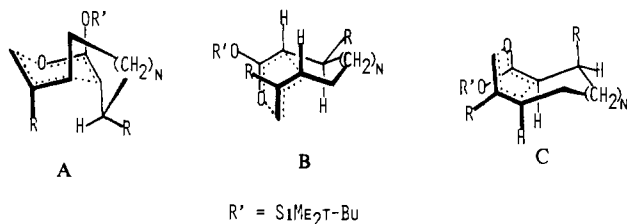
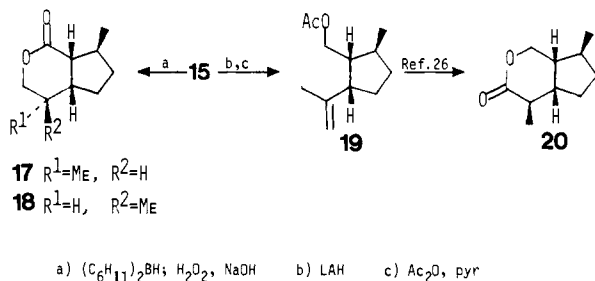


The preferential formation of the *cis*-2-alkenylcycloalkane-carboxylic acids (entries 1-7) can be understood by examining the possible transition states for rearrangement of the ketene acetals obtained upon silylation of the assumed (*Z*)-lithio lactone enolates.<sup>12</sup> Molecular models indicate the chairlike transition-state A to be much more strained than the boatlike transition-state B.



Transition-state A is accessible only when the diaxially bridging methylene chain becomes sufficient in length ( $n = 7$ ,  $R = H$ ). The preferential formation of the *trans* isomer from lactone **12** (entry 8) can be similarly rationalized. In this case, the analogous boatlike transition state for the ketene acetal derived from lactone **12** (not shown) ultimately leads to the *trans* carboxylic acid **16**. This boatlike transition state is understandably less highly favored since the analogous chairlike transition state now has a less strained axial, equatorial bridging methylene arrangement. Finally, the exclusive (>98%) formation of the *cis*,*trans*-cyclopentane-carboxylic acid **15** is a consequence of preferential rearrangement through boatlike transition state B ( $n = 1$ ,  $R = Me$ ) as opposed to the alternative boat conformer C ( $n = 1$ ,  $R = Me$ ) in which a serious A<sup>(1,3)</sup> type interaction<sup>14</sup> between the endocyclic oxygen atom and pseudoaxial methyl group is encountered, thereby precluding the eventual formation of the *cis*,*cis*-cyclopentane-carboxylic acid isomer. Similar relative asymmetric induction<sup>11</sup> is involved in the exclusive formation of the (*E*)-olefin stereochemistry in cyclopropanecarboxylic acid **13**.

The cyclopentanecarboxylic acid **15** is a useful substrate for the preparation of cyclopentanoid terpene lactones.<sup>15</sup> Thus, stereoselective hydroboration (2 equiv of (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>BH) of **15** with oxidative workup (NaOH, H<sub>2</sub>O<sub>2</sub>) directly provided the previously unsynthesized terpenes of *Nepeta cataria* (catnip oil),<sup>16</sup> ( $\pm$ )-dihydronepetalactone (**17**) and ( $\pm$ )-isodihydronepetalactone (**18**),



in a 93:7 ratio, respectively (75%).<sup>17</sup> Alternatively, reduction (LiAlH<sub>4</sub>) of carboxylic acid **15** followed by acetylation provided the known acetate **19**,<sup>18</sup> which was identical (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR) with an authentic sample.<sup>18</sup> The acetate **19** has been converted

(12) Molecular mechanics calculations predict the (*Z*)-enolate of macro-lactones to be highly preferred over the (*E*)-enolate isomer.<sup>13</sup> Highly stereoselective kinetic alkylations of nine- and thirteen-membered lactone enolates support this prediction.<sup>13</sup> Furthermore the (*Z*)-enolate is kinetically preferred even in acyclic ester enolizations.<sup>3</sup>

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(14) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

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to iridomyrmecin (**20**),<sup>18</sup> an insecticidal iridoid isolated from the Argentinian ant *Iridomyrmex humilis*. Therefore, this route constitutes a formal total synthesis of this cyclopentanoid terpene as well.

