Formation and reactions of carbanions from α-substituted perfluoroacyl fluorides*

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Abstract

Aliphatic α-substituted perfluoroacyl fluorides are converted to hindered ketones in low to moderate yields on refluxing in acetonitrile with alkali metal fluorides. Other products identified in hydrolyzed reaction mixtures include perfluoroolefins and monohydroperfluoro compounds. A mechanism involving the formation of a carbanion intermediate is proposed. Evidence for the formation of carbanions has been obtained by carrying out the reaction in the presence of bromine and also in the presence of other substrates.

Introduction

Perfluoroalkylcarbanions are important reactive intermediates in fluorocarbon chemistry [1]. They are commonly generated by the action of fluoride ions on fluoroolefins or by deprotonations of monohydroperfluoroalkanes. Other methods for their formation include the pyrolysis of alkali metal perfluoroalkane carboxylates, decomposition of perfluoroalkyl Grignard reagents [2], and Pd⁰-catalyzed thermal decomposition of esters [3], etc. Recently some stable perfluorinated carbanions have been studied spectroscopically [4] and some even isolated as tris(dimethylamino)sulfonium (TAS) salts [5].

Oligomeric α-substituted pefluoroacyl fluorides derived from hexafluoropropylene oxide (HFPO) are currently being used in this laboratory as starting material for the synthesis of perfluoroalkyl ether (PFAE) model compounds. During our studies we have observed a simple process of generating carbanions from these acid fluorides. The reactions leading to the formation as well as further reactions of these carbanions are discussed.

Experimental

Anhydrous acetonitrile was purchased from Aldrich Chemical Company in 'Sure/Seal' bottles and was used as such. KF and CsF were dried overnight

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at about 180 °C under vacuum. Only those compounds isolated were characterized completely. The structures of the others were indicated by MS and IR data. All boiling points are uncorrected. The boiling points of compounds isolated by preparative chromatography were determined by micro boiling point methods or by differential scanning calorimetry. Gas chromatographic analyses were performed on Perkin–Elmer Sigma 1 or Sigma 2B instruments using six-foot or 12-foot × 1/4-inch stainless-steel columns packed with 10% SE-30 on 80/100 mesh Supelcoport. Preparative gas chromatography was carried out on a Varex Model PSGC 10/40 instrument using 4 m or 2 m × 1 cm stainless-steel columns packed with 10% SE-30 on 60/80 mesh chromosorb PNAW. IR spectra were obtained on a Perkin-Elmer Model 600 instrument. GC/FTIR spectra were obtained on a Hewlett–Packard instrument having a model 5890 GC and a model 5965A IR detector. ^{19}F NMR spectra were obtained in $CF_2ClCFCl_2$ or its mixture with $CDCl_3$ on an NT-300 spectrophotometer at 282.3 MHz, using $CF_2ClCFCl_2$ as reference, the chemical shifts being reported as ppm. Mass spectra of compounds below 1000 amu were determined by electron impact or chemical ionization on a Finnigan 4021 mass spectrometer. Only major or significant peaks are given. All reactions were carried out under strictly anhydrous conditions, using an atmosphere of dry nitrogen.

A typical procedure for the preparation of a symmetrical ketone is described below.

Preparation of $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_2C(O)$ (IIa)

Anhydrous potassium fluoride (4.2 g, 72.4 mmol) was taken in a flask under a nitrogen atmosphere and dry acetonitrile (30 ml) was added at ambient temperature and stirred for 30 min. To this mixture, HFPO trimer acid fluoride, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ (Ia) (12.0 g, 24.1 mmol) was added, and the mixture was stirred at ambient temperature for 1 h. The reaction flask was then heated. At ~50 °C, the acetonitrile layer assumed a pale yellow color which deepened on further heating. The contents were heated to reflux (~75 °C) and maintained at this temperature for a period of 10 h. Aliquot samples were withdrawn periodically, and both the upper acetonitrile layer and the lower layer were analyzed by gas chromatography. The product IIa was present only in the lower layer. After the reaction, the flask was cooled in ice, and the reaction mixture was hydrolyzed with dilute hydrochloric acid. The lower organic layer was separated. GC/MS analysis showed products with the same retention time as Ia, which was a mixture of IIIa and IVa (~33%) and the ketone IIa (~66%) in addition to minor peaks. From the crude product, pure ketone was isolated by preparative gas chromatography (5.7 g, yield 51%) as a colorless liquid boiling at 216 °C (lit. value [7], 61 °C/0.3 mm Hg). IR: 1792(m) (C=O), 1360–1080(vs) (C−F), 1030(m), 995(vs), 980(vs), 890(m), 870(m), 815(m), 750(s) and 710(s) cm^{-1}. MS(CI): *m/z*, 949 $(M+F)^+$, 911 $(M-F)^+$, 745, 413, 335, 313, 169, 147, 119, 97 and 69. ^{19}F NMR: ($CF_2ClCFCl_2$), $\delta-80.6$ (overlapping, m), -81.4(q), -82.2 (broad), and -78 to -84 (set of weak peaks), all

