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STUDIES ON FLUOROALKYLATION AND FLUOROALKOXYLATION. PART 10. ELECTRON-TRANSFER INDUCED REACTIONS OF PERFLUOROALKYL IODIDES AND THE DIALKYL MALONATE ANION AND β-FRAGMENTATION OF THE HALOTETRAFLUOROETHYL RADICAL

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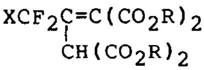
SUMMARY

Fluoroalkyl iodides, XCF_2CF_2I (X=F, perfluoroalkyl group) (1), react readily with malonic ester anion (2) in DMF to give  $XCF_2\underset{CH(CO_2R)_2}{C}=C(CO_2R)_2$ (3), 1-hydroperfluoroalkane (4) and dimer of the anion (5). The reaction is accelerated by UV irradiation and partly suppressed by p-DNB. Diallyl ether (DAE) can trap the radical intermediates to afford five-membered ring products. Interestingly, in the case of 1 (X = Cl, I) the same reaction mainly yielded tetrafluoroethylene and 5 instead of 3 and 4. The radical intermediate $XCF_2CF_2^{\cdot}$ (X=Cl) can also be trapped by DAE to yield tetrahydrofuran derivatives. All these results can be rationalized in terms of the $S_{RN}1$ mechanism.

INTRODUCTION

Perfluoroalkyl iodide is notoriously resistant to displacement of iodide under S_N1 or S_N2 conditions due to the shielding of the carbon center by the surrounding lone pair electrons on

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fluorine [1-3]. However, they are able to undergo a variety of nucleophilic substitutions via $S_{RN}1$ radical-chain processes. Perfluoroalkylation of aromatic, aliphatic thiols by perfluoroalkyl iodide in liquid ammonia [4] or DMF [5,6] with [4] or without [5,6] UV irradiation has been considered to be $S_{RN}1$ processes. Reactions of R_FI with certain enamines [7] or 2-nitropropyl anion [8] were also described as electron transfer processes. Sulfinatodehalogenations of perfluoroalkyl halides with potassium sulfite or hyposulfite were considered to involve $S_{RN}1$ mechanisms [9,10]. All these can be ascribed to the good electron accepting ability of perfluoroalkyl iodide on the one hand, and suitable electron donors on the other hand. Malonate ester anion has been reported to be a good $S_{RN}1$ donor, reacting with various p-nitrobenzyl derivatives [11] or α-halo-ketones [12]. Interaction of perfluoroalkyl iodide and malonate ion might be expected to follow an $S_{RN}1$ path. However, Feiring, in his very simple symposium abstract*, has indicated that only 1-H perfluoroalkanes and dimers of the anion were obtained, instead of the desired perfluoroalkylated product, in the reaction of perfluoroalkyl iodide and diethyl methylmalonate anion [13]. In order to perfluoroalkylate such a common and useful substrate, we have investigated the reaction of perfluoroalkyl iodide and dialkyl malonate anion. This paper presents the results of the reactions and clear evidence for the intermediacy of both radicals.

RESULTS AND DISCUSSION

Perfluoroalkyl iodide (1) reacted readily with sodium dimethyl or diethyl malonate (2) (1:2=1:4) in dimethylformamide (DMF) at 60°C for 5-10 h to give the products 3 and 4 with a small amount of 5.

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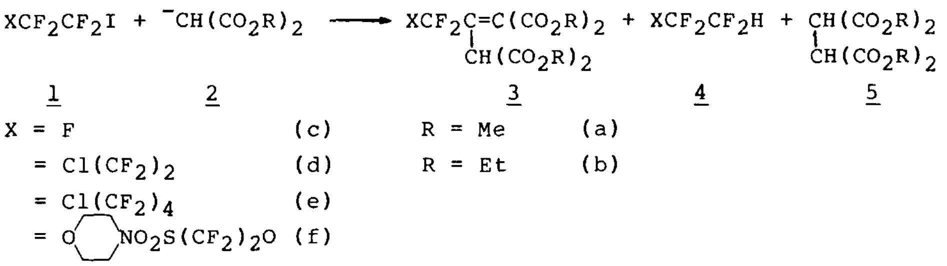
* After submission of this manuscript, Feiring published the results in more detail (J.Org.Chem., 50 (1985) 3269). However, no reaction of perfluoroalkyl iodide with sodium salt of diethyl malonate was reported.



$$XCF_2CF_2I + {}^-CH(CO_2R)_2 \longrightarrow XCF_2\underset{CH(CO_2R)_2}{\underset{|}{C}}=C(CO_2R)_2 + XCF_2CF_2H + \underset{CH(CO_2R)_2}{\underset{|}{CH(CO_2R)_2}}$$

1 2 3 4 5

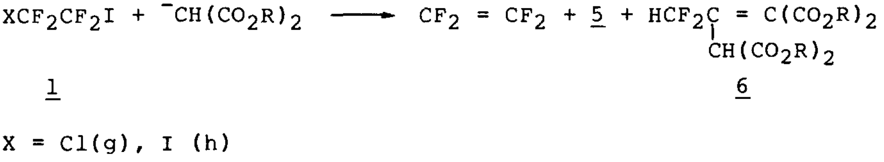
X = F (c) R = Me (a)

= $Cl(CF_2)_2$ (d) R = Et (b)

= $Cl(CF_2)_4$ (e)

= O NO$_2$S(CF$_2$)$_2$O (f)

