nucleophiles.[18] Interestingly, 19-electron organometallic radicals also appear to be substitution labile.[19]

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.[20] 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.

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(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.

(19) (a) Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265-266. (b) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238-5241.

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

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

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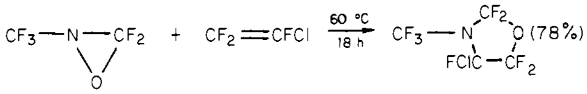
Three-membered heterocycles containing two heteroatoms have been widely investigated, but the scope of this area of heterocyclic chemistry remains small compared to that of three-membered rings with one heteroatom.[1] Oxaziridines are the most extensively studied two-heteroatom systems of this type.

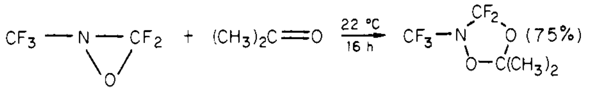
In 1976, the first example of a perfluorinated oxaziridine $\overline{CF_3NCF_2O}$ was reported.[2] This very stable but highly reactive compound exhibits a reaction chemistry very similar to the commercially important epoxide hexafluoropropene oxide (HFPO),[3] and it is attacked by a variety of nucleophiles exclusively at nitrogen.[4] With the recent availability of a variety of perhalogenated oxaziridines,[5] 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.[6]

2-(Trifluoromethyl)-3,3-difluorooxaziridine (PFAPO)[7] reacts with $CF_2{=}CFCl$ at 60 °C in glass to form 4-chloro-3-(trifluoromethyl)perfluoro-1,3-oxazolidine[8] (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 regiospecific and support the structural assignments as shown. The ^{19}F NMR shows that all ring fluorines are nonequivalent with $^2J_{FF}$ 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.[8,9] The mass spectrum (EI, 70 eV) exhibits intense $M - F^+$ ions at 246 (^{35}Cl) and 248 (^{37}Cl) and similarly in CI (70 eV, CH_4) at MH^+ 266 and 268. The compound is a colorless liquid (bp 65.3 °C) with high thermal stability.



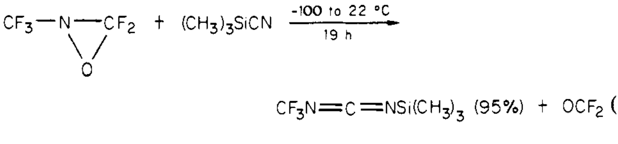
(1)

Reaction of PFAPO with acetone at 22 °C in glass yields 5,5-difluoro-2,2-dimethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine[10,11] (eq 2). The stable colorless liquid exhibits intense parent ions in both EI and CI mass spectra at M^+ 207 and MH^+ 208, respectively. The ^{19}F NMR is an A_3B_2 spin system [δ_A −68.8, m; δ_B −68.2, m (internal $CFCl_3$)] with J_{AB} = 7.0 Hz. The ^1H NMR is a singlet at δ 1.6 (external Me_4Si).



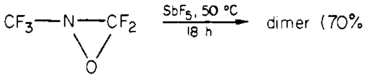
(2)

Reaction of PFAPO with $(CH_3)_3SiCN$ in Teflon FEP at low temperature results in a high yield of OCF_2 and 1-(trifluoromethyl)-3-(trimethylsilyl)carbodimide[12] (eq 3). It is reasonable to propose that an intermediate cycloaddition occurs to form a Δ^2-1,2,4-oxadiazolidine, which then undergoes loss of OCF_2 and rearranges to form the observed product. The carbodiimide is characterized by IR (ν_{NCN} 2215, vvs; 1485 cm^{-1}, s), NMR (δ CF_3 −47.0, s; CH_3 0.33, s), and mass spectra (M^+ and MH^+ at 182 and 183, respectively, for EI and CI).



(3)

Heating PFAPO with a small amount of SbF_5 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^+ and MH^+ at 298 and 299, respectively, in EI and CI and corresponding major fragments at $M^+/2$ 149 and $(M/2 + H)^+$ 150. Vapor density molecular weight also confirms the dimer (found 298, calcd 298.06). The ^{19}F NMR exhibits two CF_3 multiplets (1:1) at δ −66.5 and −69.0 and two sets of AB multiplets (1:1) at δ −73.0 and −88.3 with $J_{AB} \approx 95$ 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_3 resonances or the two CF_2 resonances with each other. The ^{13}C NMR consists of two quartets and two triplets, all with very similar chemical shifts. These data provide strong proof for



(4)

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(1) Schmitz, E. *Adv. Heterocycl. Chem.* **1979**, *24*, 63.