corresponding to CF$_2$ and CF$_3$, -130 (AB pattern) CF$_2$ next to CF$_3$, -138 (overlapping peaks), CF, and -146 ppm (broad, s) CF in the expected ratio for the structure. Analysis: Found: C, 21.07; F, 69.18%; calculated for C$_{17}$F$_{34}$O$_5$: C, 21.93, F, 69.46%.

Compounds **IIb** and **IIc** were prepared using the procedure described above for **IIa**.

{C$_3$F$_7$O[CF(CF$_3$)CF$_2$O]$_2$CF(CF$_3$)}$_2$C(O) (IIb)

Isolated by preparative gas chromatography as a colorless liquid. Boiling point, 259 °C (lit. value [7] 267–271 °C), yield 27%. IR: 1790(m) (C=O), 1350–1090(vs) (C—F), 1030(m), 995(vs), 982(vs), 890(w), 865(w), 810(m), 748(s) and 710(s) cm^{-1}. ^{19}F NMR: (CF$_2$ClCFCl$_2$), δ -80.5 (unresolved, m), -81.4 (broad), -82.2 (unresolved, m), and -78 to -84 (set of weak peaks), all corresponding to CF$_2$ and CF$_3$, -130 (unresolved) CF$_2$ next to CF$_3$, -137 (broad) CF and -145(m) CF in the expected ratio for the structure. Analysis: Found: C, 21.82; F, 69.54%; calculated for C$_{23}$F$_{46}$O$_7$: C, 21.87; F, 69.26%.

{C$_3$F$_7$O[CF(CF$_3$)CF$_2$O]$_3$CF(CF$_3$)}$_2$C(O) (IIc) (n.c.)

Isolated by preparative gas chromatography as a colorless liquid. Boiling point, 290 °C (d), yield 19%. IR: 1785(m) (C=O), 1350–1100(vs) (C—F), 1030(m), 998(vs), 985(vs), 890(2), 865(w), 810(m), 748(s) and 712(m) cm^{-1}. Analysis: Found: C, 21.89; F, 67.29%; calculated for C$_{29}$F$_{58}$O$_9$: C, 21.85; F, 69.12%.

The experimental procedure for reaction in the presence of bromine or added substrates was similar to that described for the preparation of **IIa**, except that the extra reactant was added to the reaction mixture as heating was started. The experimental details of these reactions are given in Table 2 (see below). Of the two layers obtained after the reaction, the top acetonitrile layer contained only minor amounts of the products. Other than the reactions involving pentafluorobenzoyl chloride and cyanuryl fluoride, which were filtered under nitrogen before isolation of the product, the rest were hydrolyzed and the product isolated from the lower layer or analyzed by GC/MS and GC/FTIR.

C$_3$F$_7$OCF(CF$_3$)CF$_2$OCF(CF$_3$)Br (VI) (n.c.)

Colorless liquid boiling at 128 °C. IR: 1360–1110(vs) (C—F), 1090(s), 998(s), 985(s), 948(m), 932(s), 812(w), 805(w), 750(m), 710(w), 672(w) and 650(w) cm^{-1}. MS(CI): m/z, 513, 511 (M$-$F)$^+$, 376, 335 and 181, 179 (C$_2$F$_4$Br)$^+$. ^{19}F NMR: (CF$_2$ClCFCl$_2$), δ -78.4 (t, 27.9 Hz; sextet, 4.4 Hz) CFBr, -80.3 (complex, m) CF$_3$ on CFO$-$, -81.8 (superimposed peaks and adjacent broad complex peaks), CF$_3$ attached to CF$_2$, one CF$_2$ and half of other CF$_2$, -85.3 (t, 4.9 Hz) and adjacent broad complex peaks, CF$_3$ on CFBr and other half of CF$_2$, -130.0 (unresolved m) CF$_2$ next to CF$_3$, and -145.7 (t, 21.5 Hz) CF in the expected ratio. [The broad complex peaks for two CF$_2$ groups represent AB patterns for nonequivalent fluorines, because

of the asymmetric centers in the molecule.] Analysis: Found: C, 18.14; Br, 13.83%; required for $C_8F_{17}O_2Br$: C, 18.08; Br, 15.05%.