The structure of 3 was assigned by its elemental analyses, IR, proton and fluorine NMR spectra as well as mass spectroscopy. The conversion was strongly dependent on the ratio of reactants, increasing to 94% at the ratio of 1:5 (1:2) from 24% at 1:1. The yields of 3 and 4, seemingly, changed only slightly over this range, being 45-60% for 3, 30-45% for 4. 5 (~4%) was observed only when the ratio of 1 to 2 was low (see Table 1). The reaction temperature (0-5° or 60°C) depended on the boiling point of perfluoroalkyl iodide used. Interestingly, when XCF_2CF_2I, X = Cl, (1g), I (1h) were allowed to react with malonate salt, none of 3 and 4 were obtained. Instead, tetrafluoroethylene (~ 85%), considerable amounts of 5(~50%) with a small amount of 6 (6-11%) were formed.



$$XCF_2CF_2I + {}^-CH(CO_2R)_2 \longrightarrow CF_2 = CF_2 + 5 + HCF_2\underset{CH(CO_2R)_2}{\underset{|}{C}} = C(CO_2R)_2$$

1 6

X = Cl(g), I (h)

The reaction occurred under ambient laboratory light, but was accelerated by irradiation. For example, the conversion of 1d was increased to ~20% under irradiation as compared with the control. The presence of the single electron transfer (SET) scavenger, p-dinitrobenzene (p-DNB), partly suppressed the reaction of 1 with malonate anion, i.e. the conversion of 1d was decreased about 30-40% in comparison with the control. The results are summarized in Table 2.

TABLE 1

Reaction of 1d with 2b in different ratios in DMF at 60°C for 10h

Entry	1d/2b	Conversion %	Product %		
			3	4	5
1	1/1	24.3	47.5	43.6	/
2	1/2	45.3	50.8	33.1	/
3	1/3	68.7	54.3	35.2	trace
4	1/4	87.9	55.0	40.1	trace
5	1/5	93.8	53.4	39.6	14.2

TABLE 2

Reaction of 1 with 2 (ratio 1 : 4) in DMF

Entry	Reactants	T°C	t(h)	Conversion %	Product %[a]		
					3	4	5
6	1c, 2a	5	10	86.3	53.3	40.0	trace
7	1c, 2b	5	10	75.5	61.1	33.9	trace
8	1d, 2a	60	10	79.3	57.8	37.2	trace
9	1d, 2b	60	10	87.9	55.0	40.1	trace
10[b]	1d,2b,UV	60	10	100	27.3	72.9	34.4
11	1d,2b 100mol% P-DNB	60	10	45.4	54.6	45.4	/
12	1e, 2a	60	10	88.2	55.3	39.7	trace
13	1e, 2b	60	10	82.2	55.1	32.9	trace
14	1f, 2a	60	10	86.1	47.2	40.6	trace
15	1f, 2b	60	10	83.3	50.3	38.3	trace
16	1g, 2a	15	5	100	87.3[c]	6.7[d]	53.7
17	1h, 2a	15	3	100	84.5[c]	11.2[d]	51.7

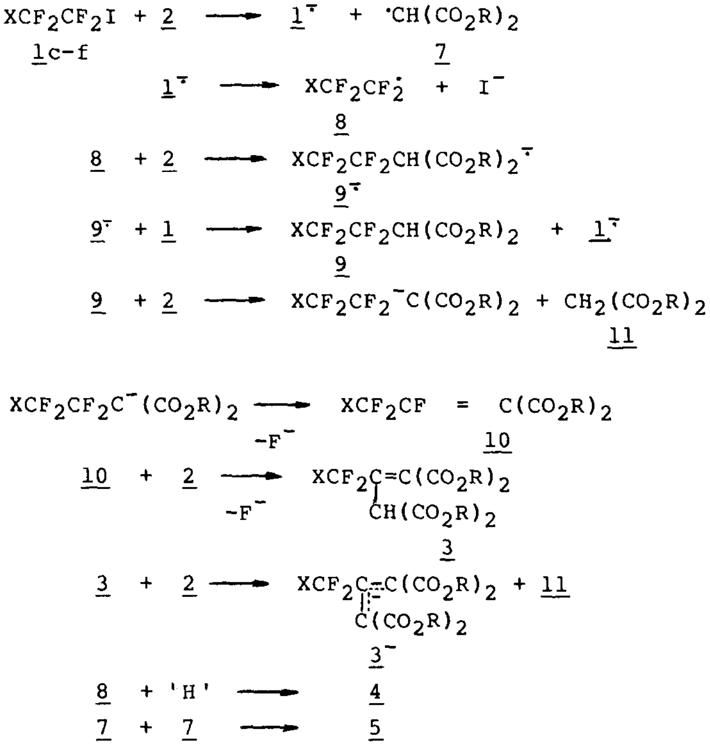
[a] isolated yield unless specified otherwise;

[b] yield determined by ^{19}F NMR;

[c] tetrafluoroethylene;

[d] yield of 6.

The results mentioned above seem to show that perfluoroalkylation of malonate anion by R_FI may involve an $S_{RN}1$ mechanism as follows:



$$\underset{\underline{1}\text{c-f}}{XCF_2CF_2I} + \underline{2} \longrightarrow \underline{1}^{\cdot-} + \underset{\underline{7}}{{}^{\cdot}CH(CO_2R)_2}$$

$$\underline{1}^{\cdot-} \longrightarrow \underset{\underline{8}}{XCF_2CF_2^{\cdot}} + I^-$$

$$\underline{8} + \underline{2} \longrightarrow \underset{\underline{9}^{\cdot-}}{XCF_2CF_2CH(CO_2R)_2^{\cdot-}}$$

$$\underline{9}^{\cdot-} + \underline{1} \longrightarrow \underset{\underline{9}}{XCF_2CF_2CH(CO_2R)_2} + \underline{1}^{\cdot-}$$

$$\underline{9} + \underline{2} \longrightarrow XCF_2CF_2{}^{-}C(CO_2R)_2 + \underset{\underline{11}}{CH_2(CO_2R)_2}$$

$$XCF_2CF_2C^-(CO_2R)_2 \xrightarrow[-F^-]{} \underset{\underline{10}}{XCF_2CF = C(CO_2R)_2}$$

