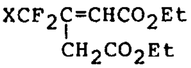
Journal of Fluorine Chemistry, *35* (1987) 343–357
Received: May 6, 1986; accepted: October 12, 1986

STUDIES ON FLUOROALKYLATION AND FLUOROALKOXYLATION. PART 16. REACTIONS OF FLUOROALKYL IODIDES WITH SOME NUCLEOPHILES BY $S_{RN}1$ MECHANISM

QING-YUN CHEN* and ZAI-MING QIU

Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu, Shanghai (China)

SUMMARY

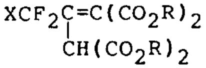
Fluoroalkyl iodides, XCF_2CF_2I ($X=ClCF_2CF_2$, $Cl(CF_2)_4$) (1), react readily with the anion of ethyl acetoacetate (2) in DMF to give  $XCF_2\underset{CH_2CO_2Et}{\underset{|}{C}}=CHCO_2Et$ (3), XCF_2CF_2H (4), $(CH_3CO)_2CHCO_2Et$ (5) and the dimer of the anion (6). The reaction can be partly suppressed with 1,4-dinitrobenzene(p-DNB) and the radical intermediate can be trapped by diallyl ether (DAE) to give the tetrahydrofuran derivatives. Anions of acetylacetone and malonitrile react also with 1 in the presence of DAE to yield the five-membered ring compounds. All these results seem to indicate that the reaction is a radical chain process induced by electron transfer. In the case of XCF_2CF_2I (X=Cl,I), tetrafluoroethylene and 6, instead of 3 and 4, are produced, showing the occurrence of β-fragmentation of the 2-halotetrafluoroethyl radical in the initiation step.

---

* Formerly spelled as Ching-yun Chen

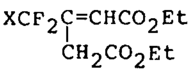
0022-1139/87/$3.50

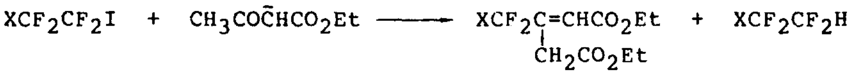
INTRODUCTION

It has been found that 1,3-dicarbonyl enolate anion is a good electron donor in organic chemistry, which can react with numerous electron accepters through the radical chain substitution reaction ($S_{RN}1$) [1-3]. There are, however, few examples involving fluoroalkyl iodide used as the electron accepter in these reactions. Yagupolskii *et al*. have reported that acetylacetone reacted with perfluoroalkyl iodide under irradiation to give the fluoroalkylated product in liquid ammonia [4]. However, the addition of perfluoroalkyl iodide to the sodium salt of diethyl methylmalonate gave only 1-H-perfluoroalkane and the dimer of the anion [5]. Recently, we found that the malonate anion could be fluoroalkylated smoothly with fluoroalkyl iodide under mild conditions to give  $XCF_2\underset{CH(CO_2R)_2}{\underset{|}{C}}=C(CO_2R)_2$ by $S_{RN}1$ mechanism [6].

This paper presents the results of the reaction of fluoroalkyl iodide with sodium acetoacetate and the evidence for the single electron transfer of the anions of acetylacetone and malonitrile to fluoroalkyl iodides in the presence of diallyl ether.

RESULTS AND DISCUSSION

Fluoroalkyl iodide (1) reacted readily with sodium ethyl acetoacetate (2) (1:2=1:4) in dimethylformamide (DMF) at 75°C for 10h to give  $XCF_2\underset{CH_2CO_2Et}{\underset{|}{C}}=CHCO_2Et$ (3, ~50%), 1-H-ω-Cl-perfluoroalkane (4, ~20%), ethyl α,α-diacetyl acetate (5) and a small amount of the dimer of the anion (6):



$$XCF_2CF_2I + CH_3CO\overset{-}{C}HCO_2Et \longrightarrow XCF_2\underset{\displaystyle CH_2CO_2Et}{C}{=}CHCO_2Et + XCF_2CF_2H$$

1 2 3 4

$$+ (CH_3CO)_2CHCO_2Et + (CH_3COCHCO_2Et)_2 + CH_3COCH_2CO_2Et$$

5 6 7

$X=Cl(CF_2)n$, $n=2(a)$, $4(b)$

The structure of 3 was identified by elemental analyses, IR, proton and fluorine NMR spectra as well as mass spectroscopy.The conversion of the reaction varied with the ratio of 1:2, and decreased to 50% when additional amounts of ethyl acetoacetate (25%) were added. If ethyl acetoacetate itself was used as the solvent instead of DMF, the reaction did not occur. Similar to the reaction of 1 with malonate anion(6),almost quantitative yields of tetrafluoroethylene (8),considerable amounts of 6, instead of the normal products 3 and 4, were obtained when X was chlorine or iodide.

