2 can be predicted for any extent of reaction. In Table II are listed the predicted and observed values for the configuration at phosphorus for the reaction of 2-[(*R*)-^{16}O,^{17}O,^{18}O]phospho-(*S*)-propane-1,2-diol that had proceeded some 23% to equilibrium. The product **1** and remaining **2** were isolated and purified by ion exchange chromatography followed (for **1**) by HPLC (see Table II). Stereochemical analysis by the ^{31}P NMR method we reported earlier[9] showed that the product **1** is predominantly formed with retention (see Figure 1[10]) and that the extent of racemization is, within experimental error, what is predicted from the rate constants determined independently.

The agreement between predicted and observed values (Table II) indicates that (i) the minimal kinetic scheme (Scheme I) is sufficient to describe the reaction course for the acid-catalyzed equilibration of **2** and **1** and (ii) the direct isomerization path proceeds with *quantitative retention of configuration at phosphorus, as predicted by the pseudorotation mechanism.* The possibility of a mechanism involving either free or caged metaphosphate species is unlikely. These results also provide the first evidence for the validity of the rules for pseudorotation[3] in a simple phosphoric monoester.

Acknowledgment. We are grateful to Dr. Joel Belasco and David Hansen for help with the computer program used to predict the isotopic content and stereochemical outcome. This work was supported by the National Institutes of Health. The Bruker NMR instrument used in this work was purchased with the help of a grant from the National Science Foundation.

Registry No. 1, 66943-89-3; **2**, 80262-60-8.

---

(9) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6601–6602.

(10) These spectra also demonstrate the power of our analytical method[9] even for a reaction where there is considerable washout of isotopic label.

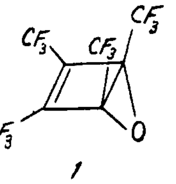
A Cyclobutadiene Oxide (Dewar Furan)

David Wirth and David M. Lemal*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received November 3, 1981

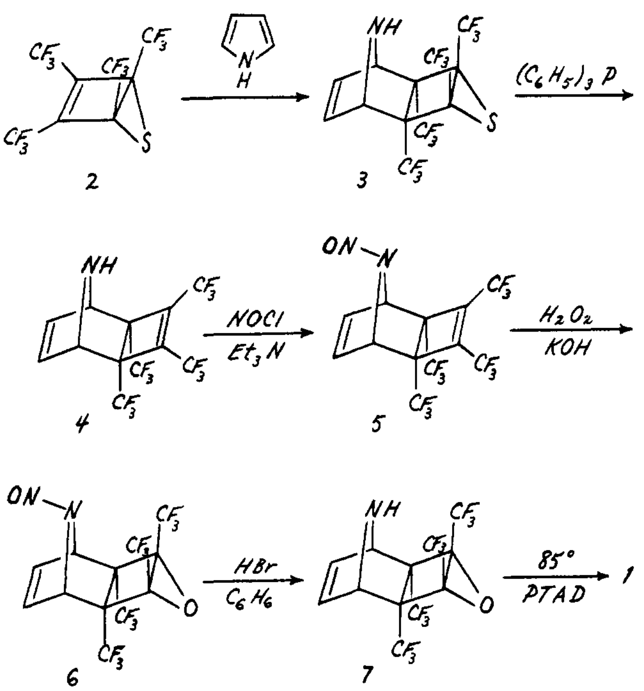
We wish to describe the synthesis and some unusual chemistry of perfluorotetramethylcyclobutadiene oxide [perfluorotetramethyl(Dewar furan), **1**], the first representative of its ring system.

