250	222
12a	407	388	360	$\underline{138}$	110
12b	507	488	460	$\underline{138}$	110
13a	393	374	346	$\underline{124}$	96
13b	493	474	446	$\underline{124}$	96
14a	409	390	362	$\underline{140}$	112
14b	509	490	462	$\underline{140}$	112

[a] The underlined value of *m/e* represents the most abundant ion.

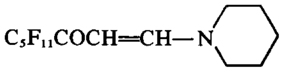
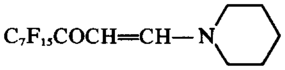
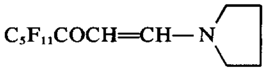
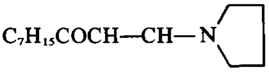
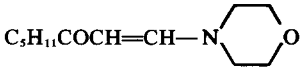
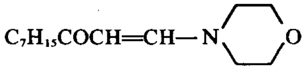
[b] The most abundant ions were due to fragmentation on the alkyl chain:

$$|M\text{-}C_3H_7|^+ \quad \text{and} \quad \underline{|M\text{-}C_4H_8\text{-}C_3H_7|^+}$$

[c] The most abundant ions involve the benzylic group:

$|M\text{-}C_7H_8|^+$ by a McLafferty rearrangement; $|M\text{-}C_7H_8\text{-}C_2H_2|^+$; $|M\text{-}R_F\text{-}C_3H_3|^+$; $|M\text{-}R_FCO\text{-}C_7H_8|^+$; $|C_7H_5N|^+$ and $\underline{|C_7H_7|^+}$.

Table 4. Analytical data for the enaminoketones **9** to **14**

Compound	b.p.† or m.p. (°C)	Yield (%)	Analysis		C%	H%	F%
$C_5F_{11}COCH{=}CHNEt_2$ **9a**	95/0.1†	39	Calc. Found	: :	36.40 36.36	3.03 3.23	52.91 52.71
$C_7F_{15}COCH{=}CHNEt_2$ **9b**	105–110/0.25†	35	Calc. Found	: :	33.94 33.80	2.42 2.25	57.58 57.15
$C_5F_{11}COCH{=}CHN(iBu)_2$ **10a**	74	40	Calc. Found	: :	42.57 42.35	4.43 4.46	46.34 46.63
$C_7F_{15}COCH{=}CHN(iBu)_2$ **10b**	80	35	Calc. Found	: :	39.20 39.24	3.63 3.73	51.72 51.64
$C_5F_{11}COCH{=}CHN(CH_2Ph)_2$ **11a**	60	15	Calc. Found	: :	50.87 52.64	3.08 3.02	40.27 40.21
$C_7F_{15}COCH{=}CHN(CH_2Ph)_2$ **11b**	56	15	Calc. Found	: :	46.53 46.88	2.58 2.72	46.04 45.52
 **12a**	76	30	Calc. Found	: :	38.33 38.27	2.95 2.98	51.35 51.79
 **12b**	78	30	Calc. Found	: :	35.50 35.47	2.37 2.35	56.21 56.07
 **13a**	82	46	Calc. Found	: :	36.64 36.49	2.54 2.56	53.18 53.14
 **13b**	86	42	Calc. Found	: :	34.08 34.16	2.03 2.09	57.95 57.66
 **14a**	88	30	Calc. Found	: :	35.20 35.08	2.44 2.37	51.10 51.01
 **14b**	91	30	Calc. Found	: :	33.01 33.07	1.96 1.98	55.99 55.75

†mm Hg.

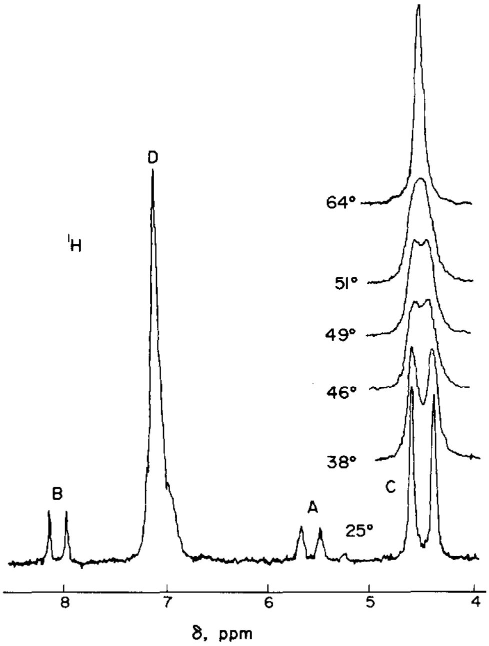


Fig. 1. Variable temperature ^{1}H NMR spectra of $C_7F_{15}CO\underset{A}{CH}{=}\underset{B}{CH}N(\underset{C}{CH_2}\underset{D}{C_6H_5})_2$ **11b** (0.5 molar solution in CCl_3F).

