New Methods for the Synthesis of Perfluorooxaziridines. Preparation of *cis*-Perfluoro-2,3-dialkyloxaziridines

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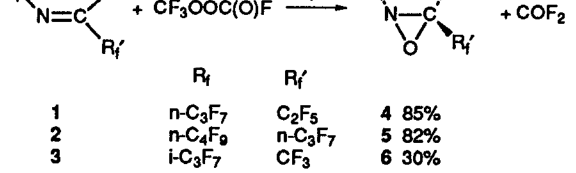
In the presence of metal fluorides $CF_3OOC(O)F$ oxidizes internal perfluoroazaalkenes forming the coresponding oxaziridines in high yields. Reaction of azaalkenes with $CF_2(OF)_2$ in the presence of CsF also gives the oxaziridines in modest yields. Evidence is presented for the intermediacy of the peroxyanion CF_3OO^- in these reactions, and the synthesis and characterization of the new oxaziridines $R_f\underset{\mathrm{O}}{\mathrm{N{-}CF}}R_f'$ (R_f, R_f' =n-C_3F_7, C_2F_5 **4**; n-C_4F_9, n-C_3F_7 **5**; i-C_3F_7, CF_3 **6**) are described.

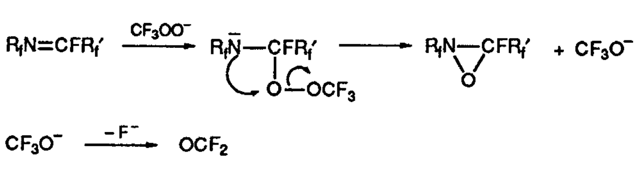
Ozaziridines are an important class of heterocyclic compounds which have been intensively studied over 40 years.[1,2] However, the first example of a perfluorinated oxaziridine was made only in 1976[3] and the number of examples of this type has remained very small. There are three methods for the preparation of polyfluorinated oxaziridines: oxidation of fluoroazaalkenes by hydrogen peroxide,[4] by chlorine gas in the presence of a metal carbonate [5] and by CF_3OOH.[3,6–8] The latter method accounts for nearly all known examples but the method is limited by the difficult preparation and potentially explosive nature of CF_3OOH.[9] This aspect has limited the development of this very interesting class of compounds which exhibit a reactivity quite different from hydrocarbon oxaziridines and which are much more potent oxidizing agents.[6–8,10–12] In this paper we present the details of two new routes for the preparation of perfluorooxaziridines, based on the reaction of perfluoroazaalkenes with $CF_3OOC(O)F$ or $CF_2(OF)_2$.

The reaction between internal perfluoroazaalkenes **1–3** and $CF_3OOC(O)F$ proceeds smoothly at 22 °C in the presence of dry CsF giving the corresponding oxaziridine and COF_2, Scheme 1.



Scheme 1 *Reagents and conditions*: i, 22 °C, 18 h, CsF

The mechanism of this reaction (Scheme 2) is probably similar to the mechanism proposed for the formation of perfluoro-2-azapropene oxide.[3] The reactive anion CF_3OO^- is generated *in situ* by the elimination of COF_2 from $CF_3OOCF_2O^-$ formed from $CF_3OOC(O)F$ and CsF. This anion attacks the carbon of the C–N bond, forming a new alkanamine anion which then undergoes an intramolecular cyclization by loss of CF_3O^- (Scheme 2).



Scheme 2

Oxaziridines **4–6** are stable, colourless liquids. Details on their characterization are given in the experimental section.‡ The IR spectra exhibit strong absorption within the range 1410–1440 cm^{-1} which is characteristic of the oxaziridine ring.[3,6–8] The CI mass spectra exhibit intense M + 1 ions for each compound and a variety of other fragment ions which are supportive of the parent compound. The ^{19}F NMR spectra, while quite complex, provide the most definitive proof of structure. The presence of two chiral centres in the molecule is responsible for the magnetic non-equivalence of the fluorines in the CF_2 groups bonded to carbon and nitrogen in **4** and **5**.

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‡ *General Procedure for Oxidation of Azalkenes with $CF_3OOC(O)F$.* The compounds **1–3**[17,18], $CF_3OOC(O)F$[14] and $CF_2(OF)_2$[19] were prepared by literature methods. Dried CsF (2 h, Bunsen burner) was placed in a 50 ml glass flask fitted with a glass–Teflon valve and a Teflon-covered magnetic stirring bar. After evacuation the azaalkene and $CF_3OOC(O)F$ were condensed into the reaction under vacuum. The reactor was warmed to 22 °C over 10–15 min and kept at this temperature for 19–24 h. The oxaziridines **4–6** were isolated by vacuum distillation through a series of traps. The reaction conditions, ratio of reactants and yields of products are summarized in Table 1. Purity of new compounds was determined by ^{19}F NMR and GLC analysis.