$$\underline{10} + \underline{2} \xrightarrow[-F^-]{} \underset{\underline{3}}{XCF_2\underset{CH(CO_2R)_2}{\underset{|}{C}}=C(CO_2R)_2}$$

$$\underline{3} + \underline{2} \longrightarrow \underset{\underline{3}^-}{XCF_2\underset{C(CO_2R)_2}{\underset{\vdots}{C}}\!\!=\!\!C(CO_2R)_2} + \underline{11}$$

$$\underline{8} + \text{'H'} \longrightarrow \underline{4}$$

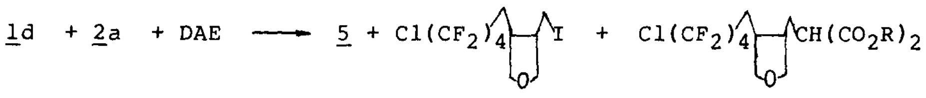
$$\underline{7} + \underline{7} \longrightarrow \underline{5}$$

This is a normal radical-chain process initiated by SET from malonate anion to perfluoroalkyl iodide.The cross coupling product (9) of the resultant radical with anion (2) was not isolated because under the reaction conditions it readily eliminated F^- to give olefin (10), which subsequently added another molecule of 2 yielding the final product (3).Owing to higher acidity of 3,dialkyl malonate was always formed.The appearance of 5, the dimer of the anion 2, was undoubtedly, a good indication for the intermediacy of malonate radical. In the case of 1 (X=Cl or I), tetrafluoroethylene was eliminated. This may be the first example of the fragmentation of β-halotetrafluoroethyl radical under such mild conditions.

$$XCF_2CF_2^{\bullet} \longrightarrow CF_2{=}CF_2 + X^{\bullet}$$
$$X^{\bullet} + 2 \longrightarrow XCH(CO_2R)_2 \longrightarrow X^{-} + 7$$
$$X{=}Cl,\ I$$

As mentioned above a small amount of 6 was also formed in the reaction. 6 is a known compound, which was prepared by the reaction of tetrafluoroethylene and malonate in dioxane at 125°C under autogenous pressure in 48.5%-yield [14,15]. The low yield of 6 in our case is a reflection of the fact that as a consequence of the mildness of the conditions, only small amounts of 6 were formed. There is, however, an alternative explaination for the appearance of 6, i.e. $XCF_2CF_2^-$ might be generated in some other ways (for example, abstraction of positive halogen by malonate anion, etc), which should eliminate β-halogen giving also tetrafluoroethylene and subsequently its derivative.

In order to elucidate the mechanism, we have used diallyl ether (DAE) as a radical trap [16,17]. Thus, treatment of 1d, 2a with DAE in the ratio of 2:1:2 gave no 3 and 4 but cyclic products 13d and 12d as well as some 5.



12d 13d

Similarly, the corresponding cyclic compound 12g or 13g was obtained in addition to $CF_2{=}CF_2$, 5 and a trace of 6 in the case of 1g, 2 and DAE (see Table 3).

$$1g + 2 + DAE \longrightarrow CF_2{=}CF_2 + 5 + 6 + 12g\ (+\ 13g)$$

The yields of 12 and/or 13 depended on the reactants ratio used. The results seem to show that the reaction of DAE with fluoroalkyl radical (8) initiated by SET was so fast that it not only suppressed the nucleophilic substitution by malonate anion but also even trapped partly unstable β-halotetrafluoroethyl radical. Such homolytic β-scission occurred only for 1 (X=Cl, I), but

TABLE 3

Reaction of 1,2 and DAE in DMF

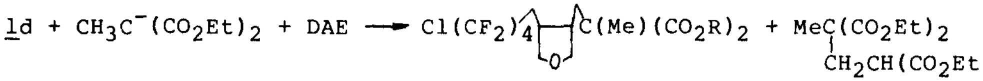
Entry	Reactants and their ratio	T(°C)	t(h)	Conversion (%)	Products (%)			
					13	12	5	CF_2=CF_2
18	1c:2a:DAE (1:1:4)	15	5	100	80.0	trace	trace	/
19	1d:2a:DAE (1:4:4)	60	5	100	87.1	trace	30.5	/
20	1d:2a:DAE (1:1:1)	60	5	100	74.6	17.0	8.5	/
21	1d:2a:DAE (2:1:2)	60	5	100	68.9	26.4	/	/
22	1d:(Me-2b)*:DAE (1:1.4:2.6)	60	5	100	67.2	5.1	trace	/
23	1e:2a:DAE (1:4:4)	60	3	100	89.3	trace	26.7	/
24	1e:2b:DAE (1:4:4)	60	3	100	92.5	trace	28.7	/
25	1e:2b:DAE (1:1:4)	60	5	100	78.6	8.8	5.6	/
26	1g:2a:DAE (5:1:5)	50	5	33.4	/	6.8	/	49.3**
27	1g:2b:DAE (1:2:4)	50	5	89.7	3.6	/	39.3	62.5**

* Me-2b = $CH_3\bar{C}(CO_2Et)_2$

** A small amount of 6 was also detected by ^{19}F NMR.

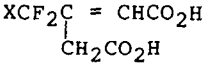
not for 1 (X=F, or R_F) is, probably, similar to that observed in the fragmentation of β-thioalkyl (or β-haloalkyl) and β -trifluoro (or β-trichloro) methyl radicals [18]. β-Fragmentation can also explain why 2,3-dimethyl-2,3-dinitrobutane was the only nonvolatile product on the photoreaction of 1,2-di-iodotetrafluoroethane with lithium 2-nitropropanide whereas the longer chain di-iodides normally afforded a mixture of mono- and di-perfluoroalkylated compounds [8]. Based on this concept, it is, then, understandable that all the yields of addition products were rather high (except for $Cl(CF_2)_2I$) when perfluoroalkyl iodides were allowed to react with trimethylsilyethylene [19] and acetylene [20] in the presence of copper.

