the BH_4^- protons by saturation of the same resonances should produce a substantial indirect (negative) NOE at boron, and it is the difference between the positive (direct) and negative (indirect) effects that is observed. Evidently, direct effects predominate at the ^{11}B nucleus upon saturation of the α-CH_2 protons, while the indirect effects predominate upon saturation of the β-CH_2.

These results indicate a close equilibrium association between the BH_4^- anion and the quaternary nitrogen, a result at odds with some predictions.[10] Figure 2 shows a model for the ion-pair structure which rationalizes the observed NOEs. This model places each of three BH_4^- hydrogens in van der Waals contact with two α-CH_2 protons and one β-CH_2 proton in a pyramidal site created by three *n*-butyl side chains and the quaternary nitrogen. The α-CH_2 and β-CH_2 groups of each *n*-butyl group are in staggered (anti) conformation, and a C_3 symmetry axis through the nitrogen and the C-α carbon of the fourth *n*-butyl side chain (not shown) is present. This packing arrangement optimizes Coulombic interaction, with CPK models indicating a N–B distance of ca. 3 Å (M–B distances in crystalline alkali tetrahydroborates range from 2.5 to 3.7 Å).[10] The van der Waals contact with two α-CH_2 protons and one β-CH_2 proton for each of three BH_4^- hydrogens rationalizes the experimental ratio of NOEs to the BH_4^- protons of ca. 2:1 obtained upon saturation of the α-CH_2 and β-CH_2 protons, respectively. The predominance of the indirect (negative) NOE to the ^{11}B nucleus upon saturation of the β-CH_2 protons is also reasonable on the basis of this model, since the BH_4^- protons are on a time average directly between the β-CH_2 protons and the boron nucleus.

Acknowledgment. We thank Sara Kunz and John Merritt for their technical assistance. This work was supported in part by a grant from the NIH to Brandeis University (BRSG-S07-RR07044).

---

(9) For comparison, we note that 12.5-s broad-band ^1H presaturation of all proton resonances gives rise to a 30.0% $^{11}B\{^1H\}$ NOE in the same sample. A more complete description of the $^{11}B\{^1H\}$ NOE, which to our knowledge has not been previously reported, is in progress.

(10) Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: Berlin, 1977; p 15.

(11) Greenwood, N. N. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., et al., Eds.; Pergamon Press, New York, 1971; Chapter 11, p 746.

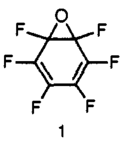
Hexafluorobenzene Oxide and Hexafluorooxepin

Natalie E. Takenaka, Robert Hamlin, and David M. Lemal*

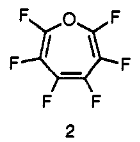
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received February 16, 1990
Revised Manuscript Received July 9, 1990

An elegant study by Vogel[1,2] revealed benzene oxide and oxepin to be a rapidly equilibrating pair of valence isomers with interesting spectroscopic properties and reactivity. We now report the synthesis of hexafluorobenzene oxide (**1**) and describe some of its chemistry, including the relationship with its valence isomer hexafluorooxepin (**2**).

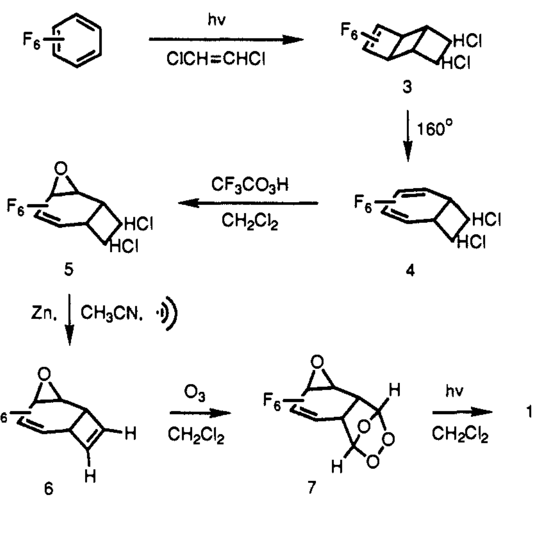


1



2

Scheme I



Earlier unavailing attempts in England[3] and in our laboratory[4] to prepare these compounds persuaded us that our quarry was very sensitive. We therefore designed a synthetic approach (Scheme I) culminating in a photoreaction that could be carried out in an inert medium in the cold.

Photocycloaddition of 1,2-dichloroethylene to hexafluorobenzene yielded a stereoisomeric mixture of *anti*-tricyclo[4.2.0.0^{2,5}]oct-3-enes (**3**) which were readily separable into cis and trans fractions by distillation.[5] Heating these at 160 °C gave bicyclic dienes *endo*-**4c** and **4t**, respectively. Each diene was epoxidized with peroxytrifluoroacetic acid[4] to yield, respectively, tricyclic oxiranes *endo*-**5c** and **5t**. Ultrasound-assisted dechlorination of the oxiranes with zinc gave the delicate diene **6** in low yield. Ozonation of **6** produced an endo/exo mixture of ozonides **7**, which was irradiated at $\lambda > 280$ nm.[6] Bulb-to-bulb distillation of the rather complex product mixture gave in addition to solvent a single volatile compound.