$$\underset{\displaystyle 1}{XCF_2CF_2I} + 2 \longrightarrow \underset{\displaystyle 8}{CF_2{=}CF_2} + 6 + I_2$$

$X=Cl(c)$, $I(d)$

This kind of reaction could be partially suppressed by the single electron transfer scavenger, 1,4-dinitrobenzene (p-DNB), and the conversion decreased to 50% in the presence of 20% mol (relative to 2) of p-DNB as compared with that of the control. In the presence of diallyl ether (DAE), the five-membered ring compounds were formed in high yield. The main products for 1 (a,b) were 9 and 10, tetrafluoroethylene and a small amount of 9 for 1c, and only tetrafluoroethylene for 1d. These results are summarised in Table 1.

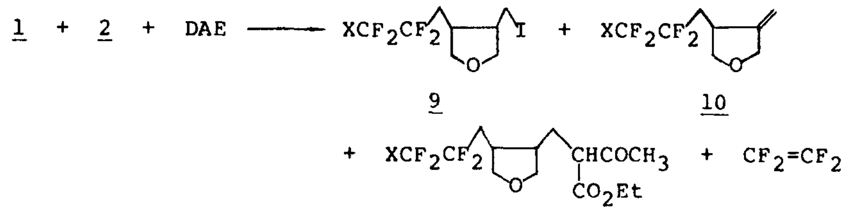
TABLE 1

The reaction of R_fI with sodium ethyl acetoacetate(2) in DMF^{a}

Entry	Reactants(ratio)	T°C	t(h)	Conv.(%)^{b}	Products(%)	
1	1a + 2 (1:4)	75	10	75.6	3(65.9)	4(20.7)
2	1b + 2 (1:4)	70	10	78.3	3(60.8)	4(24.1)
3	1a + 2 (1:6)	75	12	88.3	3(75.9)	4(19.6)
4	1b + 2 (1:6)	75	10	90.3	3(70.3)	4(22.1)
5	1c + 2 (1:2)	60	5	100	6(67.2)	8(91.2)
6	1d + 2 (1:3)	60	5	100	6(55.3)	8(96.3)
7	1a + 2 + 7(1:4:1)	75	15	52.2	3(49.2)	4(33.8)
8	1a + 2 + (p-DNB) (1:4:20%)	75	10	67.8	3(63.3)	4(19.5)
9	1a + 2 + (p-DNB) (1:4:80%)	75	10	50.9	3(58.8)	4(16.2)
10	1a + 2 + DAE (1:4:4)	75	10	94.5	9(35.6) 11(~7)	10(43.7) 6(30.3)
11	1b + 2 + DAE (1:4:4)	70	14	84.3	9(30.5) 11(~9)	10(53.9) 6(35.5)
12	1a + 2 + DAE (1:2:4)	75	10	80.5	9(40.2) 6(29.1)^{c}	10(43.8)
13	1c + 2 + DAE (1:1:4)	60	5	90.3	6(40.2) 9(19.1)	8(63.7)
14	1d + 2 + DAE (1:2:4)	60	5	93.7	6(48.3)	8(90.5)

[a] A small amount of 6 and some 5 were obtained in Entry 1 to 4 and 7 to 9.

[b] determined by ^{19}F NMR; c:a small amount of 11 was obtained.



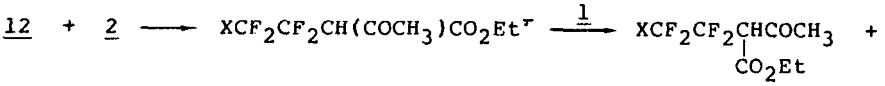
9 10

11

All these results seem to show that the reaction may involve a radical chain nucleophilic substitution ($S_{RN}1$) mechanism as follows:

$$\begin{tikzcd}[column sep=small]
\underset{\underline{1}}{XCF_2CF_2I} & + & \underset{\underline{2}}{CH_3CO\bar{C}HCO_2Et} \arrow[r] & XCF_2CF_2I^{\overline{\cdot}} \arrow[d] & + & \underset{\underline{13}}{CH_3CO\dot{C}HCO_2Et} \\
 & & & \underset{\underline{12}}{XCF_2CF_2^{\cdot}} \quad + \quad I^- & &
\end{tikzcd}$$