We have repeated Feiring's work [13] and confirmed his results. The same mechanistic probe for the reaction of diethyl methylmalonate anion and 1d has also been employed. Cyclic compound 14 was obtained in 67% yield, indicating that the radical mechanism may be also involved.



14

In agreement with the literature [21], 3a (methyl ester) is a low-melting solid whereas 3b (ethyl ester) a high-boiling liquid. For this reason the latter was sometimes difficult to purify but is very easy to hydrolyze to the corresponding dibasic acid (15) either in acidic or basic medium.



$$XCF_2\underset{\displaystyle CH_2CO_2H}{C} = CHCO_2H$$

15

EXPERIMENTAL

All boiling points and melting points were uncorrected. GC spectra were measured on Shanghai Model 102 with packing of

Porapak-Q. IR spectra were carried out on Shimadzu IR-440 except tetrafluoroethylene on Zeiss specond 75. NMR spectra (chemical shifts in ppm from external TMS for ^{1}H NMR and from external TFA for ^{19}F NMR positive for upfield shifts) were recorded on EM-360 NMR spectrometer at 60 MHz. Mass spectra were taken on MS-4021. Laser Raman spectra were made on JY-T 800.

All solvents and reagents were purified prior to use. All reactions were carried out under the atmosphere of pure nitrogen.

Preparation of 1f

42.6 g (0.1 mol) of $ICF_2CF_2OCF_2CF_2SO_2F$ [22] was added dropwise to a solution of 17.4 g (0.2 mol) of morpholine in 100 ml dichloromethane. The reaction mixture was stirred for 2h at room temperature. The reaction mixture was then washed with water, dried over $MgSO_4$. 46.1 g of 1f was obtained after evaporating the solvent and recrystallization in ether-hexane.The yield was 93.5%. 1f: m.p. 63-64°C. IR(pellet) 2850, 2750, 1450, 1380, 1335, 1290, 1265, 1200, 1180-1090, 1070, 1000, 955, 920, 845, 730, 710, 610, 580, 500 cm^{-1}. ^{1}H NMR δ 3.65(t,4H), 3.55(t,4H). ^{19}F NMR δ -14.0 (s,2F), 3.9(t,2F), 7.3(t,2F), 47.8(s,2F). MS: m/e (rel. int.) 57 (100), 493(9.92), 494(4.16),227(4.40), 177(9.83), 150(30.2), 134 (13.9), 119(7.21), 100(10.82), 88(13.29), 86(81.84), 84(11.18), 69(3.65),55(9.47),42(13.94).Analysis: Found: C, 19.44; H, 1.63; F, 31.39; S, 6.30; I. 25.54. $C_8H_8O_4NF_8SI$ requires C, 19.47; H, 1.62; F, 30.83; S, 6.49; I, 25.76.

General procedure:

In a 250 ml three-necked flask, fitted with magnetic stirrer, nitrogen inlet and condenser with a desiccator, 6.3 g (0.04 mol) of 2a and 150 ml of DMF were placed. After passing nitrogen for half an hour, 4.7 g (0.01 mol) of 1e in 10ml of DMF, was added rapidly in one portion at 60°C.The solution was stirred for 10 h at this temperature. After quenching the reaction with dilute hydrochloric acid,trace of crystalline 5a was obtained by filtration.The solution was extracted three times with 150 ml of dichloromethane. The combined extracts were washed three times with water and dried over $MgSO_4$. Distillation gave 1.34 g of 4e (23) (39.7%) and 3.9 g of malonic ester. The residue was chromatographed on silica gel (eluted with ethyl acetate and petroleum ether in ratio 2 to 8). After recrystallization in hexane and diethyl ether, 3.1 g of 3e (Me) was obtained. The yield was 55.3%. m.p. 165-167°C, IR (pellet) 2950, 1755, 1655, 1441, 1370, 1267, 1242, 1210, 1177, 1150, 1110, 985, 700 cm^{-1}. ^1H NMR δ 4.18(s,1H), 3.66(s,12H) ^{19}F NMR δ -10.6(t,2F), 32.0(t,2F), 40.8(s,2F), 42.0(t,2F), 43.1 (t,2F). MS m/e (rel. int.) 559(2.23), 561(1.01), 499(27.19), 501(12.23), 455(22.59), 457(9.82), 440(8.13), 442(2.81), 135 (2.47), 137(2.31), 185(1.53), 187(0.92), 101(46.39), 85(4.98), 87(2.50), 74(21.11), 69(10.82), 59(100), 45(30.54). Analysis: Found C, 34.12; H, 2.31; F, 34.06; Cl, 6.25. $C_{16}H_{13}O_8F_{10}Cl$ requires C, 34.36; H, 2.33; F, 34.02; Cl, 6.36.

3e (Et) b.p. 165°C/1.5mm. IR (film) 2998, 2950, 2850, 2785, 1750, 1682, 1470, 1450, 1375, 1210, 1150, 1040, 970, 785, 675cm^{-1}. ^1H NMR δ 4.22(m,9H), 1.32(t,12H). ^{19}F NMR δ -10.3(t, 2F), 31.7(t,2F), 40.8(s,2F), 42.0(t,2F), 43.1(t,2F).MS m/e (rel. int.) 425(100), 427(50.51), 471(37.54), 473(16.46), 397(53.43), 399(15.94), 369(34.06), 371(10.71), 398(21.4), 400(5.8), 379 (28.71), 381(10.54), 370(41.6), 372(12.47), 352(28.09), 354 (7.76), 185(6.69), 187 (7.83), 135(23,14), 137(8.94), 73(10.1), 69(46.29), 59(58.63), 45 (59.66). Analysis: Found: C, 39.50; H, 3.33; F, 30.76; Cl, 6.13. $C_{20}H_{21}O_8F_{10}Cl$, requires, C, 39.06; H, 3.42; F, 30.92; Cl, 5.78.