In summary, the methodology described herein represents a general and stereocontrolled route to multisubstituted cycloalkanes. Additional stereochemical control by remote chirality seems possible. Moreover, the potential for extending this process to the synthesis of heterocycles clearly exists. These topics in addition to the application of this methodology in natural product synthesis are under investigation.

**Acknowledgment.** We thank the University of Nebraska Research Council for initial financial and material support and the National Institutes of Health (Grant No. GM 28663) for current support. High-field (360 MHz) <sup>1</sup>H NMR spectra were obtained on a spectrometer purchased with funds provided, in part, by the National Science Foundation (CHE-80-24328). We thank Professor J. Wolinsky for furnishing authentic spectra of iso- and dihydronepetalactone.

**Registry No.** ( $\pm$ )-**4**, 81987-42-0; ( $\pm$ )-**8**, 81987-43-1; ( $\pm$ )-**9**, 81987-44-2; **10a**, 41979-97-9; **10b**, 41979-98-0; **10c**, 41979-99-1; **10d**, 81987-45-3; **10e**, 81987-46-4; **10e** *tert*-butyldimethylsilyl ketene acetal, 81987-47-5; ( $\pm$ )-**11**, 81987-48-6; **12**, 41980-03-4; ( $\pm$ )-**13**, 81987-49-7; ( $\pm$ )-**14a**, 81987-50-0; ( $\pm$ )-**14b**, 81987-51-1; ( $\pm$ )-**14c**, 81987-52-2; ( $\pm$ )-**14d**, 81987-53-3; ( $\pm$ )-*cis*-**14e**, 82010-05-7; ( $\pm$ )-*trans*-**14e**, 82043-25-2; ( $\pm$ )-**15**, 82041-92-7; ( $\pm$ )-**16**, 81987-54-4; 4-pentynoic acid, 6089-09-4; isobutyraldehyde, 78-84-2; ( $\pm$ )-6-hydroxy-7-methyl-4-octynoic acid, 81987-55-5; (*Z*)-3-iodo-2-methyl-2-propen-1-ol ethoxyethyl ether, 81987-56-6; 3-methyl-3-methoxy-1-butene, 13994-57-5; ethyl 4-iodo-3-methylpentanoate, 81987-57-7; ethyl ( $\pm$ )-*Z*-8-hydroxy-3,7-dimethyl-6-octenoate, 81987-58-8; **10d** *tert*-butyldimethylsilyl ketene acetal, 81987-59-9.

**Supplementary Material Available:** Experimental details for the preparation of hydroxy acids **4**, **5**, and **8**, and full spectral data for all compounds listed in Table I (9 pages). Ordering information is given on any current masthead page.

### Mechanism of Carbon Monoxide Substitution in a Metal Radical: Vanadium Hexacarbonyl

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Metal carbonyl radicals are postulated intermediates in a variety of catalytic and stoichiometric chemical transformations.<sup>2</sup> Although the substitution lability of 17-electron organometallic radicals has been recognized,<sup>3,4</sup> the precise mechanisms available are not well defined. For example, for the group 7 radicals M(CO)<sub>5</sub> (M = Mn, Re) both dissociative<sup>3</sup> and associative<sup>4</sup> substitution pathways have been proposed. Recent work favors an associative mechanism for substitution processes in Re(CO)<sub>5</sub><sup>4a</sup> and Mn(CO)<sub>3</sub>L<sub>2</sub><sup>4c</sup> species. Part of the difficulty in quantitatively discerning reactivity patterns of these radicals lies in the inherent

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(1) (a) Lanzhou, University, People's Republic of China. (b) Northwestern University.

(2) (a) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80-89. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (c) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. (d) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345-399.

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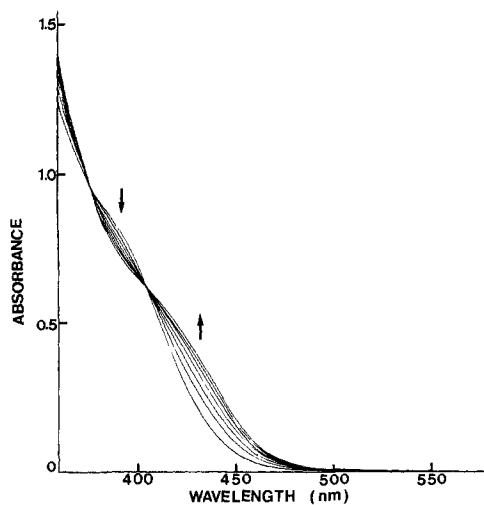
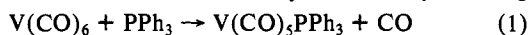