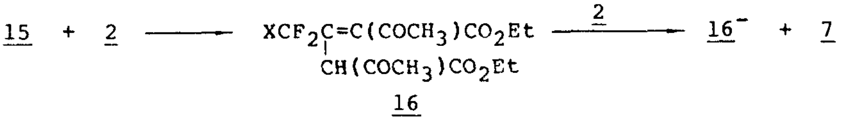
$$\underline{12} + {}^{\cdot}H^{\cdot} \longrightarrow \underset{\underline{4}}{XCF_2CF_2H}$$



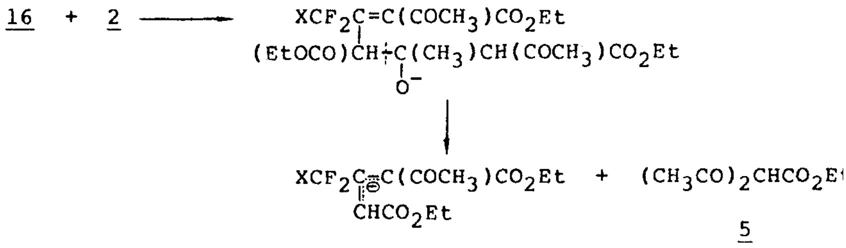
$$\underline{12} + \underline{2} \longrightarrow XCF_2CF_2CH(COCH_3)CO_2Et^{\overline{\cdot}} \xrightarrow{\underline{1}} \underset{\underline{14}}{XCF_2CF_2\underset{CO_2Et}{\underset{|}{C}}HCOCH_3} + \underline{12} + I^-$$

$$2 \times \underline{13} \longrightarrow \underline{6}$$

$$\underline{14} + \underline{2} \longrightarrow \underset{\underline{15}}{XCF_2CF{=}C(COCH_3)CO_2Et} + \underset{\underline{7}}{CH_3COCH_2CO_2Et} + F^-$$



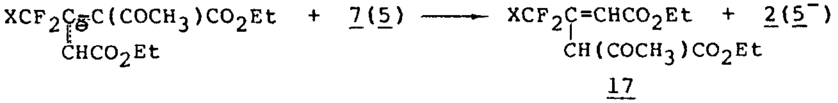
$$\underline{15} + \underline{2} \longrightarrow \begin{array}{l} \mathrm{XCF_2C{=}C(COCH_3)CO_2Et} \\ \quad \mathrm{CH(COCH_3)CO_2Et} \\ \qquad \underline{16} \end{array} \xrightarrow{\underline{2}} \underline{16}^- + \underline{7}$$



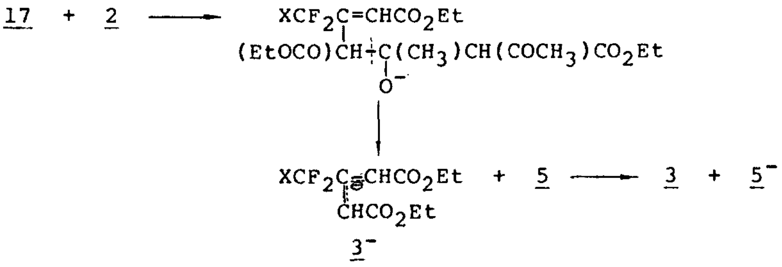
$$\underline{16} + \underline{2} \longrightarrow \begin{array}{l} \mathrm{XCF_2C{=}C(COCH_3)CO_2Et} \\ \mathrm{(EtOCO)CH{-}C(CH_3)CH(COCH_3)CO_2Et} \\ \qquad\quad \mathrm{O^-} \end{array}$$

$$\downarrow$$

$$\begin{array}{l} \mathrm{XCF_2C\overset{\ominus}{=}C(COCH_3)CO_2Et} \\ \quad \mathrm{CHCO_2Et} \end{array} + \begin{array}{c} \mathrm{(CH_3CO)_2CHCO_2E} \\ \underline{5} \end{array}$$



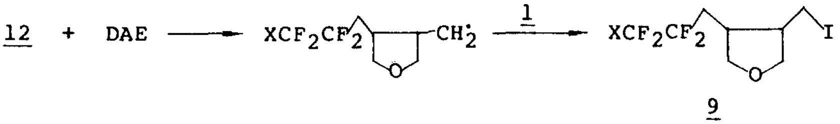
$$\begin{array}{l} \mathrm{XCF_2C\overset{\ominus}{=}C(COCH_3)CO_2Et} \\ \quad \mathrm{CHCO_2Et} \end{array} + \underline{7}(\underline{5}) \longrightarrow \begin{array}{l} \mathrm{XCF_2C{=}CHCO_2Et} \\ \quad \mathrm{CH(COCH_3)CO_2Et} \\ \qquad \underline{17} \end{array} + \underline{2}(\underline{5}^-)$$

