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Synthesis of new polyfluorinated oxaziridines

Viacheslav Petrov[a,*], Will Marshall[b]

[a] Chemours Co., Fluorochemicals, 200 Powder Mill Rd. Experimental Station 262/339, PO Box 2167, Wilmington DE, 19899, United States
[b] DuPont Experimental Station 500/1808, 200 Powder Mill Road· PO Box 8352· Wilmington, DE 19803, United States

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(1*S*,6*S*,7*R*,8*R*,10*S*)-3-(perfluoroalkyl)-4,9-dioxapentacyclo[5.3.1.02,6.03,5.08,10]undecanes
Reduction
Oxygen transfer

ABSTRACT

The article describes a synthesis of new per- and polyfluorinated oxaziridines along with some reactions of these materials.

1. Introduction

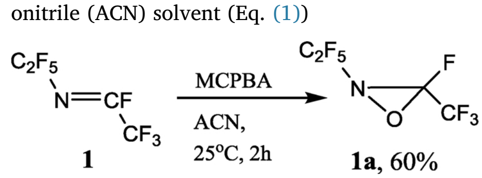
The first representative of polyfluorinated oxaziridines −oxide of perfluoro-2-azapropene [1], was shown to have an unusual and interesting reactivity [2]. The development of simple and general synthesis of perfluorinated oxaziridines, based on the reaction of dry *m*-chloroperoxybenzoic acid (MCPBA) with the corresponding perfluorinated imidoyl fluorides and imines [3,4] resulted in preparation of large number of perfluorinated oxaziridines, including $CF_3N(O)CFCF_3$ [5], $R_fN(O)CFR_f'$ [4], $Ar_fN(O)C(CF_2X)_2$ [6], $R_fSO_2N(O)C(CF_2X)_2$ [7], rapid development chemistry of these materials [2] and their application as neutral, potent oxidants for olefins [8], hydrocarbons [9,10], adamantanes [11], steroids [12], alcohols [13], sulfur- [14] and nitrogen containing compounds [15].

This article describes a synthesis of several new representatives of per- and poly- fluorinated oxaziridines and some reactions of these materials.

2. Results and discussion

Commercially available perfluorinated tertiary amines can be readily converted into the corresponding imidoyl fluorides $R_fN{=}CFR_f'$ through the reaction with catalytic amount of strong Lewis acid – antimony pentafluoride [16–18]. This reaction was also shown to be applicable to perfluorinated secondary amines [19]. For example, the cleavage of $(CF_3)CFN(F)C_2F_5$ was reported to proceed selectively under action of SbF_5, leading to the formation of $CF_3N{=}CFCF_3$ [19]. This process was successfully used for the preparation of $CF_3N{=}CFCF_3$ and it's oxide by Mlsna and DesMarteau [5].

Despite the fact, that a substantial number of perfluorinated oxaziridines was prepared at this point, the corresponding oxide of readily available [16] $C_2F_5N{=}CFCF_3$ (**1**) was never reported. In this study oxaziridine **1a** was prepared by oxidation of **1** with MCPBA in acetonitrile (ACN) solvent (Eq. (1))



(1)

Compound **1a** was isolated in 60% yield after vacuum transfer at low temperature and removal of residual solvent by washing with water. New oxaziridine was fully characterized by ^{19}F NMR, IR and mass- spectroscopy (Table 1).

The ^{19}F spectrum of oxaziridine **1a** exhibits A:B quartet ($-CF_2$ group, $J = 204.5$ Hz) due to magnetic non-equivalent fluorine substituents of CF_2- group and substantially shifted downfield signal of unique fluorine ($\delta = -146.00$ ppm in **1a** vs. -29.3 ppm in **1**), along with signals of two CF_3- groups (Table 1). Additional evidence for correct assignment of oxaziridine structure came from IR spectrum, which exhibited a band at

* Corresponding author.
E-mail address: viacheslav.petrov@chemours.com (V. Petrov).

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Table 1
NMR, IR and MS Data for New Compounds.