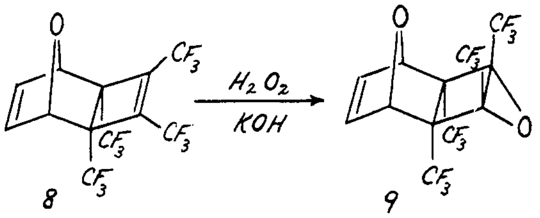


1

Although Dewar thiophene **2**, the sulfur analogue of **1**, is prepared by photocyclization of the thiophene,[1,2] this direct approach failed with the furan.[3,4] Hence **2** was chosen as the starting material from which to fashion **1**, but the disarmingly simple-looking **2** → **1** transformation required the circuitous pathway outlined in Scheme I. Since attempts to epoxidize **2** directly led to destruction of the ring system, its double bond was protected by formation of the known pyrrole adduct **3**.[5] Desulfurization with triphenylphosphine yielded diene **4**,[6] mp 43–46 °C (70% from **2**). Again attempted epoxidation of the perfluoroalkyl-substituted double bond with alkaline hydrogen peroxide[7] at room temperature resulted in thoroughgoing degradation. The problem was traced to the bridging nitrogen through the observation that the oxygen counterpart **8**[2,8] was successfully oxidized to **9** under these conditions. Accordingly, **4** was protected by nitrosation, giving **5**, mp 108–109 °C (92%). Oxidation of **5** with hydrogen peroxide in methanolic potassium hydroxide yielded oxirane **6**, mp 93–94 °C (60%). Hydrogen bromide in benzene transformed **6** into aminooxirane **7**, mp 53–84 °C[9] (80%). When **7** was heated at 85 °C and 15 torr in 1,2,4-trichlorobenzene containing a fivefold molar excess of 4-phenyl-1,2,4-triazoline-3,5-dione (to trap pyrrole), cyclobutadiene oxide **1** distilled into a cold trap (~55%). This volatile, colorless liquid displayed IR λ_{max} (vapor) 1695 cm^{-1} ($\nu_{C=C}$); ^{19}F NMR[10] (CDCl$_3$) δ 64.35 and 66.80; mass spectrum, *m/e* 321 ($M^+ - F$), 290 ($M^+ - CF_2$), 271 ($M^+ - CF_3$), 243 ($M^+ - COCF_3$), 69 (base, CF_3). The instantaneous reaction of **1** with pyrrole and furan to yield **7** and **9**, respectively, confirmed its structure.

Scheme I





Cyclobutadiene sulfide **2** undergoes a degenerate rearrangement which becomes detectable on the NMR time scale above 100 °C,[11]

---

(1) Wiebe, H. A.; Braslavsky, S.; Heicklen, J. *Can. J. Chem.* **1972**, *50*, 2721–2724.

(2) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Mochizuki, H. *Chem. Pharm. Bull. Jpn.* **1975**, *23*, 2773–2778. Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1981**, *14*, 76–82.

(3) Boriack, C. J.; Laganis, E. D.; Lemal, D. M. *Tetrahedron Lett.* **1978**, 1015–1018.

(4) Kobayashi, Y.; Hanzawa, Y.; Nakanishi, Y.; Kashiwagi, T. *Tetrahedron Lett.* **1978**, 1019–1022.

(5) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Ando, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2355–2357.

(6) Satisfactory elemental analyses were obtained for all new compounds except **1**, whose C, H analysis fell within 0.6% of the calculated values.

(7) Tarrant, P.; Allison, C. G.; Barthold, E. C.; Stump, Jr. *Fluorine Chem. Rev.* **1971**, *5*, 102.

(8) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325–4327.

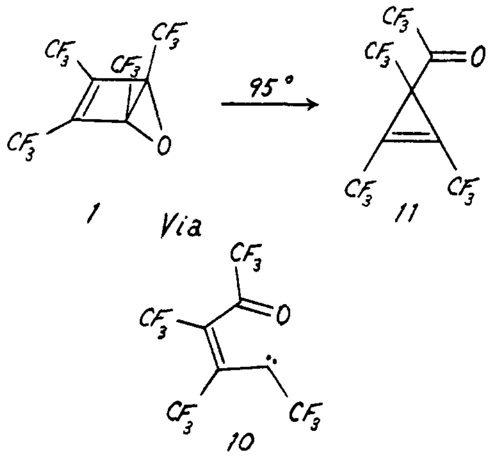
(9) Despite the broad melting range, the compound was pure as judged by ^{19}F NMR spectroscopy and gave the following analysis. Anal. Calcd: C, 35.38; H, 1.23; N, 3.44; F, 56.02. Found: C, 35.30; H, 1.30; N, 3.68; F, 56.22.