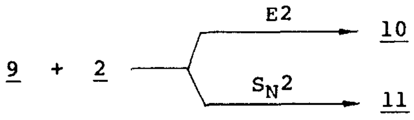


$$\underline{17} + \underline{2} \longrightarrow \begin{array}{l} \mathrm{XCF_2C{=}CHCO_2Et} \\ \mathrm{(EtOCO)CH{-}C(CH_3)CH(COCH_3)CO_2Et} \\ \qquad\quad \mathrm{O^-} \end{array}$$

$$\downarrow$$

$$\begin{array}{l} \mathrm{XCF_2C\overset{\ominus}{=}CHCO_2Et} \\ \quad \mathrm{CHCO_2Et} \\ \quad \underline{3}^- \end{array} + \underline{5} \longrightarrow \underline{3} + \underline{5}^-$$

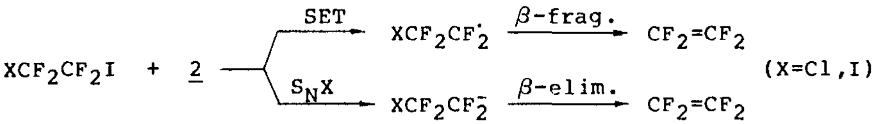




$$\underline{9} + \underline{2} \longrightarrow \begin{cases} \xrightarrow{\mathrm{E2}} \underline{10} \\ \xrightarrow{\mathrm{S_N2}} \underline{11} \end{cases}$$

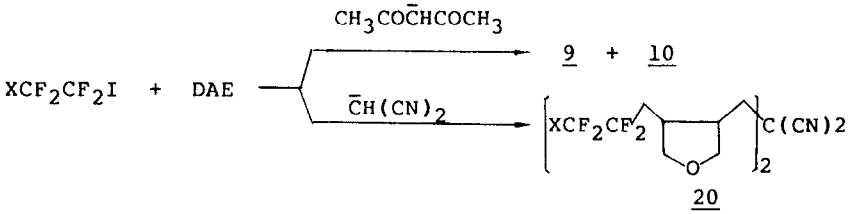
Similar to the reaction of malonate anion with R_fI(6), we could not find the presence of the products 14 and 15. The final product 3 may be explained by the $S_{RN}1$ process followed by elimination-addition steps and nucleophilic attack of 2. The formation of ethyl α,α-diacetyl acetate (5) may be evidence for the nucleophilic attack of 2 on 16. This regiospecific addition to simple carbonyl group of acetoacetate ester rather than that of Michael system probably due to the higher polarizability and lesser hindrance of the former. The products 10 and 11 in the presence of DAE, may come from the competition reactions of E2 and S_N2 for 9 with 2.

The generation of tetrafluoroethylene in the reaction of 2 with 1(c,d) could be explained by the β-fragmentation of 2-halotetrafluoroethyl radical by a SET process with or without β-elimination of 2-halotetrafluoroethyl anion as suggested previously [6,7]:



The appearance of the dimer of the anion, 6, in high yield, is undoubtedly a good indication for the intermediacy of the acetoacetate radical. In view of the synthetic application, it is a convenient, effective and cheap method for preparation of such dimers, e.g. 6, $(RS)_2$, $[CH(CO_2R)_2]_2$,$(Me_2CNO_2)_2$ etc.. Some of them are useful chemicals, e.g. 6 is an excellent perfume additive.

As mentioned above, acetylacetone has been perfluoroalkylated by perfluoroalkyl iodide through irradiation in liquid ammonia [4]. We also tried to fluoroalkylate the anions of acetylacetone (18) as well as malonitrile (19) under our conditions . However, we failed to isolate the pure products because the reactions were sluggish. The conversions were quite low (<30%),and workup of the reaction mixture met with difficulties although the fluorine NMR spectra clearly showed that $S_{RN}1$ reaction did occur.Fortunately, however, the fluoroalkyl radicals generated by SET of the anions of 18 and 19, could be trapped by DAE to give the pure fluoroalkyl tetrahydrofuran derivatives in good yield [8].



$X=Cl(CF_2)_2$, $Cl(CF_2)_4$, $CF_3(CF_2)$ (e)

The major product for 18 was 10, and single product 20 for 19. The results are given in Table 2.