Comp. No	^{1}H NMR (δ, ppm, J, Hz)[a]	^{19}F NMR (δ, ppm, J, Hz)[a]	^{13}C NMR (δ, ppm, J, Hz)[a]	IR(cm^{-1})[b]	MS (*mz*)[c]
1a	–	-81.22(3F, s), −84.39(3F,s), −104.5 (1F,dd, 204.5, 23.8), −110.10 (1F, dd, 204.5, 30.5), −146.02, 1F, dd, 30.5, 23.8)	–	1448[d]	250 (M + 1,$C_4HF_9NO^+$)[e]
1c	–	-74.74 (1F, dddt, 164.0, 15.2, 7.4, 2.1), −74.91(1F, ddtt, 164.0, 13.7, 4.1, 1.3), −76.05(1F, dtt, 151.9, 17.6, 5.0) −84.07(1F, dddt, 151.9, 17.9, 8.1, 2.9) −97.83 (1F, dt, 235.2, 18.5) −102.78(1F, ddd, 235.2, 16.9, 9.6), −132.63 (1F, t, 14.8)	96.72 (ddd, 303.1, 43.0, 8.2), 108.8o-116.40(3 overlapped multiplets)	–	227(M$^+$, $C_4F_7NO_2^+$), 228 (M +1,$C_4HF_7NO_2^+$)
2a	1.08 (2H,m), 1.19 (1H, d quint., 11.0, 1.1), 1.26(1H, d quint., 11.0, 2.1), 1.63(2H,m), 2.21 (1H, m), 2.41(1H, dq, 4.6, 1.5), 3.11(1H, dd, 3.4, 0.9), 3.97(1H, m, 2.3)	-74.32 (d, 1.6)	24.64, 26.15, 29.66, 31.50, 34.52, 51.39, 69.80, 116.75(q, 277.0), 176.20(q, 38.2)	1611 (C=N)	189 (M$^+$, $C_9H_{10}F_3N^+$)
2b	1.50(1H, dm, 11.6), 1.57(1H, dm, 11.6), 2.89(1H, m, 1.5), 2.91(1H, m, 1.2), 2.99(1H, dt, 3.7, 0.5), 3.03(1H, dd, 3.4, 0.9), 3.15(1H, dm, 3.7, 0.9), 3.48(1H, dd, 3.5, 1.5)	-74.10 (s)	17.55, 34.17, 36.37, 44.33, 45.38, 47.70, 70.63, 77.00(q, 41.7), 118.40(q, 277.0),	1466	218 [(M-H)$^+$, $C_9H_7F_3NO_2^+$]
2c	0.79(1H, d, 11.3), 1.36(1H,dm, 11.3, 1.8), 2.54(1H, quint., 1.5), 2.71(1H, quint., 1.5), 3.28(1H, dm, 3.7, 0.6), 3.54(1H,m), 4.22(1H,m), 1.5)	−74.74 (d, 1.7)	–	–	–
3a	1.59(2H, s), 2.93(2H, m), 3.00(1H, d, 3.7), 3.04(1H, dd, 3.7, 0.5), 3.13(1H, dd, 3.7, 1.5), 3.53(1H, dd, 3.7, 1.2)	-88.99(3F, t, 1.7), −123.47(1F, d, 288.0), −127.33(1F, d, 288.0)	17.39, 34.16, 36.31, 45.29, 45.40, 47.48, 47.50, 77.03(dd, 37.8, 28.1), 108.20(tq, 261.0, 38.8), 115.93(qt, 285.8, 34.9)	1467	269(M$^+$, $C_{10}H_8F_5NO_2^+$)
4a	1.58(1H, dm, 12.5), 1.61(1H, dm, 12.5), 2.90(2H, m), 2.95(1H, d, 3.7), 3.05(1H, dd, 3.4, 1.2), 3.15(1H, dd, 3.7, 1.2), 3.52(1H, dt, 3.4, 1.2)	-81.40(3F, t, 3.0), −122.00(1F, dm, 291.4), −126.52(1F dm, 291.4), −127.501F, dt, 294.3, 4.3), −128.23(1F, dt, 294.3, 4.3)	17.30, 34.25, 36.28, 45.25, 45.72, 47.44, 70.93 77.00(dd, 37.8, 24.9), 107.76(tt, 266.0, 38.8), 109.69(tt, 254.0, 32.0) 115.28(qt, 282.0, 32.9)	1467	318 [(M-H)$^+$, $C_{11}H_7F_7NO_2^+$]
4b[f]	1.85(1H,dm, ~12), 2.10(1H,dm, ~12), 2.80 (1H,m), 3.15 (1H,m), 3.19 (1H, s), 3.43(1H, dt, 4.2, 1.5), 6.10 (1H, m), 6.28(1H,m)	–	–	–	303 (M$^+$, $C_{11}H_8F_7NO^+$)

[a] $CDCl_3$ as a lock solvent, unless indicated otherwise; ^{13}C {H} spectra.
[b] liquid film, KCl plates, unless indicated otherwise; band for oxaziridine ring.
[c] electronic ionization (EI), unless indicated otherwise.
[d] Gas-phase IR.
[e] Chemical ionization (methane).
[f] Characterized in mixture with **4a**.