3c (Me) m.p. 52-54°C. IR (pellet) 2950, 1755, 1735, 1660, 1440, 1325, 1255, 1195, 1145, 1170, 978 cm^{-1}. ^1H NMR δ 4.71(s,1H), 3.7(s,12H). ^{19}F NMR δ -15.4(s). MS m/e (rel. int.) 342(1.92), 343(16.24), 325(27.58), 311(11.26), 310(9.50), 282(22.59), 283 (77.99), 280(14.25), 279(100), 251(7.47), 239(71.71), 240(8.04), 224(27.81), 211(8.02), 181(10.16), 59(36.41), 69(2.73).Analysis: Found: C, 41.95; H, 3.75; F, 16.51. $C_{12}H_{13}O_8F_3$, requires, C, 42.11; H, 3.80; F, 16.67.

3c (Et) b.p. 115°C/0.05mm. IR (film) 2950, 2800, 2755, 1740, 1675, 1470, 1450, 1372, 1210-1320, 1190, 1155, 1100, 1065, 1250, 865, 670 cm^{-1}. ^1H NMR δ 4.74(s,1H), 3.85(q,8H), 0.95(t, 12H). ^{19}F NMR δ -17.3(s). MS m/e (rel. int.) 400(20.32), 398 (14.48), 399(100), 378(2.46), 353(37.09), 352(11.19),381(11.63), 335(11.66), 326(9.39), 325(57.60), 319(17.42), 308(15.86), 309 (99.02), 280(30.18), 252(13.39), 235(16.08), 233(21.86), 232 (92,84), 206(11.27), 72(6.2), 44(11.81). Analysis: Found: C, 48.19; H, 5.27; F, 14.22. $C_{16}H_{21}O_8F_3$, requires: C, 48.24; H, 5.28; F, 14.32.

3d (Me) m.p. 62.5-63.5°C. IR (pellet) 2920, 1760, 1440, 1365, 1300, 1275, 1240, 1180, 1125, 800 cm^{-1}. Raman: 1755, 1640, 1445 cm^{-1}. ^1H NMR δ 4.11(s,1H), 3.66(s,12H). ^{19}F NMR δ -10.8 (t,2F), 31.7(t,2F), 39.4(s,2F). MS m/e (rel. int.) 459(23.47) 461(7.47), 441(30.30), 443(13.87), 426(14.37), 428(4.15), 399 (100), 401(43.78), 407(5.19), 391(22.49), 355(58.29), 356(22.75), 339(23.27), 341(8,53), 327(2,73), 329(1.04), 229(12.47), 309 (12.62), 311(5.56), 105(33.64), 59(17.89). Analysis: Found: C, 36.51; H, 2.89; F, 24.80; Cl, 8.00. $C_{14}H_{13}O_8F_6Cl$ requires: C, 36.64; H, 2.84; F, 24.86; Cl, 7.74.

3d (Et) b.p. 136°C/1.5mm IR(film) 2998, 2900, 1750, 1475, 1455, 1378, 1300, 1250, 1190, 1130, 1048, 675 cm^{-1}. Raman: 1750, 1649 cm^{-1}. ^1H NMR δ 4.15(m,2H), 1.23(t,12H). ^{19}F NMR δ -10.6 (t,2F), 30.7(t,2F), 39.0(s,2F). MS m/e (rel. int.) 514(11.20), 516(11.20), 515(29.54), 517(12.67), 478(27.59), 477(100), 469 (4,37), 471(1.59), 441(19.23), 443(8.80), 423(9.26), 425(3.02), 405(15.57), 406(15.06), 373(12.81), 347(56.11), 348(10.25), 333 (37.90), 334(7.70), 319(12.81). Elemental analyses were obtained after hydrolysis to 15d

3f (Me) m.p. 95-97°C. IR (pellet) 2992, 1770, 1750, 1660, 1450, 1395, 1335, 1270, 1240, 1200, 1160, 1128, 1070, 982, 720cm^{-1}.^1H NMR δ 4.82(s,1H), 3.81(s,6H), 3.76 (s, 6H), 3.65(t,4H), 3.45(t,4H).^{19}F NMR δ -10.7(t,2F), 4.3(m,2F), 37.3(s,2F).MS m/e (rel. int.) 590(16.25), 558(2.29), 530(23.15), 526(28.42), 486(10.21), 482(19.92), 380(13.63), 348(14.12), 291 (11.50), 250(2.50), 150(10.54), 134(61.54), 132(53.46), 100 (12.83), 86(99.23), 59(46.69), 56(100), 42(10.92). Analysis: Found: C, 36.87; H, 3.83; F, 18.79; S, 5.62. $C_{18}H_{21}O_{12}F_6NS$, requires: C, 36.67; H, 3.57; F, 19.35; S, 5.43.

3f (Et) IR (film) 2998, 2945, 1740, 1650, 1470, 1450, 1390, 1370, 1320, 1150-1300, 1120, 1070, 1030, 990, 960, 860, 710, 670 cm^{-1}. ^{1}H NMR δ 4.56(s,1H), 4.14(t,8H), 3.59(t,4H), 3.49(t,4H), 1.28(t,12H). ^{19}F NMR δ -11.9(t,2F), 4,8(t,2F), 37.2(s,2F). MS m/e (rel. int.) 646(6.26), 572(11.29), 555(3.86), 554(19.20), 450(2.50), 422(4,83), 376(4,84), 348(4,23), 250(4,36), 248(2.14), 161(21.20), 160(26.41), 150(13.40), 134(45.71), 133(30.06), 115 (46.64), 100(7.76), 88(20.29), 87(18.19), 86(84.01), 73(4.01), 60(13.28), 57(13.86), 56(100), 45(27.69), 44(14.12), 43(68.11), 42(35.29). Analysis: Found: F, 17.48; S, 5.02; H, 4.59. $C_{22}H_{29}O_{12}F_6NS$ requires F, 17.67; S, 4.96; H, 4.50.