(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 $CF_3N{=}C{=}NCF_3$: Mitsch, R. A.; Ogden, P. M. *J. Org. Chem.* **1966**, *31*, 3833.

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the proposed ring, but the choice of which isomer is not easily made. We believe the compound is 3,3,6,6-tetrafluoro-2,5-bis(trifluoromethyl)-1,4,2,5-dioxadiazine, but the 1,4,2,6- and 1,2,4,5-dioxadiazines cannot be ruled out.[13]

The above reactions clearly show the remarkable properties of PFAPO. Considerable new synthetic work is indicated by these results, and the obvious mechanistic questions raised by these examples are of interest.

Acknowledgment. The support of this research by the U.S. Army Research Office (Grant No. DAAG29-80-C-0102) is gratefully acknowledged. J. V. Paukstelis is also acknowledged for helpful assistance with the NMR.

Registry No. PFAPO, 60247-20-3; PFAPO dimer, 82135-34-0; $CF_2{=}CFCl$, 79-38-9; $(CH_3)_3SiCN$, 7677-24-9; 4-chloro-3-(trifluoromethyl)perfluoro-1,3-oxazolidine, 82135-35-1; acetone, 67-64-1; 5,5-difluoro-2,2-dimethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine, 82135-36-2; 1-(trifluoromethyl)-3-(trimethylsilyl)carbodiimide, 82135-37-3.

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[13] Examples of saturated 1,4,2,5- and 1,4,2,6-dioxadiazines are apparently unknown. Several 1,2,4,5-dioxadiazines have been prepared and their conformational equilibria have been examined: Katritzky, A. R.; Baker, V. S.; Brito-Palma, F. M. S.; Sullivan, J. M.; Finzel, R. B. *J. Chem. Soc. Perkin 2* **1979**, 1133.

*Book Reviews**

Organic Syntheses. Volume 60. Edited by O. L. Chapman. John Wiley & Sons, New York. 1981. xii + 140 + 32 pp. $22.50.

There are 27 checked procedures in this volume, mostly emphasizing new or improved methods of some generality rather than specific important products. A resurgence of interest in organic electrochemistry is demonstrated with three electrochemical preparations. The usefulness of silicon compounds in synthesis is illustrated by four examples. Carbene chemistry, once largely of interest to physical organic chemists, is finding its place in synthesis, as shown by the introduction of a formyl group on styrene by means of dichloromethylene to prepare atropaldehyde, and the preparation of a cyclopropene from a carbene generated by thermolysis of a diazirine. These are merely examples of the good things to be found in this volume.

This venerable aid to the organic chemist has now reached its sixtieth anniversary, unheralded by jubilee celebrations, but nevertheless widely and deeply appreciated. The Editor alerts future submitters of methods that this occasion is marked by the adoption of a new style guide. The variety and timeliness of the preparations included in this volume demonstrate the health and vigor of this institution, with which most of us have been familiar from the beginning of our careers.

Chemistry and Physics of Carbon. Volumes 15, 16, and 17. Edited by P. L. Walker, Jr., and P. A. Thrower. Marcel Dekker, Inc., New York. 1979, 1980, and 1981, respectively. Volume 15: 320 pp. $36.50. Volume 16: 336 pp. $42.50. Volume 17: 320 pp. $45.00.

Lest anyone might be misled, it should be stated that the title of this series is not meant to include organic chemistry; the volumes are concerned with the element. Each contains a group of contributed reviews. In volume 15, these are Pyrocarbon Coating of Nuclear Fuel Particles, by Guilleray, Lefevre, and Price; Acetylen Black: Manufacture, Properties, and Applications, by Schwab; and The Formation of Graphitizable Carbons via Mesophase: Chemical and Kinetic Considerations, by Marsh and Walker. Volume 16 contains two reviews: The Catalyzed Gasification Reactions of Carbon, by McKee; and The Electron Transport Properties of Graphite, Carbons, and Related Materials, by Spain. In Volume 17 are to be found reviews on Electron Spin Resonance and the Mechanism of Carbonization, by Lewis and Singer; Physical Properties of Noncrystalline Carbons, by Delhaës and Carmona; The Effect of Substitutional Boron on Irradiation Damage in Graphite, by Brocklehurst, Kelly, and Gilchrist, and Highly Oriented Pyrolytic Graphite and its Intercalation Compounds, by Moore.