(10) Chemical shifts are reported relative to internal CCl$_3$F.

(11) Bushweller, C. H.; Ross, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 629–631.

0002-7863/82/1504-0847$01.25/0

but it suffers irreversible change—quantitative aromatization[12]—only only under rather vigorous conditions ($t_{1/2} = 5$ h at 160 °C[2,13]). In contrast, cyclobutadiene oxide **1** valence isomerizes cleanly by a different pathway at temperatures below 100 °C ($t_{1/2} \simeq 20$ min at 95 °C), yielding the extremely stable cyclopropenyl ketone **11**.[3,14] We interpret this unexpected rearrangement of **1** in terms of fragmentation to carbene **10** followed by the amply precedented cyclization of a vinylcarbene to a cyclopropene.[15,16] For the parent heterocycle, cyclobutadiene oxide itself, one can estimate from strain and bond energies that formation of the carbene should be close to thermoneutral. Facile thermal access to a carbene from a ground state may be attributed here to relief of approximately 70-kcal/mol strain in two small rings[17] and the generation of a C–O π bond.[18] MNDO calculations[21] yield an energy difference of 17 kcal/mol between fully optimized cyclobutadiene oxide and the (singlet) carbene, *s-cis*-(*Z*)-2-buten-4-yliden-1-al. The dichotomous behavior of **1** and **2** on thermolysis is understandable on the basis that (1) the difference between single and double bond energies is more than 20 kcal/mol greater for C–O than for C–S[22] and (2) thiophene enjoys significantly greater aromatic stabilization than furan.[23]



1 Via 10 11

The retro-Diels–Alder reaction of **9**, carried out in a flow apparatus, required temperatures approaching 200 °C, and thus gave ketone **11** unaccompanied by the presumed intermediate **1**. It was this discovery which stimulated us to synthesize **7**, whose fragmentation was expected to proceed under milder conditions by virtue of the greater stabilization energy of pyrrole as compared to furan.[23]

Kobayashi has shown that Dewar thiophene **2** is a talented dienophile which undergoes Diels–Alder addition to many unhindered dienes at ambient temperatures.[5] Competition experiments now reveal that its oxygen counterpart **1** reacts with furan at 25 °C *three orders of magnitude faster than* **2**. We ascribe the high reactivity of both dienophiles to low-lying LUMO's, which confer upon them cyclobutadienoid character.[24] Perhaps the more reactive **1** has the lower lying LUMO, as predicted by simple molecular orbital theory. The cycloaddition chemistry of **1** will be discussed more fully in a future report.

We plan to synthesize and study cyclobutadiene oxide itself.

Acknowledgment. We thank the National Science Foundation for generous support of this research.

Registry No. 1, 80326-57-4; **2**, 39091-73-1; **3**, 66008-14-8; **4**, 80326-58-5; **5**, 80326-59-6; **6**, 80326-60-9; **7**, 80326-61-0; **9**, 80326-62-1; **11**, 67705-04-8.

---

[12] The corresponding aziridine (Dewar pyrrole) also aromatizes on heating, but automerization has not been detected. Kobayashi, Y.; Ando, A.; Kawada, K.; Kumadaki, I. *J. Org. Chem.* **1980**, *45*, 2966–2968.

[13] This appears to be another manifestation of the perfluoroalkyl effect. Lemal, D. M.; Dunlap, L. H., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 6562–6564.

[14] The assignments of ^{19}F NMR signals to the nonvinyl CF_3 groups in this compound were inadvertently switched in ref 3.

[15] Hartzler, H. In "Carbenes", Moss, R. A., Jones, M., Eds.; Wiley: New York, 1975; Vol. II, p 57ff.

[16] For a closely related example, see: Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6634–6636.