4f b.p. 111-112°C/3mm. IR (film) 2995, 2900, 2755, 1470, 1430, 1360, 1310, 1298, 1260-1140, 1105, 1010, 985, 850, 770, 730 cm^{-1}. ^{1}H NMR δ 5.74(t-t, 1H), 3.49(t,4H), 3.39(t,4H). ^{19}F NMR δ 4.1(t,2F), 11.0(t,2F), 38.7(s,2F), 60.8(d,2F). MS m/e (rel. int.) 367(0.90), 368(11.36), 338(39.96), 168(26.09), 150(1.52), 137(7.85), 136(100), 138(6.93), 133(35.71), 120(35.46), 119 (15.30), 101(66.06), 100(8.49), 86(6.58), 72(27.13), 69(5.14), 59(19.83), 57(33.00), 56(44.8), 45(14.23), 44(68.61), 43(20.65), 42(49.09). Analysis: Found: C, 26.10; H, 2.35. $C_8H_9O_4F_8NS$ requires C, 26.16; H, 2.45.

Reaction of 1g, 1h with 2a

A solution of 4.3 g (0.027 mol) of 2a in 80 ml of DMF was treated with 1.8g (0.0069 mol) of 1g at 15°C.The reaction mixture was stirred vigorously at this temperature for 3 h and 143 ml (84.5%) of gas was collected, which was identified to be tetrafluoroethylene by GC, MS and IR by comparison with authentic sample. The reaction mixture was hydrolysed with dilute hydrochloric acid, 1.8g (51.7%) of 5a was obtained by filtration the solution, m.p. 134.5-136°C (lit, [24], m.p. 135-136°C). The residue was extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$ and concentrated on a rotary evaporator to oily solid. After chromatographed on silica gel, 0.25 g (11.2%) of 6 was obtained, m.p. 55-56.5°C (lit, [14], m.p. 56-58°C).

6 MS m/e (rel. int.) 325(6.90), 304(2.73), 293(5.45), 292 (2.78), 273(3.16), 266(5.35), 265(46.90), 264(13.35),261(53.73), 241(10.91), 233(8.85), 221(23.59), 206(15.36), 207(13.36), 203 (20.49), 175(9.69), 171(27.21), 159(15.67), 132(4.15),145(9.14), 113(19.09), 105(16.85), 101(38.29), 93(13.95), 74(14.51), 75 (10.33), 69(15.15), 59(100), 45(13.87).

Similarly, tetrafluoroethylene, 5a and 6 were obtained in the reaction of 1h with 2a.

Reaction of 1d with 2b in the presence of p-DNB

0.7 g (0.00185 mol) of 1d and 1.3 g (0.0074 mol) of p-DNB were added into the solution of 1.4(0.0074 mol) of 2b in 50 ml of DMF. The vigorously stirred mixture was maintained at 60°C for 10 h. The conversion was 45.4% shown by ^{19}F NMR, and the product 3d (Et) was 54.6% (See Table 2).

The reaction of 1d and 2b under UV irradiation

A solution of 3.8 g (0.021 mol) of 2b, 1.89 g (0.0052 mol) of 1d in 150 ml of DMF was irradiated for 3 h at 50°C. ^{19}F NMR showed that the conversion was complete and the product 3d (Et) was 27.0%. After hydrolysis with dilute hydrochloric acid, 1.15 g (34.4%) of 5b was obtained.

Reactions of 1 with 2 or methylmalonate salt in the presence of DAE, (See Table 3).

Typical procedure

To a solution of 4.8 g (0.031 mol) of 2a in 100 ml of DMF was added 2.9 g (0.0078 mol) of 1d and 3.1 g (0.031 mol) of DAE. The mixture was stirred for 5 h at 60°C. 1.25 g (30.5%) of 5a was obtained by filtering the solution after hydrolysis of the mixture with dilute hydrochloric acid. Distillation gave 1.56 g of DAE, trace of 12 and 3.16 g of 13d (CH_3) (87.2%).

13d (Me) b.p. 164°C/2mm. IR (film) 2980, 2800, 1742, 1445, 1345, 1245, 1200, 1140, 1055, 980, 850, 800, 675cm^{-1}. ^{1}H NMR δ 4.44 (s,1H), 3.68(s.2H), 1.6-3.7(m). ^{19}F NMR δ -10.5(t,2F), 35.2(s.2F), 41.6(s,2F), 44.4(s,2F). MS m/e (rel. int.) 465(10.42), 467 (3.41), 433(3.82), 435(1.26), 331(17.29), 332(8.10), 318(6.50), 320(1.92), 145(100), 135(1.87), 137(1.19),132(36.73),113(30.69), 100(19.27), 98(8.25), 87(25,35),85(13.60), 83(21.72), 81(16.62), 74(30.73), 69(71.08),67(15.74), 59(43.17), 55(36.83), 45(13.16), 44(9.04), 43(11.02), 41(27.16). Analysis: Found C, 38.59; H, 3.72; F, 32.64; Cl, 7.49. $C_{15}H_{17}O_5F_8Cl$ requires C, 38.75; H, 3.66; F, 32.72; Cl, 7.64.

12d b.p. 119°C/4mm (lit. [17] b.p. 107°C/2mm.). MS, ^{1}H NMR, ^{19}F NMR and IR spectra were agreed with lit, [17].