The product 10 may be explained by subsequent elimination of 9, and 20, the product of malonitrile anion with 1, may come from a double nucleophilic substitutions on 9:

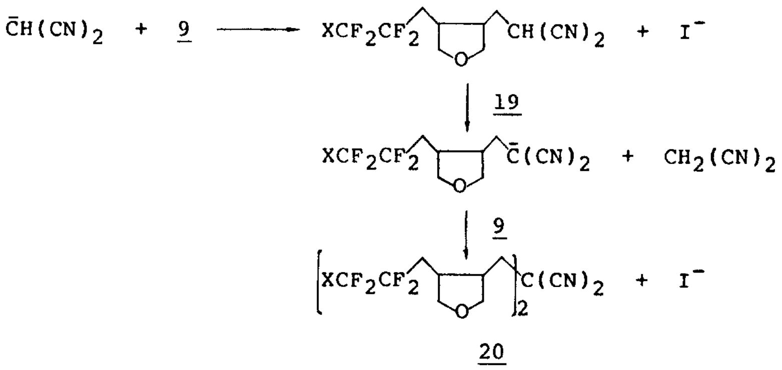


TABLE 2

The reaction of R_fI with the anions of acetylacetone(18) and malonitrile (19) in the presence of DAE[a]

Entry	Reactants(ratio)	T°C	t(h)	Conv.(%)[b]	Products(%)[c]
15	18+1a+DAE(3:1:3)	70	10	86.1	4(~4) 9(11.2) 10(69.3)
16	18+1b+DAE(3:1:3)	70	10	82.7	4(7.5) 9(8.8) 10(63.4)
17	18+1d+DAE(2:1:3)	75	5	95.3	8(90.2) 6(58.3)
18	19+1a+DAE(4:1:4)	90	5	91.2	4(7.8) 20(62.2)
19	19+1b+DAE(4:1:4)	85	5	93.5	4(14.8) 20(54.8)
20	19+1e+DAE(4:1:4)	90	5	88.2	4(8.3) 20(64.3)

[a] In DMF.

[b] Determined by ^{19}F NMR.

[c] Isolated yield, a small amount of 11 was detected (^1H; ^{19}F and MS) in Entry 15 and 16.

EXPERIMENTAL

All boiling points and melting points were uncorrected. GC spectra were measured on a Shanghai Model 103 with column packing with oxaperfluoroalkyltriazine polymer on 100 mesh 102 support.IR spectra were taken on a Shimedzu IR-440 spectrometer. NMR spectra (chemical shifts in ppm from external TMS for ^1H NMR and from external TFA for ^{19}F NMR positive for upfield shifts) were recorded on a EM-360 NMR spectrometer at 60 MHz. ^{13}C NMR spectrum was taken on FX-90 Q (90MHz). Mass spectra were measured on MS-4021. All solvents and reagents were purified prior to use and all reactions were carried out under the atmosphere of pure nitrogen.

General procedure

In a 250 ml three-necked flask, fitted with a magnetic stirrer, nitrogen inlet and condenser with a desiccator, were placed 6.1 g (40 mmol) dried powder of 2, which was made by the reaction of ethyl acetoacetate with sodium in ethanol, and 50 ml of DMF. While heating the solution at 75°C, 3.6 g of (10m mol) of 1a was added rapidly in one portion. The colour of the solution rapidly became red-black. After stirring the mixture at this temperature for 10h, 75% conversion was reached.Distillation gave 0.7 g of 1a and 0.5 g of 4a(20.7%).After quenching the reaction with dilute hydrochloric acid the mixture was extracted three times with 150 ml of dichloromethane. The combined extracts were washed three times with water and dried over anhydrous $MgSO_4$.After evaporation of solvent,the residue was distilled to give a small amount of 5,[b.p. 82°C/2mmHg (lit.[9], 45°C/0.2mmHg), MS m/e 173($M+1^+$), 172,(M^+),157, 143, 127, 129, 99, 85, 43;], 6 as well as 2.4 g of 3a (65.8%) b.p. 120°C/ 5mmHg. IR (film) 2995, 2850, 1750, 1728, 1665, 1375, 1325, 1180, 1120, 1030, 845, 668 cm^{-1}; ^{1}H NMR δ 6.20(s,1H),3.93(q,2H), 3.71(q,2H), 3.46(s,2H), 1.02(t,3H), 0.97(t,3H) ppm; ^{19}F NMR δ -10.3(t,2F), 35.8(t,2F), 42.6(s,2F) ppm; MS m/e: 373, 371, 327, 325, 297, 299, 270, 269, 197, 185, 183, 137, 135, 131, 130, 100, 87, 85,74, 73, 43; Analyses: Found, C,38.32,H,3.70, F,30.75, Cl, 9.02; $C_{12}H_{13}O_4F_6Cl$,requires, C,38.87, H,3.51, F,30.77, Cl,9.58.