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CF_2Cl$ (VIII) (n.c.)

Colorless liquid boiling at 64 °C/40 mmHg. IR: 1798(m) (C=O), 1380–950(vs) (C—F), and 880(m), 850(m) (C—Cl) cm^{-1}. MS(EI): m/z, 529 $(M-Cl)^+$, 451 $(M-C(O)CF_2Cl)^+$, 381, 379 $(C_3F_6OC_2F_4C(O)CF_2Cl)^+$, 363, 335, 215, 213, 169 and 87, 85 $(CF_2Cl)^+$. Analysis: Found: C, 21.26; Cl, 6.09; F, 64.86%; required for $C_{10}F_{19}ClO_3$: C, 21.27; Cl, 6.28; F, 63.94%.

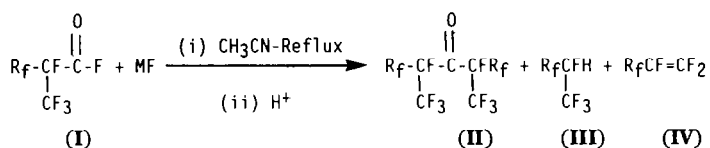## $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6F_5$ (IX)

This ketone was obtained from pentafluorobenzoyl chloride as a colorless liquid boiling at 217 °C (lit. value [14] b.p. not reported). IR: 1745(m) (C=O), 1648(m), 1520(vs), 1500(vs), 1420(m), 1350–1100(vs) (C–F), 1070(s), 990(vs), 978(s), 958(m), 808(m), 785(w), 742(m), 702(m) and 640(w). MS(EI): m/z, 461 $(M-C_3F_7O)^+$, 361, 295 $(C_6F_5C(O)C_2F_4)^+$, 267, 217, 195, 167, 117 and 69. ^{19}F NMR: $(CF_2ClCFCl_2)$, δ -77 to -83 (several multiplets) CF_3+CF_2O, -129(d) CF_2 next to CF_3, -136.3(m) para fluorine in C_6F_5, -139.1(m) ortho fluorines in C_6F_5, -144.8 (t, each broad) $-CFO$, -145.8 (t, each q) $-CFO$, -160.5 (t, each complex) meta fluorines in C_6F_5 in the expected ratio. Analysis: Found: C, 27.63; F, 67.13%; calculated for $C_{15}F_{22}O_3$, C, 27.86; F, 64.71%.

Compound XIII (n.c)

This 2-fluoro-4,6-bis(perfluoroalkylether)triazine was obtained as a colorless liquid boiling at 97–98 °C/1 mmHg. It is easily hydrolyzed by moisture, and therefore the isolation was carried out under a dry nitrogen atmosphere. IR: 1575 and 1565(s), 1445(s), 1392(m), 1360–1100(vs) (C–F), 1050(m), 998(vs), 985(s), 942(m), 890(w), 812 (m, broad), 752(m), 742(m) and 718(m) cm^{-1}. MS(EI): m/z, 814 $(M-C_3F_7O)^+$, 714 $(M-C_3F_7OC_2F_4)^+$, 648 $(M-C_3F_7OC_3F_6O)^+$, 486, 335, 316 $[C_3N_3(C_2F_5)(C_2F_4)F]^+$, 266, 216, 169, 126 $(C_3N_3F_2)^+$, 119 and 69. Analysis: Found: C, 22.91; N, 4.11; F, 64.78%; required for $C_{19}F_{35}N_3O_4$: C, 22.82; N, 4.20; F, 66.56%.