12g b.p. 101°C/4mm. (lit. [25] b.p. 116°C/8mm). All analytic data were in accord with lit, [25].

13c (Me) m.p. 109-111°C. IR (pellet) 2950, 2800, 1745, 1445, 1340, 1280, 1240, 1200, 1165, 1120, 1055, 1025, 675 cm^{-1}. ^{1}H NMR δ 4.38(t,1H), 3.77(s,6H), 1.6-3.7(m). ^{19}F NMR δ 6.9(s, 3F), 38.4(m,2F). MS m/e (rel. int.) 349(80.39), 350(7.40), 347 (9.45), 317(26.40), 288(10.0), 289(1.30), 217(2.55), 215(66.02), 202(14.87), 203(2.46), 145(100),132(20.86),131(8.85), 125(9.71), 113(14.60), 100(17.27),87(11.02), 69(42.97), 59(31.53).Analysis: Found: C, 44.80; H, 4.84. $C_{13}H_{17}O_5F_5$ requires: C, 44.83; H, 4.89.

13e (Me) m.p. 94-96°C. b.p. 154°C/2.5mm. IR (pellet) 2900, 2800, 1730, 1440, 1255, 1205, 1150, 1120, 1000, 685 cm^{-1}. ^{1}H NMR δ 3.76(s,6H), 1.6-3.7(m). ^{19}F NMR δ -11.6(t,2F), 34.9(s,2F), 41.8(s.2F), 43.1(m,4F), 45(s,2F). MS m/e (rel. int.) 564(2.02), 520(4.04), 518(13.68), 488(5.72), 486(13.13), 432(49.35), 430 (100), 429(8.38), 419(5.97), 417(17.56), 384(1.20), 382(3.53), 145(32.19), 132(12.76),113(10.20),100(4.50), 97(2.62), 87(3.65), 85(6.35), 69(17.88), 59(5.73). Analysis: Found: Cl, 6.57; H, 3.06. $C_{17}H_{17}O_5F_{12}Cl$ requires: Cl, 6.29; H, 3.01.

13e (Et) b.p. 154°C/0.2mm. IR (film) 2995, 2900, 2850, 1740, 1465, 1440, 1370, 1360-1000, 920, 860, 780, 670 cm^{-1}. ^{1}H NMR δ 4.06(q,4H), 1.7(t,6H), 1.7-4.0(m). ^{19}F NMR δ -10.3(t, 2F), 35.3(s,2F), 42.1(t,2F), 43.3(m,4F), 45.2(s,2F). MS m/e (rel. int.) 595(7.40), 593(15.51), 549(6.00), 547(12.31), 503 (2.30), 501(5.80), 457(1.60), 455(3.70), 447(2.10), 445(3.30), 433(19.72), 431(64.56), 420(4.40), 418(13.81), 413(10.11), 397 (2.30), 395(5.90), 187(2.70), 185(3.30), 173(100), 101(16.71), 99(10.81), 97(11.71), 87(8.90), 85(16.11), 83(19.62), 81(10.31), 73(11.21), 69(56.06), 67(11.91), 59(10.41), 55(26.52), 45(6.60), 43(40.24). Analysis: Found: C, 39.10; H, 3.96; Cl, 5.36. $C_{19}H_{21}O_5F_{12}Cl$ requires: C, 38.48; H, 3.54; Cl, 5.99.

13g (Et) b.p. 151°C/2.5mm IR (film) 2995, 2990, 2900,2785, 1730, 1470, 1445, 1390, 1370, 1300, 1210, 1155, 1090, 1045, 940, 910, 860, 760, 670 cm^{-1}. ^{1}H NMR δ 3.96(q,4H), 1.5-3.7 (m), 1.05(t,6H). ^{19}F NMR δ -6.4(s,2F), 35.3(m,2F). MS m/e (rel.int.) 393(67.58), 395(22.20), 347(30.40), 349(13.60), 301(8.71), 303(2.92), 231 (71.05), 233(26.83),218(18.84), 220(6.20),213(12.08), 215(3.91), 173(100), 174(12.17), 160(28.38), 133(14.10), 127(43.94), 120 (15,86), 101(21.45), 83(10.80), 81(11.55), 73(13,82), 69(48.12), 55(35.15), 41(13.91). Analysis:Found C, 45.77; H, 5.40; F, 18.94; Cl, 8.84. $C_{15}H_{21}O_5F_4Cl$. requires C, 45.86; H, 5.35; F, 19.36; Cl, 9.04.

14d b.p. 155°C/1.5mm IR (film) 2995, 2900, 2850, 2750, 1740, 1465, 1450, 1380, 1370, 1330, 1300, 1250, 1190, 1135,1020, 970, 860, 840, 800, 670 cm^{-1}. ^{1}H NMR δ 4.02(q,4H), 1.26(s,3H), 1.18(t,6H), 1.6-3.7 (m). ^{19}F NMR δ -9.4(t,2F), 36.0(s,2F), 42.7 (t,2F), 45.5(t.2F). MS m/e (rel. int.) 507(29.04), 509(11.56), 432(19.69), 434(8.41), 404(4.95),406(1.39),387(6.28), 389(1.39), 375(6.50), 377(2.77),359(7.10),361(1.76), 331(74.0), 333(23.87), 318(31.42), 320(8.58), 301(12.31), 295(11.90), 173(37.87), 174 (66.83), 141(13.25), 127(21.02), 128(31.67), 115(40.25), 100 (12.42), 87(14.0), 85(5.19), 83(14.71), 69(100), 59(10.37), 55 (19.23), 43(12.87), 41(27.96). Analysis: Found Cl, 6.76; F, 29.91; $C_{18}H_{23}O_5F_8Cl$. requires Cl, 7.01; F, 30.00.

The procedure of hydrolysis of 3d, 3f in basic medium to form dibasic acids according to lit, [14.]