Its mass spectrum displayed a parent peak at m/e 202 for C_6F_6O, together with fragment peaks corresponding to loss of O, CO, CO + F, and CO + CF_2 (base, $C_4F_4^+$). The ^{19}F NMR spectrum (CH_2Cl_2) comprised three signals of equal area at 149.2, 152.8, and 154.3,[7] a finding consistent with the hexafluorobenzene oxide but not the hexafluorooxepin structure. Signal assignments, shown below, are based on comparison with model cyclohexadienes and on variable temperature NMR behavior to be discussed. Note that the fluorines geminal to oxygen appear ~60 ppm upfield from their expected position in the oxepin, as judged from model compounds **8** and **9**.[8] The presence of a fluorinated oxirane ring was indicated by an IR band at 1445 cm^{-1}.[9] A UV maximum at 246 nm ($\epsilon = 7400$, s-C_6H_{12}) confirmed the presence of the cyclohexadiene chromophore.

While solutions of **1** in typical nonpolar solvents were found to be quite stable at room temperature, the benzene oxide rearranges spontaneously and cleanly to hexafluorocyclohexa-2,4-

---

(1) Vogel, E.; Schubart, R.; Boll, W. A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 510. Vogel, E.; Boll, W. A.; Günther, H. *Tetrahedron Lett.* **1965**, 609.

(2) For a review, see: Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385.

(3) Barlow, M. G.; Haszeldine, R. N.; Peck, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 158.

(4) Dailey, W. P.; Ralli, P.; Wasserman, D.; Lemal, D. M. *J. Org. Chem.* **1989**, *54*, 5516.

(5) For other examples of haloolefin photocycloadditions to hexafluorobenzene, see: (a) Roberts, B. E.; Goldman, G. D.; Lemal, D. M. *J. Fluorine Chem.*, in press. (b) Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292. (c) Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. L. *J. Org. Chem.* **1980**, *45*, 3118. (d) Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.*, in press.

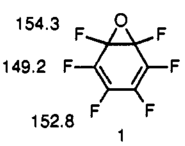
(6) Developed by Story, the photolysis of ozonides has been reviewed by Adam: Adam, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *86*, 638.

(7) ^{19}F NMR chemical shifts are reported in parts per million upfield from internal trichlorofluoromethane.

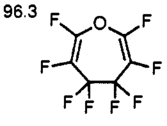
(8) Toy, M. S.; Stringham, R. S. *J. Org. Chem.* **1979**, *44*, 2813. Toy, M. S.; Stringham, R. S. *J. Fluorine Chem.* **1978**, *12*, 23.

(9) Fluorinated epoxides typically absorb at somewhat higher frequencies; diene epoxide **6**, for example, has a band at 1495 cm^{-1}.

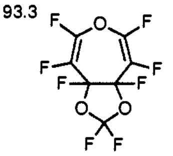
0002-7863/90/1512-6715$02.50/0



1

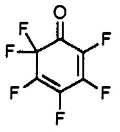


8

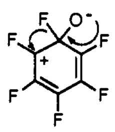


9

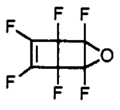
dienone (**10**)[3,10] in acetonitrile or acetone. Warming of solutions in nonpolar solvents gave the same result. These observations are consistent with ring opening of **1** to zwitterion **11** followed by a 1,2-shift of fluoride. Our finding that the reaction is accelerated by Lewis or Brønsted acids lends credence to this pathway. Barlow found that heating hexafluoro Dewar benzene oxide (**12**) in the liquid or gas phase gave dienone **10** as the principal product.[3] Presumably **1** formed as an intermediate in that transformation and rearranged via **11**, as suggested by the authors, or perhaps via the analogous biradical in the case of high-temperature gas-phase pyrolysis.



10



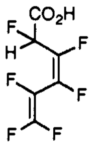
11



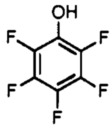
12

Irradiation of **1** in the presence of benzophenone at wavelengths >340 nm, to insure excitation only of the triplet sensitizer, yielded again the dienone **10**. Direct photolysis of the benzene oxide gave the unsaturated acid **13**, presumably via **10**. The same acid is formed when **10** is irradiated similarly, via electrocyclic ring opening to a ketene which is hydrolyzed by traces of water in the solvent.[11] Thus, benzene oxide **1** rearranges cleanly to dienone **10** in the ground state and upon excitation into either its S_1 or T_1 state.