Perfluoro-2-propyl-3-ethyloxaziridine **4** (−100 °C trap), b.p. 68–69 °C, IR (gas) 1420(m), 1342(s), 1288(s), 1237(s), 1208(s), 1168(s), 1145(s), 1109(m), 1066(m), 1033(m), 952(m), 844(s), 815(s), 742(s) cm^{-1}; MS (CI, major), *m*/*z* 350 [$(M+1)^+$,100], 330[$(M-F)^+$,33], 312[$(M-F_2)^+$,17], 289[$(M-CF_3)^+$,17], 250($C_5F_{10}^+$,24), 184($C_3F_6N^+$,33) 169($C_3F_7^+$,56), 119($C_2F_5^+$,66); ^{19}FNMR ($CF_3^ACF^FF^{F'}CF^CF^D\overline{N O C}F^ECF^IF^{I'}CF_3^B$) A −81.4(3F, t), B −82.4(3F, d), C −99.6(d-q), D −107.4(d-q) (2F, typical AB pattern), E −140.8 (1F, br. m), F(I) −128.9, F′(I′) −129.1 (2F, typical AB pattern), I(F) −127.5, I′(F′) −128.6 (2F, typical AB pattern), $J_{C\text{-}D}=208$, $J_{I\text{-}I'}=284$, $J_{F\text{-}F'}=292$, $J_{D\text{-}E}=32$, $J_{C\text{-}E}=21$, $J_{A\text{-}C}=J_{A\text{-}D}=9$ Hz.

Perfluoro-2-butyl-3-propyloxaziridine **5** (−70 °C trap), b.p. 78–79/190 mm Hg; IR (liq.) 1414(m), 1353(m), 1220(s), 1193(s), 1159(m), 1139(s), 1073(m), 1024(m), 988(m), 956(m), 932(m), 909(m), 887(m), 737(m), 690(m) cm^{-1}; MS (CI, major), *m*/*z* 450[$(M+1)^+$,100], 434[$(M+1-O)^+$,40], 414[$(M\text{–}OF)^+$,31], 300($C_6F_{12}^+$,34), 169($C_3F_7^+$,100); ^{19}F NMR ($CF_3^ACF_2^GCF_2^FCF^CF^D\overline{N O C}F^ECF^I\text{-}F^{I'}CF_2^KCF_3^B$) A,B −81.4 (6F,q), C −99.5 (d-d-t), D −106.5 (d-d-t) (2F, AB pattern), E −139.8 (1F,m), I −124.5 (d-q), I′ −126.2 (d-q) (2F, AB pattern), F(K) −126.8 (2F,m), K(F) −125.3 (2F, m), G −127.3 (2F, d), $J_{C\text{-}D}=208$, $J_{I\text{-}I'}=294$, $J_{C\text{-}E}=23$, $J_{D\text{-}E}=31$, $J_{A\text{-}F}=J_{B\text{-}I,I'}=9$ Hz.

Perfluoro-2-isopropyl-3-methyloxaziridine **6** (−100 °C trap, mixture 1:1 with **3**, pure compund was isolated by preparative GLC: Halocarbon K-352, 3 m, He, 20 ml min^{-1}, oven temperature 50 °C), b.p. 45–46 °C; IR (gas) 1439(m), 1358(m), 1297(s), 1256(s), 1217(s), 1173(s), 1111(s), 997(s), 821(m), 710(m), 624(m) cm^{-1}; MS (CI, major), *m*/*z* 300[$(M+1)^+$, 85], 284 [$(M+1-O)^+$, 35], 280 [$(M-F)^+$,21)], 169 ($C_3F_7^+$,30), 145 ($C_3F_5N^+$,100). ^{19}F NMR ($CF_3^ACF_3^BCF^D\text{–}\overline{N O C}F^E\text{–}CF_3^C$) A −75.4 (3F, d-pent.), B −78.1 (3F,d-q), C −81.4 (3F, d), D −162.8 (1F,d-hept), E −140.5 (1F,d-q-q), $J_{D\text{-}E}=60$, $J_{A\text{-}D}=J_{B\text{-}D}=4$, $J_{A\text{-}B}=8$, $J_{A\text{-}E}=7$, $J_{C\text{-}E}=2$ Hz.

