

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

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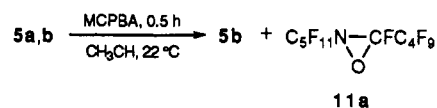
### Introduction

Oxaziridines are an important class of reactive heterocyclic compounds which have been intensively studied over 40 years.<sup>2,3</sup> However the first example of a perfluorinated oxaziridine was made only in 1976<sup>4</sup> and the number of examples of this type has remained very small. Until recently, there were only three methods for the preparation of polyfluorinated oxaziridines: oxidation of fluoroazaalkenes by hydrogen peroxide,<sup>5</sup> by chlorine gas in the presence of metal carbonate<sup>6</sup> and by CF<sub>3</sub>OOH.<sup>4,7-9</sup> The latter method accounts for nearly all known examples but this method is limited by the difficult preparation and potentially explosive nature of CF<sub>3</sub>OOH.<sup>10</sup> Recently two new methods for the preparation of perfluorinated *cis*-2,3-dialkyloxaziridines were reported based on the reaction of CF<sub>3</sub>OOC(O)F and CF<sub>2</sub>(OF)<sub>2</sub><sup>11</sup> with readily available azaalkenes obtained from reactions of commercial perfluorotrialkylamines with SbF<sub>5</sub>.<sup>12</sup> However these methods also involve highly reactive oxidizers and would not be attractive to most chemists. This aspect has limited the development of this very interesting class of compounds which exhibit a reactivity quite different from hydrocarbon oxaziridines.<sup>7-9,13-17</sup> The very promising use of these compounds as neutral selective oxidants in organic chemistry includes the oxidation of alkenes to epoxides,<sup>9,15,16</sup> sulfides to sulfoxides and sulfones,<sup>9,15</sup> and alcohols to ketones.<sup>16</sup> Very recently these oxaziridines were shown to effect in good yields and high regio- and stereoselectivity the hydroxylation of unactivated tertiary aliphatic C-H

bonds.<sup>17</sup> These and other results led us to reinvestigate earlier unsuccessful attempts to use a readily available oxidant for their preparation. In this paper we present the facile synthesis of perfluorinated oxaziridines using the common oxidant MCPBA.

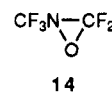
**Oxidation of Perfluoroazaalkenes by *m*-Chloroperoxybenzoic Acid (MCPBA).** For some time we have tried to apply more traditional oxidants to the conversion of fluorinated azaalkenes to oxaziridines, with little success.<sup>18</sup> Results with hydrogen peroxide were encouraging but the necessary concentrated H<sub>2</sub>O<sub>2</sub> is not readily available and it is also difficult to handle safely.<sup>5,9</sup> A stable readily available oxidant like *m*-chloroperoxybenzoic acid, which is widely used for hydrocarbon oxaziridine formation, would be ideal. We decided to reinvestigate earlier unsuccessful attempts with this reagent based on reports of the successful oxidation of highly electrophilic fluorinated alkenes to epoxides with MCPBA.<sup>19,20</sup> This proved successful with azaalkenes when the MCPBA was sufficiently concentrated (>80%) and well-dried and when CH<sub>3</sub>CN was used as a solvent (Table I). The oxidation is rapid in CH<sub>3</sub>CN (0.5-3 h), much slower in less polar benzonitrile, and does not proceed in CH<sub>2</sub>Cl<sub>2</sub> (2 d, 22 °C).

The isomeric azaalkenes **5** provide insight into the steric requirements in this reaction.

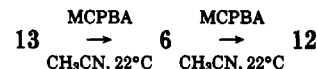


Clearly, greater steric bulk at the N=C carbon inhibits the oxidation by MCPBA. Only traces (if any) of the oxaziridine **11b** from **5b** could be detected by <sup>19</sup>F NMR, under this condition.

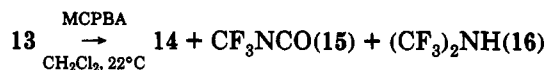
Finally of particular long-standing interest was an alternative method for the preparation of **14** from



CF<sub>3</sub>N=CF<sub>2</sub> (**13**). The azaalkenes **13** is rapidly dimerized by fluoride ion<sup>21</sup> and thus any oxidation method involving a source of active fluoride ion would lead to **12** via **6**. In addition **13** is extremely susceptible to hydrolysis and any oxidation in the presence of H<sub>2</sub>O would likely give CF<sub>3</sub>NCO as a major product.<sup>12</sup> Use of MCPBA in CH<sub>3</sub>CN gave only **12**.



However in the much less polar solvent CH<sub>2</sub>Cl<sub>2</sub>, the oxidations with MCPBA gave reasonable yields of **14**.