3b: b.p. 103°C/1.2mmHg; IR (film) 2995, 2900, 2805, 1755, 1725, 1665, 1470, 1450,1420, 1375, 1275, 1220-1140, 1105, 1080, 1025, 780, 710 cm^{-1}; ^{1}H NMR δ 6.25(s,1H), 4.04(q,2H), 3.91(q,2H), 3.52(s,2H), 1.15(t,3H), 1.10(t,3H) ppm; ^{19}F NMR δ -10.3(t, 2F), 35.9(s,2F), 42.3(m,4F), 43.2(m.2F) ppm; MS m/e: 471, 473, 425, 427, 379, 399, 396, 398, 368, 370, 351, 353, 135, 137, 85, 87, 74, 69, 45; Analyses: Found, C,35.73, H,2.77, F,40.29; Cl, 7.29; $C_{14}H_{13}O_4F_{10}Cl$, requires: C,35.71, H.2.78, F,40.38, Cl,7.55.

Reaction of 1a with 2 in the presence of p-DNB

To a solution of 6.1 g(40 mmol) of 2 in 40 ml of DMF, 3.6 g (10mmol) of 1a and 1.3 g (0.8 mmol) of p-DNB were added. The vigorously stirred mixture was maintained at 75°C for 10h. The conversion decreased to 50.9% as shown by ^{19}F NMR as compared with that of control (75.6%). The products, 3 to 4, were in a ratio 3.7:1 (see Table 1).

Reaction of 1c,1d with 2

A solution of 1.5 g (10 mmol) of 2 in 20 ml of DMF was treated with 1.8 g (5mmol) of 1c at 60°C. The reaction mixture was stirred at this temperature for 5h,and 123 ml of tetrafluoroethylene was collected (91.2%). After hydrolysis of the mixture with dilute hydrochloric acid, 0.87 g (3.4 mmol) of 6 was obtained by filtration (67.2%), m.p. 87-88°C (lit.[10], m.p.88°C).

Reactions of 1 with 2 in the presence of DAE

Typical procedure:

To a solution of 6.0 g (40mmol) of 2 in 30 ml of DMF was added 3.9 g (40mmol) of DAE and then 4.6 g (10 mmol) of 1b. The mixture was stirred at 70°C for 14h. The conversion reached 84%(^{19}F NMR).After hydrolysis with dilute hydrochloric acid and filtration, 1.5 g (5.8 mmol) of 6 was obtained. Distillation gave 2.2 g (3.9mmol) of 9b(39%), 1.9 g (4.4 mmol) of 10b (43.7%) and trace of 11b.

9b:b.p. 132°C/3mmHg; IR (film), 2995, 2800,1440,1380,1400,1100-1280, 1090, 1000, 945, 790, 740, 700, 640 cm^{-1}; ^{1}H NMR δ 2.2-4.5(m) ppm; ^{19}F NMR δ -10.2(s,2F), 35.6(s,2F), 42.3(s,2F), 43.5(s,4F), 45.5(s,2F) ppm; MS m/e: 561, 563, 433, 435, 403, 405, 383, 385, 335, 213, 100, 97, 85, 87, 77, 73, 69, 65, 59, 55, 43, 41; Analyses: Found, C,26.04, H,1.80, F,40.54; $C_{12}H_{10}OF_{12}ClI$, requires: C,25.69, H,1.78, F,40.68.

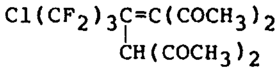
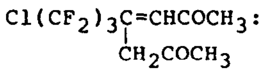
10a: b.p.57°C/3mmHg; IR (film) 3025, 3005, 2995, 2900, 2895, 1675, 1440, 1365, 1315, 1265, 1190, 1140, 1080, 1030, 975, 940, 900, 845, 800, 745, 705, 670 cm^{-1}; ^1H NMR δ 4.95(m,2H), 4.22 (s,2H), 2.0-4.2(m,7H) ppm; ^{19}F NMR δ -10.2(t,2F), 35.3(s,2F), 41.9(s,2F), 44.9(s,2F) ppm; MS m/e : 332, 334, 315, 317, 302, 239, 151, 85, 87, 83, 43; Analyses: Found, C, 35.99, H,2.71, F,45.91, Cl,10.40; $C_{10}H_9OF_8Cl$, requires, C,36.09, H,2.71, F,45.71, Cl,10.68.