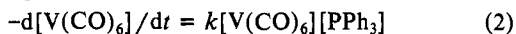
Figure 1. Visible spectral changes during the reaction between  $3.88 \times 10^{-4} \text{ M V(CO)}_6$  and  $7.10 \times 10^{-3} \text{ M PPh}_3$  in hexane at  $26^\circ \text{C}$ .

instability of the  $\text{M(CO)}_5$  species of interest. Therefore, we have examined ligand substitution kinetics of vanadium hexacarbonyl, the only stable homoleptic metal carbonyl radical. Although  $\text{V(CO)}_6$  has been the subject of a number of physical<sup>5</sup> and synthetic<sup>6</sup> investigations, herein we report the first quantitative kinetic study of ligand replacement in  $\text{V(CO)}_6$ .<sup>7</sup>

Vanadium hexacarbonyl reacts cleanly with triphenylphosphine in hexane solution to give the monosubstitution product according to eq 1.<sup>6</sup> The reaction can be conveniently monitored by observing



changes in the visible spectrum as a function of time as illustrated in Figure 1. Isosbestic points at 404 and 377 nm are maintained throughout the course of the reaction. Further substitution to yield  $\text{V(CO)}_4(\text{PPh}_3)_2$  is slow under the experimental conditions. The rate<sup>8</sup> of eq 1 varies with the  $\text{PPh}_3$  concentration and temperature as in Figure 2. Substitution proceeds solely by a second-order process ( $k = 2.53 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$ ) according to the rate law given in eq 2. As can be seen from Figure 2, no ligand-in-



dependent (i.e., dissociative) pathway exists under these conditions. In addition, carbon monoxide replacement by triphenylarsine, a poorer nucleophile than triphenylphosphine, is an order of magnitude slower at  $15^\circ \text{C}$ .<sup>9</sup> The better nucleophile  $\text{P}(n\text{-C}_4\text{H}_9)_3$

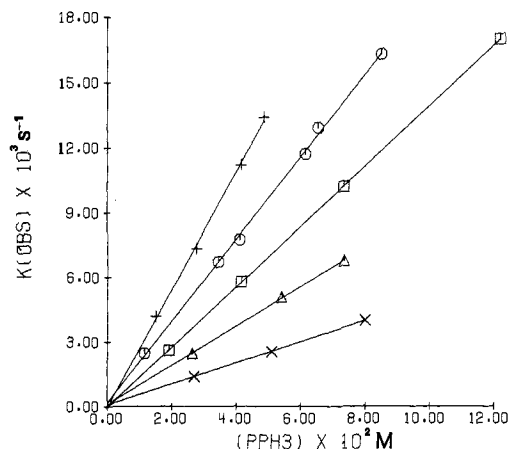


Figure 2. Plot of  $k_{\text{obsd}} (\text{s}^{-1})$  vs.  $\text{PPh}_3$  concentration (M) for the substitution of  $\text{V(CO)}_6$  by  $\text{PPh}_3$  in hexane solution: +,  $T = 26.0^\circ \text{C}$ ; O,  $T = 20.0^\circ \text{C}$ ; □,  $T = 15.0^\circ \text{C}$ ; Δ,  $T = 8.9^\circ \text{C}$ ; X,  $T = 0.0^\circ \text{C}$ .

substitutes CO about 200 times faster than  $\text{PPh}_3$ . Thus, carbon monoxide substitution appears to take place by an associative ( $\text{S}_{\text{N}}2$ ) process. This is corroborated by the observed activation parameters:  $\Delta H^\ddagger = 10.0 \pm 0.4 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -27.8 \pm 1.6 \text{ cal/(mol K)}$ . The relatively large, negative entropy of activation is similar to other CO-substitution reactions that proceed via a transition state of higher coordination number.<sup>10</sup> A seven-coordinate transition state seems reasonable since vanadium can expand its coordination sphere as evidenced by complexes of the type  $\text{EV(CO)}_6$ , where E is a bulky polarizable electrophile.<sup>12</sup> An alternative mechanism involving substitution of a 16-electron  $[\text{V(CO)}_6]^+$  intermediate formed by electron transfer<sup>11</sup> or by the action of trace oxidants may be eliminated on the basis of the highly reproducible kinetics observed and the fact that  $k_{\text{obsd}}$  does not depend on the  $\text{V(CO)}_6$  concentration, added  $[\text{V(CO)}_6]^-$ , or CO. Likewise the 18-electron  $[\text{V(CO)}_6]^-$  cannot be involved, because of its very slow rate of substitution (see below).