15d Yield, 65.3%, m.p. 150-152^{o}C. IR (pellet) 2500-3500, 1704, 1672, 1428, 1305, 1225, 1180, 1120, 840, 768 cm^{-1}. ^{1}H NMR δ 5.95(s,1H), 4.63(s,2H), 3.25(s,2H). ^{19}F NMR δ -10.9(t,2F), 35.7(t,2F), 42.3(s,2F). MS m/e (rel. int.) 315(3.71), 317(1.18), 297(21.45), 299(7.41), 296(9.41),298(4.74),279(1.64), 269(6.26), 271(2.34),268(22.08),270(7.37),197(100), 179(22.37), 169(43.13), 165(15.7), 152(9.85),151(33.7),141(17.29), 135(5.26), 137(3.21), 133(27.30),125(15.7), 123(61.67),105(9.31), 51(5.92), 45(33.44). Analysis: Found: C, 30.62; H, 1.76; F, 36.27; Cl, 10.83. $C_8H_5O_4F_6Cl$. requires C, 30.52; H, 1.59; F, 36.25; Cl, 11.29.

15e Yield 79.6%. m.p. 162-163^{o}C. IR (pellet) 3540-2500, 1705, 1672, 1418, 1320, 1285, 1220, 1200, 1135, 1085, 1040, 920, 740 cm^{-1}. ^{1}H NMR δ 6.42(t,1H), 5.95(s,2H), 3.67(s,2H). ^{19}F NMR δ -10.2(t,2F), 35.9(t,2F), 42.6(m,4F), 43.4(t,2F). MS m/e (rel. int.) 415(80.46), 417(25.83), 416(7.43), 418(2.37), 398 (11.63), 400(2.95), 399(33.66), 397(100), 379(9.31), 381(2.71), 369(11.1), 371(5.36), 368(17.86), 370(9.32), 165(19.64), 133 (30.42), 129(1.30), 87(12.06), 85(22.71), 69(10.74), 59(5.90), 45(11.77). Analysis: Found: C, 29.00; H, 1.09; F, 45.56; Cl, 8.58. $C_{10}H_5O_4F_{10}Cl$, requires, C, 28.95; H, 1.21; F, 45.84; Cl, 8.56.

The acid could be also obtained by hydrolysis in acid medium [26]. The yield of 15e was 74.2%.

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REFERENCES

1 R.D.Chambers, 'Fluorine in Organic Chemistry', Wiley-Interscience, New York, 1973, pp 98,99.

2 B.E.Smart, 'Fluorocarbons' in 'The Chemistry of Halides, Pseudohalides and Azides', Part I, ed. by S.Patai and Z.Rupport, Wiley, New York, 1983, p.603.

3 Q.-Y.Chen and S.-Z.Zhu, Acta Chimica Sinica, 41 (1983) 1044.
4 V.N.Boid, M.G.Shupak and L.M.Yagupolskii, J.Org.Chem.USSR, 13 (1977) 1055; V.I.Popov, V.N.Boik and L.M.Yagupolskii, J.Fluorine Chem, 21 (1982) 365.
5 A.E.Feiring, J.Fluorine Chem., 24 (1984) 191.
6 D.-B.Su,Q.-Y.Chen and R.-X.Zhu, Org.Chem., to be published.
7 D.Cantacuzene, C.Wakselman and R.J.Dorme, J.Chem.Soc., Perkin Trans., I (1977) 1365.
8 A.E.Feiring, J.Org.Chem., 48 (1983) 347.
9 W.-Y.Huang, B.-N.Huang and C.-M.Hu, J.Fluorine chem., 23 (1983) 193.
10 W.-Y.Huang, B.-N.Huang and W.Wang, Acta Chimica Sinica, 41 (1983) 1193.
11 N.Kornblum, P.Ackermann and R.T.Swiger, J.Org.Chem., 45 (1980), 5294.
12 G.A.Russell and F.Ros, J.Am.Chem. Soc, 104 (1982) 7349.
13 A.E.Feiring, Sixth Winter Fluorine Conference Abstracts, Florida, 1983 p. 9.
14 D.C.England, L.R.Melby, M.A.Dietrich and R.V.Lindsey, Jr, J. Am. Chem. Soc, 82 (1960) 5116.
15 A.Rozov, Yu.V.Zeifman, Y.A.Cheburkov and I.L.Knunyants, Izvest. Akak. Nauk SSSR, Ser.Khim, (1975) 188.
16 A.L.J.Beckwith, C.J.Easton, T.Lawrence and A.K.Serelis, Aust.J.Chem., 36 (1983) 545.
17 Q.-Y.Chen and Z.-Y.Yang, J.Fluorine Chem., 28 (1985) 399.
18 D.C.Nonhebel and J.C.Walton, 'Free-radical Chemistry', Cambrige Univ.Press, 1974 pp. 212-214, 472-475.
19 Q.-Y.Chen and Z.-Y.Yang, Acta Chimica Sinica, to be published.
20 Q.-Y.Chen and Z.-Y.Yang, Acta Chimica Sinica, to be published.
21 A.A.Chiu, R.R.Gorby, J.E.H.Hancock and E.J.Hunstedt, J.Org. Chem. 49 (1984), 4313.
22 Perfluorosulfonic Acid Research Group (Shanghai Inst. Org. Chem.) Scientia sinica, 21 (1978) 773.
23 Y.-X.Chen and Q.-Y.Chen, Org.Chem., to be published.
24 D.A.White in 'Organic Syntheses' Vol 60, Ed, by O.L.Chapman Wiley-Interscience, 1981, p. 78.
25 Q.-Y.Chen and Z.-Y.Yang, to be published.
26 T.J.Otterbacker in 'Organic syntheses, Collective' vol 1 Ed. by H.Gilman, Wiley N.Y. 1947, sec. ed. p. 291.