Table 1 Oxidation of perfluoroazaalkenes by $CF_3OOC(O)F$ in the presence of CsF

Azaalkene[a]	CsF[a]	$CF_3OOC(O)F$[a]	Time/h[b]	Products (%)
1, 2.0	13.2	2.2	19	**4** (85), COF_2 (30)
2, 3.0	13.2	3.5	18	**5** (82), COF_2 (67)
3, 2.0	39.5	2.2	20	**6**(30)[c], COF_2(9)

[a] mmol. [b] 22 °C. [c] Isolated by preparative GLC.

The large $^2J_{FF}$ values ($\sim$208 and 290 Hz) result in characteristic AB patterns for these fluorines. Large $^4J_{FF}$ couplings across the C–N bond of the ring between the ring carbon–fluorine and the CF_2 groups attached to nitrogen (23 and 31 Hz in **4**, 21 and 32 Hz in **5**) confirm the *trans* arrangement of the fluorocarbon groups in the oxaziridine as in the starting azaalkene. For **6** this ^4J coupling is a remarkable 60 Hz, suggesting a preferred eclipsed arrangement for these fluorines. All assignments and coupling constants were confirmed by homonuclear decoupling experiments and by COSY for **6**.

In previous work with CF_3OOH, the use of KF was necessary in order to observe the oxidation of $CF_3N{=}C(CF_3)_2$ to the oxaziridine. It was assumed that either CF_3OO^- or a complex $CF_3O_2H \cdots KF$ was responsible for the enhanced reactivity of CF_3OOH.[8] Trifluoromethyl hydroperoxide does not react with this or other internal azaalkenes without KF. The generation of CF_3OO^- by attack of fluoride ion on $CF_3OOC(F)$ has previously been inferred by chemical trapping of the anion with ClF to form CF_3OOCl and both $CF_3OOC(O)F$ and CF_3OOH react with MF (K, Rb, Cs) to give COF_2 and O_2, along with other products, depending on the conditions.[9,13] Thus it is very reasonable that CF_3OO^- is the oxidizing species as shown in Scheme 1.

In the synthesis of $CF_3OOC(O)F$, by reaction of $CF_2(OF)_2$ with COF_2 and CsF, the reaction is believed to proceed *via* an intermediate CF_3OO^- anion. (Scheme 3).[14,15] Evidence for the intermediate CF_3OO^- anion was also obtained in low-temperature reactions of $CF_2(OF)_2$ with $KOC(CF_3)_3$.[16] At −111 °C, $(CF_3)_3COF$ is formed in high yield and an explosive salt can be isolated. The latter decomposes above −78 °C to give O_2 and COF_2 quantitatively and if allowed to decompose rapidly, red light is emitted. If COF_2 is added to the unstable salt at −196 °C and allowed to warm to −20 °C, a high yield of $CF_3OOC(O)F$ is obtained. From these results it was reasoned that $CF_2(OF)_2$ might react directly with an azaalkene in the presence of CsF to give the oxaziridine. The alkanamine ion formed from CsF and the azaalkene would first be oxidized by $CF_2(OF)_2$ generating $CsOOF_3$ *in situ*. At 22 °C, a reasonable yield of oxaziridine **5** was obtained from **2** [−196 to 22 °C, 10 h; 22 °C, 12 h; 2 fold excess of **2** (16 mmol), 2 g CsF] (Scheme 4).

$$COF_2 + CsF \rightleftharpoons CsOCF_3$$

$$CF_2(OF)_2 + CsOCF_3 \longrightarrow CF_3OF + CsOCF_2OF$$

$$CsOCF_2OF \xrightarrow{O} CsOOCF_3 \xrightarrow{COF_2} CF_3OOC(O)F + CsF$$

Scheme 3

$$\mathbf{2} \rightleftharpoons CsN(C_4F_9)_2 \xrightarrow{CF_2(OF)_2} \text{"}CsOOCF_3\text{"} + (C_4F_9)_2NF$$

$$\text{"}CsOOCF_3\text{"} + \mathbf{2} \longrightarrow CsF + COF_2 + \mathbf{5}$$

Scheme 4

The ratio of $(C_4F_9)NF$[17b] to **5** (2 g total) was 78:28 and a substantial amount of O_2 was observed. In the absence of CsF, **2** and $CF_2(OF)_2$ did not react at 22 °C after 1 day. Collectively, we believe these results strongly support the intermediary of CF_3OO^- in these oxidations.

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