The substitution lability of  $\text{V(CO)}_6$  contrasts with the behavior of the isostructural<sup>13</sup> (but not isoelectronic) analogues chromium hexacarbonyl and vanadium hexacarbonyl anion.<sup>14</sup> Chromium hexacarbonyl substitutes CO very slowly even at elevated temperatures.<sup>15</sup> Indeed, extrapolation of high-temperature data<sup>15</sup> gives a second-order rate constant for CO replacement by tri-*n*-butylphosphine of  $10^{-9} \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$ . Associative substitution is about  $10^{10}$  times faster in  $\text{V(CO)}_6$  than in  $\text{Cr(CO)}_6$ . Similarly,  $\text{V(CO)}_6^-$  resists nucleophilic attack even under forcing conditions, and only photolytically induced substitutions of this anion have been reported.<sup>16</sup>

These results show that oxidation of  $\text{V(CO)}_6^-$  to the 17-electron  $\text{V(CO)}_6$  radical results in an extraordinary enhancement in the rate of CO substitution. Recent work of Kochi and Hershberger<sup>17</sup> demonstrates that electrochemical oxidation of the substitution inert  $\text{CpMn(CO)}_2(\text{CH}_3\text{CN})$  complex to the 17-electron Mn(II) cation results in facile replacement of the acetonitrile ligand by

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(8) Kinetic runs were conducted under pseudo-first-order conditions (with  $[\text{PPh}_3] > 10[\text{V(CO)}_6]$ ) by observing the change in optical density at 440 nm. Since  $\text{V(CO)}_6$  is very air sensitive, all manipulations were carried out under an atmosphere of prepurified nitrogen. Hexane was dried (Na/benzophenone) and rigorously degassed prior to use. Reactions were carried out in 1.00-cm quartz cells in the thermostated cell compartment of a Perkin-Elmer 320 spectrometer or in 4.00-cm Pyrex cells, constructed with an integral Dewar for temperature control, on a Cary 14. Plots of  $\ln(A_\infty - A_t)$  vs. time were linear for more than 3 half-lives, and  $k_{\text{obsd}}$  was obtained from the slope of this line by least-squares analysis. Rate constants were reproducible to  $\pm 5\%$ . Infrared monitoring of the reaction mixture showed  $\text{V(CO)}_5\text{PPh}_3$  ( $\nu_{\text{CO}}$  2050 (m), 1930 (s)  $\text{cm}^{-1}$ ) to be the only detectable product; no intermediates were observed. See ref 6 for a complete discussion of the properties of  $\text{V(CO)}_5\text{PPh}_3$ .

(9)  $\text{V(CO)}_5\text{AsPh}_3$  ( $\nu_{\text{CO}}$  2051 (m), 1934 (s)  $\text{cm}^{-1}$ ) forms as the initial product in the reaction of  $\text{V(CO)}_6$  with  $\text{AsPh}_3$ . The infrared spectrum of  $\text{V(CO)}_5\text{AsPh}_3$  is similar to that of  $\text{V(CO)}_5\text{PPh}_3$ . However,  $\text{V(CO)}_5\text{AsPh}_3$  is thermally unstable at room temperature. Isosbestic points at 415 and 350 nm were observed when the substitution reaction was monitored by visible spectroscopy. At  $15^\circ \text{C}$ ,  $k_2 = 1.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ .  $\text{V(CO)}_4(\text{AsPh}_3)_2$  has been reported to be thermally unstable: Werner, R. P. M. *Z. Naturforsch. B.* **1961**, *16*, 477.

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nucleophiles.<sup>18</sup> Interestingly, 19-electron organometallic radicals also appear to be substitution labile.<sup>19</sup>

Our results provide a quantitative foundation for understanding the reactivity of 17-electron organometallic radicals and suggest that their substitution lability may result from the availability of low-energy associative reaction pathways.<sup>20</sup> For octahedral  $d^5$  complexes the hole in the bonding  $t_{2g}$  orbital set permits nucleophilic attack on a triangular face of the octahedron. Further studies on the reactivity of  $V(CO)_6$  with small molecules are in progress along with parallel mechanistic work on other stable organometallic radicals.