Compounds **15** and **16** are the hydrolysis products of **13** under conditions of excess **13**, reflecting the fact that

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(2) Schmitz, E. *Adv. Heterocycl. Chem.* **1963**, *2*, 83-130.

(3) Schmitz, E. *Adv. Heterocycl. Chem.* **1979**, *24*, 63-107.

(4) Falardeau, E. R.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1976**, *98*, 3529-3532.

(5) Navarrini, W.; DesMarteau, D. D., U.S. Pat. 4,874,875, 1989; *Chem. Abstr.* **1990**, *112*, 159140Y.

(6) Ratcliffe, C. T. (Allied Corp.) U.S. Pat. 4,287,128, 1981; *Chem. Abstr.* **1982**, *96*, 6550 h.

(7) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1980**, *19*, 1330-1333.

(8) Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 4844-4847.

(9) Bragante, L.; DesMarteau, D. D. *J. Fluorine Chem.* **1991**, *53*, 181-197.

(10) Bernstein, P. A.; Hohorst, F. A.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 3882-3886.

(11) (a) Petrov, V. A.; DesMarteau, D. D. *Mendeleev Commun.* **1993**, 87-88. (b) Petrov, V. A.; DesMarteau, D. D.; Bragante, L. Eur. Pat. Appl. EP 496414, 1992; *Chem. Abstr.* **1992**, *117*, 191830n.

(12) Petrov, V. A.; DesMarteau, D. D. *Inorg. Chem.* **1992**, *31*, 3776-3779.

(13) Sekiyama, A.; DesMarteau, D. D. *J. Org. Chem.* **1979**, *44*, 1131-1133.

(14) Lam, W. Y.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 4034-4035.

(15) O'Brien, B. A.; Lam, W. Y.; DesMarteau, D. D. *J. Org. Chem.* **1986**, *51*, 4466-4470.

(16) DesMarteau, D. D.; Petrov, V. A.; Montanari, V.; Pregnoto, M.; Resnati, G. *Tetrahedron Lett.* **1992**, *33*, 7245-7248.

(17) DesMarteau, D. D.; Petrov, V. A.; Montanari, V.; Donadelli, D.; Resnati, G. *J. Am. Chem. Soc.* **1993**, *115*, 4897-4898.

(18) DesMarteau, D. D., unpublished results.

(19) Zeifman, Yu. V.; Rokhlin, E. M.; Utebaev, U.; Mysov, E. I. *Dokl. AN USSR* **1975**, *226*, 1337-1340.

(20) Kadyrov, A. A.; Rokhlin, E. M.; Knunyants, I. L. *Izv. AN USSR. Ser. Khim.* **1982**, 2344-2347.

(21) (a) Knunyants, I. L.; Gontar, A. F. *Sov. Sci. Rev., Sect. B*: **1984**, *5*, 219-254.

Table I

azaalkene	R <sub>f</sub>	R <sub>f</sub> '	product
1	<i>n</i> -C <sub>3</sub> F <sub>7</sub>	C <sub>2</sub> F <sub>5</sub>	7
2	<i>n</i> -C <sub>4</sub> F <sub>9</sub>	<i>n</i> -C <sub>3</sub> F <sub>7</sub>	8
3	<i>i</i> -C <sub>3</sub> F <sub>7</sub>	CF <sub>3</sub>	9
4	<i>n</i> -C <sub>6</sub> F <sub>13</sub>	<i>n</i> -C <sub>5</sub> F <sub>11</sub>	10
5a	<i>n</i> -C <sub>6</sub> F <sub>11</sub>	<i>n</i> -C <sub>4</sub> F <sub>9</sub>	11a
5b	<i>n</i> -C <sub>5</sub> F <sub>11</sub>	CF <sub>3</sub> CF <sub>2</sub> CF(CF <sub>3</sub> )	11b <sup>a</sup>
6	CF <sub>3</sub>	N(CF <sub>3</sub> ) <sub>2</sub>	12

<sup>a</sup> Traces detected by <sup>19</sup>F NMR.

complete removal of H<sub>2</sub>O from MCPBA is difficult. This result also indicates that 1,1-difluoro-2-azaalkenes are more easily oxidized than internal azaalkenes, which do not react with MCPBA under the same conditions in CH<sub>2</sub>Cl<sub>2</sub>, in agreement with earlier work using CF<sub>3</sub>OOH.

Extension of the MCPBA oxidations to several other imines and azaalkenes, CF<sub>3</sub>CF=NBr, (CF<sub>3</sub>)<sub>2</sub>C=NCl, (CF<sub>3</sub>)<sub>2</sub>C=NCCL<sub>2</sub>CF<sub>3</sub>, and C<sub>3</sub>F<sub>7</sub>CF=NC(C<sub>2</sub>F<sub>5</sub>)=C(F)C<sub>2</sub>F<sub>5</sub>, failed. The double bonds in the *N*-halo imines are too electrophilic for oxidation by MCPBA and the two azaalkenes containing bulky substituents inhibit the oxidations as earlier mentioned for 5b.