10b: b.p. 85°C/3mmHg; IR (film) 3020, 3000, 2900, 2850, 2730. 1672, 1438, 1360, 1315, 1210, 1150, 1075, 1025, 990, 940, 900, 780, 670 cm^{-1}; ^1H NMR δ 4.38(m,2H), 4.13(s,2H), 4.02(d,1H), 2.97(t,1H), 1.9-2.2(m,3H) ppm; 19F NMR δ -9.1(t,2F), 36.3 (s,2F), 43.2(s,2F),44.3(s,4F), 46.5(s,2F)ppm; MS m/e: 435, 433, 434, 432, 415, 417, 117, 85, 87, 83, 69, 67, 57, 55, 43, 41; Analyses: Found,C,32.89, H,1.98, F,52.52, Cl,8.09; $C_{12}H_9OF_{12}Cl$, requires, C,33.29, H,2.08, F,52.72, Cl,8.21.

11a: b.p. 138°C/3mmHg; IR (film) 3020, 2995, 2820, 1750, 1725, 1630, 1445, 1370, 1190, 1140, 1066, 980, 850, 800, 675 cm^{-1}; ^1H NMR δ 4.08(q,2H), 2.11(s,3H), 1.22(t,3H), 1.55-3.94(m,11H) ppm; ^{19}F NMR δ -10.3(t,2F), 34.5(s,2F), 41.0(t,2F), 44.0(s, 2F) ppm; MS m/e: 465, 463, 419, 417, 373, 371, 333, 331, 143, 130, 101, 99, 97, 73, 69, 55, 43; Analyses: Found, C,41.39, H,4.15, F,32.69, Cl,7.22; $C_{16}H_{19}O_4F_8Cl$,requires,C,41.51,H,4.11, F,32.86, Cl,7.68.

11b: b.p. 163°C/3mmHg; IR (film) 3010, 2950, 2800, 1740, 1720, 1625, 1440, 1360, 1300-1000, 930, 860, 825, 780, 735, 690 cm^{-1}; ^1H NMR δ 4.05(q,2H), 2.20(s,3H), 1.19(t,3H), 1.5-3.5(m,11H) ppm; ^{19}F NMR δ -9.3(t,2F), 35.6(s,2F), 43.0(s,2F), 44.0(s,4F), 46.0(s,2F) ppm; MS m/e: 564, 562, 536, 534, 511, 509, 433, 425, 255, 213, 131, 129, 85, 87, 69, 43; Analyses: Found, C,39.00, H, 3.59, Cl, 6.59 ; $C_{18}H_{19}O_4F_{12}Cl$, requires, C,38.40, H,3.38, Cl,6.31.

Reaction of 1a with 18

To a solution of 12 g of 18 (0.12mol) in 50 ml of DMF was added 10.8 g (30mmol) of 1a at 80°C. The mixture was maintained at this temperature for 15h. ^{19}F NMR spectra showed that the conversion was only ~20%,and the main product was 1-H-4-Cl-perfluoroalkane, 4,(~80%). After workup, besides 1a, 7.7 g and 4a, 0.74 g (13.8%), 0.87g of oilly products were obtained. ^{19}F NMR spectrum showed that it was the mixture of several products, in which a group of CF_2 resonances disappeared as compared with 1a, e.g. δ -11.0(t), 30.6(t), 39.5(s) and -10.8(t), 41.2(t), 42.5(s) ppm in ratio of 1:1:1 respectively. GC-MS analyses also confirmed this result, two of them might be  $\underset{\mathrm{CH(COCH_3)_2}}{\mathrm{Cl(CF_2)_3C}}\mathrm{=C(COCH_3)_2}$: 395(M+1$^+$), 397, 351, 353, 309, 295, 297, 271, 173, 165, 131, 129, 101, 100, 85, 87, 74, 69, 43; and  $\underset{\mathrm{CH_2COCH_3}}{\mathrm{Cl(CF_2)_3C}}\mathrm{=CHCOCH_3}$: 310(M$^+$), 295, 297, 266, 268, 253, 238, 223, 211, 135, 137, 87, 85, 67, 69, 43.

Reaction of 1a with 19

7.9 g (80mmol) of 19 (dried powder, made from malonitrile and sodium ethylate) in 40 ml of DMF was treated with 7.2 g (20 mmol) of 1a in 10 ml of DMF at 90°C. The colour of the solution rapidly turned to deep red-black . After stirring at this temperature for 10h, ^{19}F NMR spectra showed that the conversion was ~30%. More than 70% product was 1-H-ω-Cl-perfluoroalkane, 4a. A CF_2 group sign also disappeared in ^{19}F NMR spectrum as compared with that of 1a. Workup of the reaction mixture met with difficulties due to the deep colour of the solution.