**Acknowledgment.** We thank Professor T. L. Brown for advice and for communicating his results prior to publication. This research was supported in part by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the Ministry of Education of the People's Republic of China for their support.

**Registry No.**  $V(CO)_6$ , 14024-00-1;  $PPh_3$ , 603-35-0;  $V(CO)_5PPh_3$ , 72622-82-3.

(18) Chemical oxidation also induces unusual lability in organometallic systems. See, for example: Magnuson, R. H.; Zulu, S.; Tsai, W.-M., Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887-6888.

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(20) It should be noted the  $V(CO)_6$  differs somewhat from  $Mn(CO)_5$  and  $Re(CO)_5$ . The latter  $C_{4v}$  species possess a stereochemically active odd electron.

## Unusual Cycloaddition Reactions with 2-(Trifluoromethyl)-3,3-difluorooxaziridine

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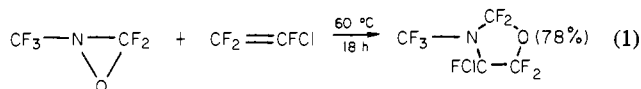
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Received March 11, 1982

Three-membered heterocycles containing two heteroatoms have been widely investigated, but the scope of this area of heterocyclic chemistry remains small compared to that of three-membered rings with one heteroatom.<sup>1</sup> Oxaziridines are the most extensively studied two-heteroatom systems of this type.

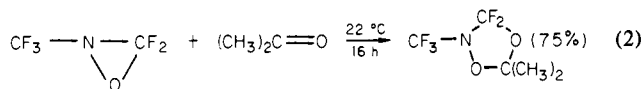
In 1976, the first example of a perfluorinated oxaziridine  $CF_3NCF_2O$  was reported.<sup>2</sup> This very stable but highly reactive compound exhibits a reaction chemistry very similar to the commercially important epoxide hexafluoropropene oxide (HFPO),<sup>3</sup> and it is attacked by a variety of nucleophiles exclusively at nitrogen.<sup>4</sup> With the recent availability of a variety of perhalogenated oxaziridines,<sup>5</sup> the chemistry of these novel heterocycles warrants continued investigation. We report here some unusual cycloadditions, most of which have not been observed for HFPO and which do not appear to be duplicated in kind by nonfluorinated oxaziridines.<sup>6</sup>

2-(Trifluoromethyl)-3,3-difluorooxaziridine (PFAPO)<sup>7</sup> reacts with  $CF_2=CFCl$  at 60 °C in glass to form 4-chloro-3-(trifluoromethyl)perfluoro-1,3-oxazolidine<sup>8</sup> (eq 1). Only a single regioisomer is formed, and other examples with  $CF_2=CBr_2$  and  $CF_2=CCl_2$  indicate that this reaction is regioselective and support



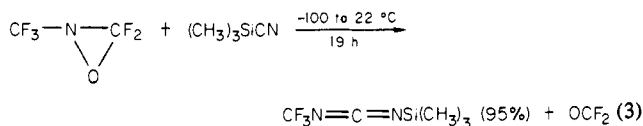
the structural assignments as shown. The <sup>19</sup>F NMR shows that all ring fluorines are nonequivalent with <sup>2</sup>J<sub>FF</sub> for carbons 2 and 5 equal to 93 and 111 Hz, respectively. The nonequivalence of the ring fluorines is clearly due to the chiral center at C-4, since the related compound 3-(trifluoromethyl)perfluoro-1,3-oxazolidine does not exhibit similar properties.<sup>8,9</sup> The mass spectrum (EI, 70 eV) exhibits intense M - F<sup>+</sup> ions at 246 (<sup>35</sup>Cl) and 248 (<sup>37</sup>Cl) and similarly in CI (70 eV, CH<sub>4</sub>) at MH<sup>+</sup> 266 and 268. The compound is a colorless liquid (bp 65.3 °C) with high thermal stability.