In conclusion, a variety of perfluorinated oxaziridines can now be obtained in excellent yield from commercially available perfluoro tertiary amines in two steps: conversion of (R<sub>f</sub>)<sub>3</sub>N to R<sub>f</sub>N=CFR<sub>f</sub>' by SbF<sub>5</sub>, followed by oxidation with MCPBA in acetonitrile. These oxaziridines have excellent potential as potent neutral oxidizing agents in organic chemistry and further applications will be described in forthcoming publications.

### Experimental Section

Manipulations of reactants and products were carried out as described in recent publications.<sup>12</sup> Infrared, NMR, and mass spectra were similarly determined. *m*-Chloroperoxybenzoic acid (Aldrich, 80–85%, balance *m*-chlorobenzoic acid) was washed three times with a phosphate buffer (pH 7) and then was dried over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator for 5–10 h.<sup>22</sup> Acetonitrile and CH<sub>2</sub>Cl<sub>2</sub> were distilled over P<sub>4</sub>O<sub>10</sub>.

The compounds 1–5,<sup>12,23–24</sup> 6, 13,<sup>27</sup> (CF<sub>3</sub>)<sub>2</sub>C=NCCL<sub>2</sub>CF<sub>3</sub>,<sup>24</sup> CF<sub>3</sub>CF=NBr,<sup>25</sup> (CF<sub>3</sub>)<sub>2</sub>C=NCl,<sup>26</sup> and C<sub>3</sub>F<sub>7</sub>CF=NC(C<sub>2</sub>F<sub>5</sub>)=C(F)C<sub>2</sub>F<sub>5</sub><sup>28</sup> were prepared by literature methods. Compounds 7–9,<sup>11</sup> 12,<sup>5</sup> 14,<sup>4</sup> and 15 and 16<sup>29–30</sup> were identified by comparison of IR and NMR spectra were literature data. Purity of all compounds was

(22) Schwartz, N. N.; Blumberg, J. H. *J. Org. Chem.* 1964, 29, 1976–1979.

(23) Petrov, V. A.; Belen'kii, G. G.; German, L. S. *Izv. AN USSR. Ser. Khim.* 1985, 1934–1935.

(24) Peterman, K. E.; Shreeve, J. M. *Inorg. Chem.* 1975, 14, 1223–1228.

(25) O'Brien, B. A.; DesMarteau, D. D. *J. Org. Chem.* 1984, 49, 1467–1469.

(26) Ruff, J. K. *J. Org. Chem.* 1967, 32, 1676–1677.

(27) (a) Hauptschein, M.; Braid, F. E. *J. Org. Chem.* 1958, 23, 323. (b) Barr, D. A.; Haaszeldine, R. N. *J. Chem. Soc.* 1955, 1881–1889.

(28) Petrov, V. A.; Shevchenko, N. V.; Grinevskaya, V. K.; Parnes, Z. N.; Bardin, V. V.; Furin, G. G.; German, L. S.; Vol'pin, M. E. *Bull. AN USSR. Ser. Khim.* 1990, 2566–2570.

(29) Young, J. A.; Tsoukolas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* 1960, 82, 396–400.

Table II. Oxidation of Perfluoroazaalkenes by MCPBA

azaalkene <sup>a</sup>	MCPBA <sup>b</sup>	solvent (mL) <sup>d</sup>	time, h	products, % <sup>c</sup>
1, 21	24	30	1	7 (80)
2, 21	22	40	0.5	8 (68)
3, 12	17	20	0.5	9 (38)
4, 20	24	50	3	10 (77)
5a, b, 7 <sup>e</sup>	18	35	0.25	11a (95) <sup>f</sup>
6, 4	10	12	2	12 (80)
13, 5	10	25	0.5	12 (50)
13, 3	7	25 <sup>g</sup>	0.25	14 (53)
				15 (10)
				16 (25)

<sup>a</sup> Millimoles. <sup>b</sup> Millimoles based on 85% MCPBA. <sup>c</sup> Isolated yield. <sup>d</sup> Dry CH<sub>3</sub>CN. <sup>e</sup> Mixture of isomers, ratio 52:48, R<sub>f</sub>' = *n*-C<sub>4</sub>F<sub>9</sub>; CF<sub>3</sub>CF<sub>2</sub>CF(CF<sub>3</sub>). <sup>f</sup> Calculated yield, 5b recovered. <sup>g</sup> Dry CH<sub>2</sub>Cl<sub>2</sub>.

checked by GLC. Compounds 7–10, 12, and 14 were >98% pure. In the case of 5, 5a and 5b could not be separated before reaction with MCPBA and product 11a contained unreacted 5b, which also could not be readily separated.