The orientation of the contributions is toward materials science and industrial concerns, although there is much fundamental chemistry to be found. Each volume is provided with a subject index and a complete author index, as well as the tables of contents of all prior volumes. The text is reproduced from typescripts which have apparently been retyped on the publisher's premises to provide a uniform appearance.

Energy Storage and Transportation. Edited by G. Beghi. D. Reidel Publishing Co., Dordrecht, Holland, and Boston, Mass. 1980. x + 497 pp. $39.50.

A course of lectures held at Ispra, Italy, in 1979, sponsored by The Joint Research Centre of the Commission of European Communities, provided the content of this book. There are 17 lectures plus an introduction and a subject index. Some of the topics are directly related to applied chemistry, such as: Hydrogen as Chemical Storage, by G. De Beni; Perspectives for Hydrogen Hydride Technology, by H. Buchner; Advanced Secondary Batteries, by M. Dell; Phase Change Heat Storage, by F. Fittipaldi; Coal Gasification and Liquifaction, by H. G. Rörtgen and U. Lenz; and Solar Energy Conversion and Storage by Semicondutor Liquid Junction Cells, by W. Gissler.

The papers are all in English and are reproduced from typescripts with several different typefaces, and there are a few ugly corrections. The lack of running headings makes the book difficult to use. There are bibliographies at the end of each paper, but they are rather short. Nevertheless, this book gives a useful, comprehensive insight into recent research and development activity.

Nitrogenous Air Pollutants: Chemical and Biological Implications. Edited by D. Grosjean. Ann Arbor Science Publishers, Ann Arbor, Mich. 1979. x + 349 pp. $33.00.

A symposium on the title subject, held at the 175th National Meeting of the A.C.S., generated the papers in this book of proceedings. The 20 contributed papers consist of book reports or original research and reviews. Those that are reviews are shorter than most of the primary papers and are therefore less useful than might be expected. Nevertheless, the wide variety of subjects covered provides a helpful introduction to the recent investigations. The variety of nitrogenous compounds found in polluted air is as interesting as it is disturbing, and includes not only oxides of nitrogen but amines, nitrosamines, peroxynitrates, and nitroarenes.

The volume concludes with a 4-page subject index, a feature pleasant to find in a book of proceedings, but a list of contributors (there must be over 50) is unfortunately lacking.

Solubility Data Series. Volume 7. Oxygen and Ozone. Edited by R. Battino (Wright State University). Pergamon Press, New York and Oxford. xviii + 519 pp. 1981. $100.00.

This volume continues the pattern of the series by presenting carefully sifted and evaluated data on solubilities in a form that is thorough, useful, and clear, to the extent that published information allows, guided by the motto quoted in the foreword: "If the knowledge is undigested or simply wrong, more is not better". The importance of the solubility of oxygen and ozone is exceptionally great, owing to the dependence of life processes on it. It is therefore appropriate that this volume indicates not only solubilities in water, numerous salt solutions, and organic solvents but also in various biological fluids, such as tissue, blood, vegetable oils, and wines. The editor notes with surprise the absence of information on the solubility of oxygen in deuterium oxide, but he expresses no surprise at "the paucity of high pressure solubility measurements for oxygen", and offers the hypothesis, perhaps resulting from an unhappy experience, that this paucity is "no doubt due to the probability of converting the dissolution vessel into a bomb calorimeter".

Encyclopedia of Chemical Technology. Third Edition. Volume 16. Edited by M. Grayson and D. Eckroth. John Wiley & Sons, New York. 1981. xxvi + 971 pp. $145.00.

This newest volume in the major revision of the Kirk-Othmer Encyclopedia covers topics from Noise Pollution to Perfumes. Two topics—Nuclear Reactors and Olefin Fibers and Polymers—make up about one-fourth of the book. Oxygen, ozone, and oxalic acid are each given a section. Organometallics are divided into σ-bonded and π-bonded compounds in separate sections. Paint, paper patents, and perfumes are among the important topics in the P portion. Nonwoven textile fabrics

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* Unsigned book reviews are by the Book Review Editor.