Results and discussion

When HFPO oligomeric acid fluorides (I) which contain a trifluoromethyl group as an α-substituent are refluxed in dry acetonitrile with anhydrous KF or CsF, hindered ketones (II) are formed as one of the products. Examination of the hydrolyzed reaction mixture showed the presence of monohydro perfluoroalkylethers (III) as the major by-product along with smaller amounts of olefins (IV).

$$\underset{(I)}{\overset{\displaystyle O}{\underset{\underset{CF_3}{|}}{R_f-CF-\overset{||}{C}-F}}} + MF \xrightarrow[\text{(ii) H}^+]{\text{(i) CH}_3\text{CN-Reflux}} \underset{(II)}{\overset{\displaystyle O}{\underset{\underset{CF_3}{|}\;\underset{CF_3}{|}}{R_f-CF-\overset{||}{C}-CFR_f}}} + \underset{(III)}{\underset{\underset{CF_3}{|}}{R_fCFH}} + \underset{(IV)}{R_fCF=CF_2}$$

$R_f = CF_3CF_2CF_2O[CF(CF_3)CF_2O]_n-$; $M = K$, Cs; (I–IV: **a**, $n = 1$; **b**, $n = 2$; **c**, $n = 3$)

Diglyme and tetraglyme were also used as solvents, but were less satisfactory than acetonitrile. The yields of the ketones (**II**) were only low to moderate. Higher ratios of MF to acid fluoride (up to 3:1) led to an increase in the yield of the ketone. The yield decreased with increasing molecular weight which may be due to a lower solubility in acetonitrile. These results are summarized in Table 1. These hindered ketones do not readily form hydrates, a behavior similar to that of bis(perfluoroiso-propyl)ketone [6]. Some of these symmetrical ketones have been prepared before by the reaction of acid fluoride with olefins in the presence of CsF in glyme solvents [7], the olefin being used as a precursor of the carbanions.

The unique ability of fluorinated acid fluorides to react reversibly with fluoride ions to form isolable alkoxides is well documented [8, 9].

$$\overset{\displaystyle O}{\overset{||}{R_f-C-F}} + MF \rightleftharpoons \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{R_f-C-O^-M^+}}$$
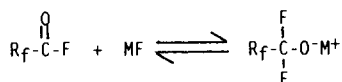
The speed and extent of equilibrium is dependent on temperature, solvent, structure of R_f and metal fluoride. Our results discussed here suggest that the alkoxides formed from **I** can also undergo a different mode of decomposition, leading to elimination of carbonyl fluoride and formation of the metal salt of a secondary carbanion. Such as intermediate (**V**) can readily explain the formation of the ketones (**II**) and the side products **III** and **IV**.

TABLE 1

Reaction of $R_fCF(CF_3)C(O)F$ (I) and MF in acetonitrile [$R_f = C_3F_7O(CF(CF_3)CF_2O)_n-$]

I (n)	MF	Ratio I:MF	Temp. (°C)	Time (h)	Products (GC area %)[a]	
					II	**III and IV**[b]
1	CsF	1:1	60	16	32	64
1	KF	1:1	75	10	19	80
1	KF	1:3	75	10	66 (51)	33
1	KF	1:4	75	10	60 (48)	34
2	KF	1:3	75	15	33 (27)	64 (19)[c]
3	KF	1:3	75	20	26 (19)	72

[a]Small amounts of unknowns were present in most reactions. Isolated yields are indicated in parentheses.
[b]Since **III**, **IV** and any unreacted **I** present were difficult to separate by GC in our hands, they were estimated together.
[c]This sample isolated by preparative GC, gave elemental analysis values in agreement with **III**, but GC/FTIR spectra showed small amounts of the olefin, **IV**.

This is represented in Scheme 1.

$$\underset{(I)}{R_f\text{-}\underset{CF_3}{\overset{O}{\overset{\|}{C}}}\text{F-C-F}} \quad \underset{-MF}{\overset{+MF}{\rightleftharpoons}} \quad R_f\text{-}\underset{CF_3\ F}{\overset{F}{\overset{|}{C}F\text{-}C\text{-}O^-M^+}}$$

$$-C(O)F_2 \Big\updownarrow +C(O)F_2$$

$$\underset{(II)}{R_f\text{-}\underset{CF_3\ CF_3}{\overset{O}{\overset{\|}{C}}F\text{-}C\text{-}CF\text{-}R_f}} \quad \underset{+MF}{\overset{-MF}{\Big\updownarrow}}$$

$$R_f\text{-}\underset{CF_3\ F}{\overset{O^-M^+}{\overset{|}{C}}F\text{-}C\text{-}CF\text{-}R_f} \xleftarrow{\ I\ } \underset{(V)}{R_f\text{-}\underset{CF_3}{\overset{|}{C}}F^-M^+} \xrightarrow{+H^+} \underset{(III)}{R_f\text{-}\underset{CF_3}{\overset{|}{C}}FH}$$