**General Procedure for Oxidation of Perfluoroazaalkenes with *m*-Chloroperoxybenzoic Acid (MCPBA).** Dried MCPBA was dissolved in very dry CH<sub>3</sub>CN and the azaalkenes was then added with rapid stirring in one portion. After 1–3 h at 22 °C, the reaction mixture was diluted with dry CH<sub>3</sub>CN until the precipitated *m*-chlorobenzoic acid dissolved giving two liquid layers. The lower layer was then separated and distilled under vacuum. The reaction conditions, ratio of reactants, and yields of products are summarized in Table II. Compound 10 was checked by GLC after distillation and showed a purity of >98%. <sup>19</sup>F NMR (supplementary material) showed no fluorine-containing impurities and <sup>1</sup>H NMR showed no signals other than the reference.

**Perfluoro-2-hexyl-3-pentylloxaziridine (10):** bp 67–68 °C/20 mmHg; IR (liq) 1411 (m), 1361 (m), 1236 (s), 1202 (vs), 1143 (s), 1089 (s), 1025 (m), 985 (m), 860 (m), 813 (m), 792 (m), 734 (m), 718 (m) cm<sup>-1</sup>; MS (CI) *m/z* 650 [(M + 1)<sup>+</sup>, 60%], 634 [(M + 1 - O)<sup>+</sup>, 100], 630 [(M - F)<sup>+</sup>, 17], 614 [(M - OF)<sup>+</sup>, 81], 380 [(M - C<sub>6</sub>F<sub>11</sub>)<sup>+</sup>, 14], 319 (C<sub>6</sub>F<sub>13</sub><sup>+</sup>, 21); 119 (C<sub>2</sub>F<sub>5</sub><sup>+</sup>, 99); <sup>19</sup>F NMR (CF<sub>3</sub><sup>A</sup>(CF<sub>2</sub>)<sub>4</sub><sup>F</sup>CF<sup>D</sup>NOCF<sup>E</sup>CF<sub>2</sub><sup>I</sup>(CF<sub>2</sub>)<sub>5</sub><sup>G</sup>CF<sub>3</sub><sup>B</sup>) A, B -81.3 (6F, t), C -99.2 (ddtt) and D -106.2 (dtt) (2F, typical AB pattern), E -139.6 (1F, br m), I -124.5 (2F, m), F, G -122.4, -122.9, -123.3, -124.5, -126.6 (14F), *J*<sub>C-D</sub> = 208, *J*<sub>C-E</sub> = 24, *J*<sub>D-E</sub> = 31 Hz. Compound 11a was not identified as a pure compound and spectra (<sup>19</sup>F, IR, MS [CI]) were obtained on the distilled mixture of 5b and 11a. GC/MS of the mixture showed a 40/60 mixture of 5b/11a.

**Perfluoro-2-pentyl-3-butylloxaziridine (11a):** IR (liq) 1412 (NOCF) cm<sup>-1</sup>; MS (CI) *m/z* 550 [(M + 1)<sup>+</sup>, 100%]; <sup>19</sup>F NMR (CF<sub>3</sub><sup>A</sup>CF<sub>2</sub><sup>G</sup>(CF<sub>2</sub>)<sub>2</sub><sup>F</sup>CF<sup>D</sup>NOCF<sup>E</sup>CF<sub>2</sub><sup>I</sup>(CF<sub>2</sub>)<sub>2</sub><sup>F</sup>CF<sub>3</sub><sup>B</sup>) A, B -81.3 (overlaps 5b), C, D -99.3 (ddtt), and -106.1 (dtt) (2F, typical AB pattern), E -139.6 (1F, m), I -124.0 (m) and I' -125.2 (dt) (2F, AB pattern), F -123.3, 123.7, 124.6 (overlaps 5b), G -126.3 (overlaps 5b), *J*<sub>C-D</sub> = 208, *J*<sub>I-I'</sub> = 285, *J*<sub>C-E</sub> = 24, *J*<sub>D-E</sub> = 31, *J*<sub>C-F</sub> = 13, *J*<sub>D-F</sub> = 12 Hz.

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**Supplementary Material Available:** <sup>19</sup>F NMR spectrum of 10 (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(30) Fawcett, F. S.; Smith, W. C. (E.I. du Pont de Nemours and Co.) U.S. Pat. 3,118,923, 1960/64; *Chem. Abstr.* 1964, 60, 9148.