Reactions of 1 with 18,19 in the presence of DAE

Typical procedure

To a solution of 3.9 g (40mmol) of 19 in 30 ml of DMF was added 3.9 g (40mmol) of DAE and then 3.5 g (10mmol) of 1e. The mixture was stirred at 90°C for 5h. The conversion reached 88% A small amount of 4e (~ 5%) was found. After workup, besides a small amount of 4e and 9, 2.2 g of 20e was obtained (64.3%) m.p. 132-134°C; IR (pellet) 2940, 2860, 2240, 1440, 1360, 1220, 1135, 1160, 1025, 910, 755, 600, cm^{-1}; ^{1}H NMR δ 3.35-4.2(m, 8H), 1.80-2.80(m,12H) ppm; ^{19}F NMR δ 3.1 (s,6F), 35.2(s,4F), 46.4(s,4F), 48.2(s,4F) ppm; MS m/e: 700, 699, 396, 395, 382, 370, 315, 316, 302, 301, 287, 267, 227, 107, 97, 83, 79, 69,65, 55, 41; ^{13}C NMR δ 117.8 ppm; Analyses: Found, C,39.53, H,2.82, F,48.73; $C_{23}H_{20}O_2F_{18}N_2$, requires, C,39.54, H,2.87, F,49.00.

20a: m.p. 105-106.5°C; IR (pellet) 2950,2850, 2250, 1440, 1260, 1185,1135,1055,875, 845, 760,700 cm^{-1}; ^{1}H NMR δ 3.3-4.3(m,8H), 1.5-2.9(m,12H) ppm; ^{19}F NMR δ -10.5(t,4F), 35.0(s,4F), 41.6 (s,4F), 44.4(s,4F) ppm; MS m/e: 733, 731, 730, 411, 413, 397, 399, 385, 387, 330, 332, 317, 319, 302, 304, 282, 284, 163, 98, 97, 87, 85, 83, 79, 73, 69, 65, 59, 55, 53, 47, 41; Analyses: Found, C,37.58, H,2.65, F,41.65, Cl,9.41; $C_{23}H_{20}O_2N_2F_{16}Cl_2$, requires, C,37.76, H,2.74, F,41.59, Cl,9.71.

20b: m.p. 127-128°C; IR (pellet), 2905, 2850, 2255, 1475, 1435, 1100-1300,1080, 1050, 985, 905, 860, 780, 735, 675, 635, 565, 545 cm^{-1}; ^{1}H NMR δ 3.4-4.2(m,8H), 2.55(m,4H), 2.20(m,8H) ppm;

^{19}F NMR δ -10.7(t,4F),34.8(s,4F),41.8(s,4F),42.9(s,8F),44.8(S, 4F) ppm; MS m/e : 499, 501, 471, 473, 431, 433, 430, 432, 417, 419, 403, 405, 383, 385, 343, 345, 163, 165, 135, 137, 131, 133, 117, 119, 103, 97, 95, 91, 85, 87, 77, 69, 67, 65, 59, 54, 51, 47, 44, 41; Analyses: Found, C,35.03, H,2.10, $C_{27}H_{20}O_2N_2F_{24}Cl_2$, requires, C,34.80, H,2,15.

ACKNOWLEDGMENT

We would like to thank Prof. Wei-Yuang Huang for his helpful discussion and the financial support by Chinese Academia Sinica.

REFERENCES

1 G.A.Russell, B.Mudryk and M.Jawdosuk, Synthesis, 62 (1981)

2 N.Kornblum, S.D.Boyd and N.Ono, J.Am.Chem.Soc.,96 (1974) 2580.

3 R.K.Norris, E.J.Panek, J.Am.Chem.Soc., 93 (1971) 5839.

4 L.M.Yagupolskii, G.I.Matyuschecheva, N.V.Pavlenko and V.N. Boiko, J.Org.Chem. USSR. (Engl.Transl.) 18 (1982) 14.

5 A.E.Feiring, J.Org.Chem., 50 (1985) 3269.

6 Q.Y.Chen and Z.M.Qiu, J.Fluorine Chem., 31 (1986) 301.

7 Q.Y.Chen and Z.M.Qiu,Acta.Chimica Sinica,to be published.

8 Q.Y.Chen and Z.Y.Yang, J.Fluorine Chem.,28 (1985) 399.

9 M.W.Rathke and P.J.Cowab, J.Org.Chem., 50 (1985) 2622.

10 O.Dann,H.Distler and H.Merkel, Chem.Ber., 85 (1952) 457.