$$-MF \Big\updownarrow +MF$$
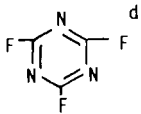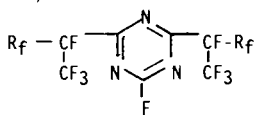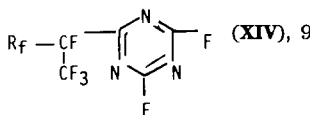
$$\underset{(IV)}{R_f\text{-}CF=CF_2}$$
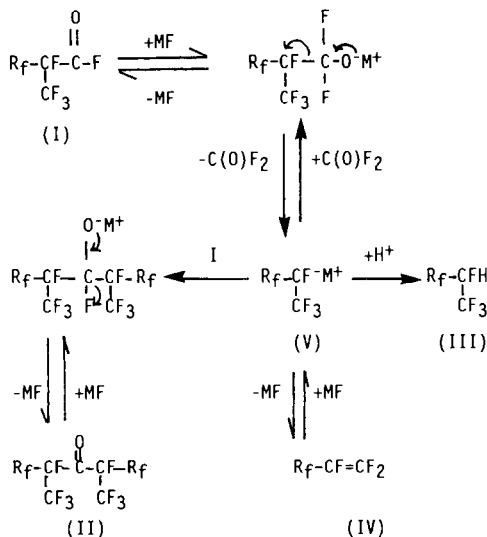
Scheme 1.

The representative reaction shown in Scheme 1, *i.e.* the addition of carbonyl fluoride to carbanions generated from olefins and metal fluorides, has been reported earlier [10] using hexafluoropropylene. The addition of carbanions to acid fluorides yielding ketones is also known [6, 7], but the elimination of carbonyl fluoride from these HFPO oligomeric acid fluorides does not appear to have been recognized. Analogous elimination of carbonyl fluoride has been reported [11] in $FSO_2CF_2CF_2O^-K^+$ yielding the carbanion $FSO_2CF_2{}^-K^+$, well stabilized due to its ease of conversion to difluorosulfene $(CF_2{=}SO_2)$ and KF. Similar elimination of carbonyl fluorides from $(CF_3)_2CFCF(SO_2F)C(O)F$ in the presence of fluoride ion was also postulated to account for the products isolated [12].

It may be remarked that when a linear acid fluoride, *i.e.* $C_2F_5O(CF_2CF_2O)_5CF_2C(O)F$, was subjected to the same experimental conditions, no ketone was detected though some lower oligomeric acid fluorides were formed.

Further evidence for the formation of a carbanion intermediate comes from trapping experiments with bromine as well as other substrates. These reactions were carried out with HFPO trimer acid fluoride (**Ia**). Reactions in the presence of added substrates led to competition between the added substrate and **Ia** for the intermediate **V** (Scheme 1), and appropriate products are formed depending on relative reactivities. The results are presented in Table 2. It may be noted that the structures of compounds $C_6F_5C(O)F$, $C_6H_5C(O)F$, **IIIa**, **IVa**, **VIII**, **X**, **XI**, **XII** and **XIV** were determined by mass spectra alone. It can be seen that chlorodifluoroacetic anhydride reacted readily with the anion giving rise to a mixed ketone **VII** whereas the carbanion **V** did not react with the ester carbonyl group in methyl chlorodifluoroacetate.

TABLE 2

Reactions of $R_f CF(CF_3)C(O)F$ (**Ia**) with MF and CH_3CN in the presence of added substrates (S) $[R_f = C_3F_7OCF(CF_3)CF_2O-]$