Reaction of PFAPO with acetone at 22 °C in glass yields 5,5-difluoro-2,2-dimethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine<sup>10,11</sup> (eq 2). The stable colorless liquid exhibits intense parent



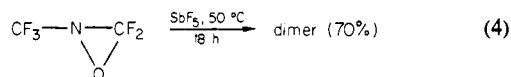
ions in both EI and CI mass spectra at M<sup>+</sup> 207 and MH<sup>+</sup> 208, respectively. The <sup>19</sup>F NMR is an A<sub>3</sub>B<sub>2</sub> spin system [ $\delta_A$  -68.8, m;  $\delta_B$  -68.2, m (internal CFCI<sub>3</sub>)] with J<sub>AB</sub> = 7.0 Hz. The <sup>1</sup>H NMR is a singlet at  $\delta$  1.6 (external Me<sub>4</sub>Si).

Reaction of PFAPO with (CH<sub>3</sub>)<sub>3</sub>SiCN in Teflon FEP at low temperature results in a high yield of OCF<sub>2</sub> and 1-(trifluoromethyl)-3-(trimethylsilyl)carbodiimide<sup>12</sup> (eq 3). It is reasonable



to propose that an intermediate cycloaddition occurs to form a  $\Delta^2$ -1,2,4-oxadiazolidine, which then undergoes loss of OCF<sub>2</sub> and rearranges to form the observed product. The carbodiimide is characterized by IR ( $\nu_{NCN}$  2215, vs; 1485 cm<sup>-1</sup>, s), NMR ( $\delta$  CF<sub>3</sub> -47.0, s; CH<sub>3</sub> 0.33, s), and mass spectra (M<sup>+</sup> and MH<sup>+</sup> at 182 and 183, respectively, for EI and CI).

Heating PFAPO with a small amount of SbF<sub>5</sub> in glass results in an unusual self-cycloaddition (eq 4). The structure of this



dimer is not yet proven but all evidence supports a saturated six-membered dioxadiazine ring. The IR and Raman spectra are consistent with that expected for the saturated ring. The mass spectrum shows intense ions M<sup>+</sup> and MH<sup>+</sup> at 298 and 299, respectively, in EI and CI and corresponding major fragments at M<sup>+</sup>/2 149 and (M/2 + H)<sup>+</sup> 150. Vapor density molecular weight also confirms the dimer (found 298, calcd 298.06). The <sup>19</sup>F NMR exhibits two CF<sub>3</sub> multiplets (1:1) at  $\delta$  -66.5 and -69.0 and two sets of AB multiplets (1:1) at  $\delta$  -73.0 and -88.3 with J<sub>AB</sub> ≈ 95 Hz for both. The two AB patterns coalesce into two somewhat broad singlets at 100 °C, but it is not possible to equilibrate the two CF<sub>3</sub> resonances or the two CF<sub>2</sub> resonances with each other. The <sup>13</sup>C NMR consists of two quartets and two triplets, all with very similar chemical shifts. These data provide strong proof for

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

(3) Tarrant, P.; Allison, C. G.; Barthold, K. P.; Stump, E. C., Jr. *Fluorine Chem. Rev.* **1971**, *5*, 77.

(4) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1979**, *14*, 289.

(5) Zheng, Y.; DesMarteau, D. D., to be submitted for publication.

(6) Some organic oxaziridines have been shown to undergo cycloadditions with some heterocumulenes: Komatsu, M.; Ohshiro, Y.; Hotta, H.; Sato, M.; Agawa, T. *J. Org. Chem.* **1974**, *39*, 948. Kormatsu, M.; Ohshiro, Y.; Yasuda, K.; Ichizima, S.; Agawa, T. *Ibid.* **1974**, *39*, 957.

(7) PFAPO stands for pentafluoroazapropene oxide after HFPO for hexafluoropropene oxide.

(8) Only one example of a perhalogenated oxazolidine has been reported: Banks, R. E.; Burling, E. D. *J. Chem. Soc.* **1965**, 6077.

(9) Lam, W. Y.; DesMarteau, D. D., to be submitted for publication.

(10) We are not aware of any previously reported fluorinated analogues of this type, but a related perfluoro compound is known, 2,2,4,5,5-pentakis-(trifluoromethyl)-1,3,4-dioxazolidine: Varwig, J.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 646.

(11) A related reaction with HFPO has been reported: Sianesi, D.; Pasetti, A.; Tarli, F. *French Patent* 1 503 361; *Chem. Abstr.* **1969**, *70*, 4100a.

(12) The only other reported analogue is CF<sub>3</sub>N=C=NCF<sub>3</sub>: Mitsch, R. A.; Ogden, P. M. *J. Org. Chem.* **1966**, *31*, 3833.