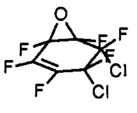
Benzene oxide **1** is reduced under very mild conditions to pentafluorophenol (**14**). Sodium iodide in acetone, for example, effects this transformation cleanly at room temperature. The reaction takes place faster than the spontaneous rearrangement to dienone **10** in acetone, and **10** was ruled out as an intermediate by the finding that it yields other products under the reaction conditions. Whether reduction of **1** by iodide ion proceeds via electron transfer or nucleophilic attack is not known. The great susceptibility of the benzene oxide to reduction accounts for the fact that our earlier attempts to synthesize it via reductive dechlorination of **15** gave only **14**.[4]



13



14



15

The behavior of the ^{19}F NMR spectrum of **1** as a function of temperature is striking. At -40 °C in chlorobenzene the spectrum is sharp, with well-resolved spin–spin splitting. All three resonances broaden and then narrow again as the temperature is increased, but the extent of broadening and the temperature where it becomes maximal are different for each signal. *These observations reveal the existence of a dynamic equilibrium between the benzene oxide and a species that is not independently observed, undoubtedly the oxepin **2**.*

On the basis of the spectra of model compounds, the four fluorines distal to oxygen in the oxepin are expected to have chemical shifts in the 140–160 ppm range where the entire spectrum of **1** appears; those geminal to oxygen should appear close to 95 ppm, as noted above. In the intermediate exchange rate regime, therefore, the signal for the fluorines geminal to oxygen in **1** should be much broader than the other two, reach maximum breadth at a higher temperature, and move downfield as the temperature is raised (expectations confirmed by computer simulation). This is precisely the behavior we observe for the highest field resonance of **1**, which broadens more than 10-fold and shifts downfield rapidly as it resharpens above 50 °C. We have not yet been able to detect the oxepin directly, even with high signal-to-noise ratios at temperatures low enough that its spectrum should be sharp. The equilibrium between **1** and **2** clearly lies far on the side of the benzene oxide.

In contrast, the parent benzene oxide–oxepin equilibrium is quite evenly balanced.[12] This fact together with the powerful destabilization of three-membered rings which results from fluorine substitution[13] led us to speculate at the outset of our work that **2** would predominate very heavily over **1**. We regard the gulf between this prediction and the experimental facts as one of the most interesting observations to emerge from our study.

Acknowledgment. We express our gratitude to Wayne P. Casey for expert assistance with NMR problems, and we thank the Air Force Office of Scientific Research for supporting this work.

---

(10) Soelch, R. S.; Mauer, G. M.; Lemal, D. M. *J. Org. Chem.* **1985**, *50*, 5845.

(11) See, for example: Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; pp 321-3.

(12) Günther, H. *Tetrahedron Lett.* **1965**, 4085.

(13) Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141. Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195. O'Neal, H. E.; Benson, S. W. *J. Chem. Phys.* **1968**, *72*, 1866.

Near-Infrared-Excitation Resonance Raman Spectra of the Primary Electron Donor in Photosynthetic Reaction Centers from *Rhodobacter sphaeroides*

Robert J. Donohoe,[†] R. Brian Dyer,[‡] Basil I. Swanson,[†]
Carol A. Violette,[§] Harry A. Frank,[§] and David F. Bocian*[,∥]

Isotope and Structural Chemistry Group
(INC-4, Mail Stop C-345)
and Photochemistry and Photophysics Group
(CLS-4, Mail Stop J-567)
Los Alamos National Laboratory
Los Alamos, New Mexico 87545
Department of Chemistry, University of Connecticut
Storrs, Connecticut 06269
Department of Chemistry, Carnegie Mellon University
Pittsburgh, Pennsylvania 15213

Received April 19, 1990

The X-ray crystal structures of bacterial photosynthetic reaction centers (RCs)[1-3] serve as bench marks for establishing a detailed description of the light-induced electron-transfer process.[4,5] Much recent work has focused on the characterization of the electronic properties of the primary electron donor state (P*), which is an

---

[†] Isotope and Structural Chemistry Group, Los Alamos National Laboratory.

[‡] Photochemistry and Photophysics Group, Los Alamos National Laboratory.

[§] University of Connecticut.

[∥] Carnegie Mellon University.

(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385-398.

(2) Allen, J. P.; Feher, G.; Yeates, T. O.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8589-8593.

(3) Chang, C.-H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J.; Schiffer, M. *FEBS Lett.* **1986**, *205*, 82-86.

(4) (a) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225-260. (b) Kirmaier, C.; Holten, D. In *Photosynthetic Bacterial Reaction Center: Structure and Dynamics*; Breton, J., Vermeglio, A., Eds.; Plenum: New York; Vol. 149, pp 219-228.

(5) Budil, D.; Gast, P.; Schiffer, M.; Norris, J. R. *Annu. Rev. Phys. Chem.* **1987**, *38*, 561-583.