[17] From the heat of isomerization of bicyclo[2.1.0]pent-2-ene to cyclopentadiene (47.8 kcal/mol), the strain energy of the former is almost 75 kcal/mol; about 10 kcal of this has been attributed to homoantiaromaticity.[19]

[18] Gordon, A. J.; Ford, R. A. "The Chemists' Companion, A Handbook of Practical Data, Techniques, and References", Wiley-Interscience: New York, 1972; p 113.

[19] Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818–1829.

[20] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; pp 273, 276.

[21] These were performed by R. Dave Mitchell and David Wirth at Columbia University, through the kind courtesy of Professor Ronald Breslow. See: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558–5561 and references contained therein.

[22] Johnson, D. A. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 2, pp 58–60.

[23] Pihlaja, K.; Taskinen, E. In "Physical Methods in Heterocyclic Chemistry"; Katritzky, A. R., Ed.; Academic Press: New York, 1974; Vol. VI, pp 240–246.

[24] Antihomoaromaticity in bicyclo[2.1.0]pent-2-ene has been predicted[25] and recently documented.[19,26] Enhanced Diels–Alder reactivity is one of its manifestations.[19]

[25] Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784–6789; **1975**, *97*, 3082–3090. Borden, W. T.; Jorgensen, W. L. *Ibid.* **1973**, *95*, 6649–6654.

[26] Andrews, G. D.; Baldwin, J. E.; Gilbert, K. E. *J. Org. Chem.* **1980**, *45*, 1523–1524.

Silver Ion Affinities of Alcohols As Ordered by Mass Spectrometry/Mass Spectrometry

S. A. McLuckey, A. E. Schoen, and R. G. Cooks*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 24, 1981

Interest in gas-phase organometallic and inorganic complexes is at a high level[1] due to successful studies of intrinsic chemistry of organic ions[2] and the availability of laser desorption techniques for metal ion production.[3] The affinities of molecules for metal ions and the structures of the products of this interaction are key aspects of organometallic chemistry to which the technique of mass spectrometry/mass spectrometry (MS/MS)[4] should contribute. We now show that MS/MS can be used to order metal ion affinities for various ligands through the following sequence: (i) the metal ion is generated by laser desorption from the metal in the presence of the vaporized ligand(s); (ii) among the resulting products is the metal-bound dimer ion $(L_1 \cdots M \cdots L_2)^+$ (L = ligand, M = metal) which is mass selected; (iii) its structure is established by recording a collision-induced dissociation spectrum of fragment ions; (iv) finally, relative affinities of L_1 and L_2 for M^+ are assigned from the fragment intensity ratio $[L_1M^+]/[L_2M^+]$. We conclude inter alia that silver ion affinities depend upon the nature of the heteroatom in the ligand (ammonia solvates Ag^+ more strongly than does water) and upon polarizability and inductive effects which favor larger and more branched solvent molecules.

Consider the following data as an illustration of the basis for the method. An aluminum foil irradiated in the presence of diethylamine and isopropylamine by 1.06-μm radiation from a Nd:YAG laser in a combined chemical ionization/laser desorption

---

[1] (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 455. (b) Holland, P. M.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 6174. (c) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 784. (d) Kappes, M. M.; Staley, R. H. *Ibid.* **1981**, *103*, 1286. (e) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Ibid.* **1981**, *103*, 4360.

[2] Levsen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie: New York, 1978.

[3] Conzemius, R. J.; Capellen, J. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 197.

[4] (a) Kruger, T. L.; Litton, J. F.; Kondrat, R. W.; Cooks, R. G. *Anal. Chem.* **1976**, *48*, 2113A. (b) Kondrat, R. W.; Cooks, R. G. *Ibid.* **1978**, *50*, 81A (c) Yost, R. A.; Enke, C. G. *Ibid.* **1979**, *51*, 1251A. (d) Hunt, D. F.; Shabanowitz, J.; Giodani, A. B. *Ibid.* **1980**, *52*, 386. (e) McLafferty, F. W. *Acc. Chem. Res.* **1980**, *13*, 33.

0002-7863/82/1504-0848$01.25/0 © 1982 American Chemical Society