Substrate (S)	MF	Ratio Ia:MF:S	Conditions	Products (GC area %) [isolated yield][a,b]
Br_2	KF	1:3:4.3	75 °C, 10 h	$R_fCF(CF_3)Br$ (**VI**), 83 [40] IIIa, 13
$(ClCF_2\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-)_2O$	KF	1:3:1.1	70 °C, 4 h	$R_fCF(CF_3)C(O)CF_2Cl$, (**VII**), 91 [64] IIIa + IVa + Ia, 8 IIa, trace
$ClCF_2C(O)OCH_3$[c]	KF	1:1:1	70 °C, 16 h	$R_fCF(CF_3)C(O)OCH_3$ (**VIII**), 15 IIIa + IVa, 16 IIa, 60
$C_6F_5C(O)Cl$[d]	KF	1:3:1	75 °C, 15 h	$R_fCF(CF_3)C(O)C_6F_5$ (**IX**), 58 [34] IVa + Ia, 40 IIa, trace $C_6F_5C(O)F$, trace
$C_6H_5C(O)Cl$	KF	1:3:1	75 °C, 20 h	$R_fCF(CF_3)C(O)C_6H_5$ (**X**), 3 IIIa + IVa, 28 IIa, 6 $C_6H_5C(O)F$, 55
$C_6H_5CH_2Br$[c]	KF	1:3:1	75 °C, 10 h	$R_fCF(CF_3)CF_2OCH_2C_6H_5$ (**XI**), 20 $R_fCF(CF_3)C(O)OCH_2C_6H_5$ (**XII**), 5 IIIa + IVa, 50 IIa, 22
cyanuric fluoride (trifluorotriazine)[d]	CsF	3:4.4:1	75 °C, 4 d	$R_f-\underset{CF_3}{\overset{\|}{C}}F-$[triazine ring with F]$-CF-R_f$ $\overset{\|}{CF_3}$ (**XIII**), 48 [45] $R_f-\underset{CF_3}{\overset{\|}{C}}F-$[triazine ring with F]$-F$ (**XIV**), 9 IVa, 39

[a]Minor amounts of unidentified products were present in most reactions.
[b]Compound IIIa was seen only in hydrolyzed reaction mixtures. GC analysis immediately after hydrolysis still showed the presence of acid fluorides in some reactions, which on storage changed to acid.
[c]Substantial amounts of substrates remained unreacted in these reactions.
[d]These reaction products were processed without hydrolysis under dry N_2 atmosphere.

Pentafluorobenzoyl chloride gave fair yields of the mixed ketone **IX**. In contrast, benzoyl chloride acts as a fluoride-ion acceptor giving benzoyl fluoride as the major product, and only 3% of the mixed ketone **X**. Cyanuric fluoride gave mainly a disubstituted fluorotriazine (**XIII**). Even when the experiment (Table 2) was repeated with excess **Ia** and under pressure to 200 °C, no trisubstituted triazine was formed. Preparations of substituted

triazines have been reported from the carbanion generated from hexafluoropropylene and KF with cyanuryl fluoride under pressure [13]. Benzyl bromide did not give a product derived from the carbanion, but gave the ether **XI** derived from the alkoxide. An explanation of this behavior is not readily apparent. Hydrolysis of the reaction mixture led to the slow conversion of this ether to an ester **XII**.

Acknowledgements

References

1 R. D. Chambers, *Fluorine in Organic Chemistry*, Wiley–Interscience, New York, 1973; B. L. Dyatkin, N. I. Delyagina and S. R. Sterlin, *Russ. Chem. Rev. (Engl. Transl.)*, *45* (1976) 607; B. E. Smart, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Functional Groups, Supplement D*, Wiley, Chichester, 1983, part 1, chapt. 14.
2 R. N. Haszeldine, *J. Chem. Soc.*, (1952) 3423, 4259; *ibid.*, (1953) 1748.
3 Q. Chen and J. Chen, *Huaxue Xuebao, 46* (1988) 252 [*Chem. Abstr., 110* (1988) 7788m].
4 A. E. Bayliff and R. D. Chambers, *J. Chem. Soc., Perkin Trans. 1*, (1988) 201.
5 B. E. Smart, W. J. Middleton and W. B. Farnham, *J. Am. Chem. Soc., 108* (1986) 4905.
6 R. D. Smith, F. S. Fawcett and D. D. Coffman, *J. Am. Chem. Soc., 84* (1962) 4285.
7 T. Martini, *Tetrahedron Lett.*, (1976) 1861.
8 J. A. Young, *Fluorine Chem. Rev., 1* (1967) 389.
9 H. Millauer, W. Schwertfeger and G. Siegemund, *Angew. Chem., Int. Ed. Engl., 24* (1985) 161.
10 F. S. Fawcett, C. W. Tullock and D. D. Coffman, *J. Am. Chem. Soc., 84* (1962) 4275.
11 G. C. Krespan, *J. Fluorine Chem., 16* (1980) 385.
12 I. W. Cookson, R. N. Haszeldine, J. S. Kilburn and W. D. Morton, *Euchem Symposium*, Menton, France, June 27–30, 1976.
13 R. L. Dressler and J. A. Young, *J. Org. Chem., 32* (1967) 2004.
14 H. Gopal and C. Tamborski, *J. Fluorine Chem., 13* (1979) 337.