Variable-temperature NMR studies show that the rotation around the C–N bond is strongly hindered, the activation barrier being about 17–18 kcal.mode^{-1}, i.e. 3–4 kcal.mole^{-1} higher than that for the hydrocarbon analogues.[16] This is in accordance with the enhanced polar character of the ethylenic bond where the nitrogen is the positive end and the perfluoroacyl group the negative one. As a consequence the magnetic inequivalence of the two CH_2 groups bound to nitrogen is already observed at room temperature for all the perfluoroalkylenaminoketones reported here. This is exemplified in Fig. 1, which displays the variable-temperature ^{1}H NMR spectra of **11b**.

The mass spectra of the perfluoroalkylenaminoketones (Table 3) exhibit many characteristic features: in most cases the base peak corresponds to the $(O{\equiv}C{-}C{=}CHNR_2)^+$ ion. Another fragmentation path consists in an extrusion of CO from the parent ion, as shown by the observation of the $(M{-}F{-}CO)^+$ ion in all the spectra.

The aldehydes $R_FCF{=}CH_ACH_B{=}O$ **8** were easily characterized by their IR ($\nu(C{=}C) = 1.680\,cm^{-1}$; $\nu(C{=}O) = 1.705\,cm^{-1}$) and ^{1}H NMR spectra ($\delta\ H_A = 7.00$; $\delta\ H_B = 11.75$ ppm). The value of J_{H_AF} (36 Hz) indicates that these compounds adopt the *E* configuration.

EXPERIMENTAL

General. The ^{1}H and ^{19}F NMR spectra were run on a JEOL C-60 HL spectrometer, the IR spectra on a Perkin–Elmer 577 and the mass spectra on an AEI MS 12 spectrometer. The VPC analyses were performed on a CARLO ERBA Fractovap 2400 T, filled with a 3 m × 2 mm column packed with 10% QFl on Chromosorb CWR 80–100.

Preparation of enamines **2** *to* **7**. The amine (46 mmoles) in 20 ml of solvent (ether, dioxan, $CHCl_3$, CCl_4 or CF_2ClCCl_2F) is added dropwise to a molar solution of the 1-hydryl perfluoroalk-1-ynes (40 mmole). The temperatures and reaction times are as follows: **2** (0°, 3 h); **3** (0°, 3 h); **4** (50°, 36 H); **5** (20°, 6 h); **7** (35°, 6 h). The solutions can be stored for several days at 0°.

Preparation of the enaminoketones **9** *to* **14**. 50 ml of 20% aqueous HCl is added to the enamine solution at 0°. The mixture is then heated under agitation to 35–40° for 30 min. After cooling and separation of the aqueous phase, the organic phase is washed with 10 ml H_2O, then with 3 × 10 ml of a saturated $NaHCO_3$ solution, and again with 2 × 10 ml H_2O, and is dried over molecular sieves. The solvent is distilled off and the residue recrystallized from pentane. Melting points, yields and microanalyses are given in Table 4.

Isolation of the aldehydes **8**. The aldehydes **8** were separated from the *N,N*-dibenzylenaminoketones **11** by vacuum distillation of the residue obtained after the evaporation of the solvent (see above). **8a**: $C_5H_{11}CF{=}CH{-}CHO$; b.p. 32° (12 mm); (Found: C, 28.40; H, 0.86; F, 60.93. Calc. for $C_8H_2F_{12}O$: C, 28.07; H, 0.57; F, 66.67%). **8b**: $C_7F_{15}CF{=}CHCHO$; b.p. 59° (12 mm); (Found: C, 27.93; H, 0.56; F, 66.39. Calc. for $C_{10}H_2F_{16}O$: C, 27.15; H, 0.45; F, 68.78%).

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