90% yield. In the instance of other alkenes of Table I, there is a marked decrease in the percentage yield of didealkylation product, *p*-CN-A, relative to monodealkylated product, *p*-CN-NMA (with norbornane the percentage yields are in an 81:14:5 ratio of *p*-CN-DMA:*p*-CN-NMA:*p*-CN-A). Epoxidation with this system is competitive with dealkylation of *p*-CN-NMA.

In conclusion, the reaction of *p*-CN-DMANO with TPPFe^{III}Cl in CH_2Cl_2, in the absence of O_2, represents a catalysis with rapid turnover in which the "oxygen" moiety is transferred to TPPFe^{III} (Scheme I) and hence employed in N-dealkylations of *N*,*N*-dimethyl- and *N*-methylanilines, epoxidation of alkenes, and hydroxylation of alkanes. The use of *p*-CN-DMANO has distinct advantages over iodosobenzene as an "oxygen" donor to TPPFe^{III}, and these advantages should be observable with other metalloporphyrin systems. The reagent *p*-CN-DMANO is soluble in most organic solvents, and in solution it is monomeric. Also, *p*-CN-DMANO does not destroy, by oxidation, the porphyrin ring system. We are continuing work on the kinetics of the *p*-CN-DMANO + TPPFe^{III}X systems, the reaction of *p*-CN-DMANO in the presence of other metalloporphyrins, and the use of other *N*-oxides.

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Registry No. TPPFe^{III}Cl, 16456-81-8; *P*-CN-DMANO, 62820-00-2; *P*-CN-DMA, 1197-19-9; *P*-CN-NMA, 4714-62-9; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; norbornene, 498-66-8; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; cyclohexane, 110-82-7; cytochrome P-450, 9035-51-2.

Cyclophanes. 15. Thermolysis of 1,1',4,4'-Tetrahydro-1,4:1',4'-diepoxy[2.2](1,4)-naphthalenophane. Intracavity Nonbonded Interaction and Evidence for the Intermediacy of an Isobenzofuranophane

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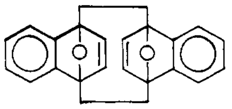
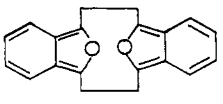
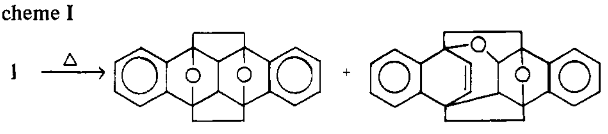
Though 1,1',4,4'-tetrahydro-1,4:1',4'-diepoxy[2.2](1,4)-naphthalenophane (**1**) has been known for some time,[2-4] little has been reported on the chemistry of this system. Molecular models of **1** indicate that severe nonbonded interactions exist between the two oxygen atoms within the cavity. We report here on the thermolysis of **1** and present evidence for the intermediacy of isobenzofuranophane **5** and the unusual strain-induced isomerization of **1** to **4**.



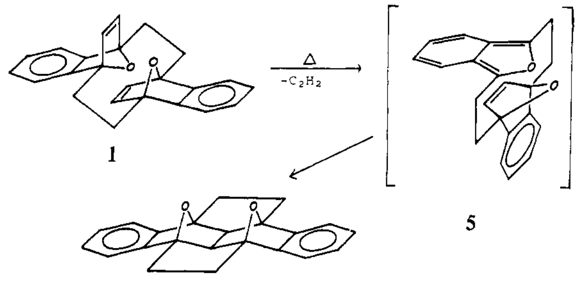
1



2



3 4



1 5 3

When **1** was heated in DMF or xylene at 150 °C (see Scheme I), a brilliant burgundy color was observed.[5] After dissipation of the color (4 h) the reaction mixture was cooled (0 °C), and a white crystalline material precipitated. Filtration afforded polycyclic diether **3** (26.7%).[6] Evaporation of the solvent from the mother liquor and chromatography of the residue (silica gel; 4:1 benzene:ethyl acetate) afforded an unidentifiable oil and polycyclic diether **4** (53.2%) as a foam. Recrystallization from methanol afforded pure **4** (mp 232.5–233.5 °C).

Compound **3** was easily identified by spectral and microanalytical[7] means. The ultraviolet spectrum of **3** ($\lambda_{max}$$CHCl_3$ (ϵ): 255 mm (981), 262 (1570), 269 (2452), 275 (2845)) indicated the presence of the benzenoid units[8] and the mass spectrum (*m/e* 314 (M^+), 170, 144) showed that its molecular weight was 26 amu (C_2H_2) less than the starting material. The ^1H NMR spectrum was simple ($CDCl_3$; δ 7.13 (AA'BB', 8 H), 2.75 (AA'BB', 8 H), 2.06 (s, 2 H)[9]), indicating aromatic and aliphatic protons and the absence of vinyl protons.[10] The highly symmetric nature of **3** was reflected in the ^{13}C NMR spectrum ($CDCl_3$; δ 147.9, 125.6, 117.8, 94.9, 64.3, 28.5) in which only six absorptions were observed.[11] The above data are compatible with the structure assignment for **3**.

Compound **4** was also identified by spectral and microanalytical methods,[12] but the structure elucidation was more complicated. The ultraviolet spectrum of **4** ($\lambda_{max}$$CHCl_3$ (ϵ) 258 nm (sh) (6484), 268 (9141), 273 (9035), 279 (8928), 292 (4677), 301.5 (1275)) was similar to **1**,[8] but the extinction coefficients were as much as 4 times greater, and an additional two absorptions above 290 nm were observed. Mass spectral analysis (*m/e* = 340 (M^+), 267, 225, 154) indicated that **4** was isomeric with **1**, but the fragmentation pattern was different. The presence of a single olefinic unit was indicated by the absorption of 1 equiv of Br_2,[13] and the ^1H NMR spectrum of **4** confirmed the presence of two nonequivalent vinylic protons ($CDCl_3$; δ 7.17 (m, 8 H), 6.03 (ABq, 2 H, J = 10 Hz) 3.10–2.10 (m, 10 H)). In addition to the presence of eight aromatic protons, the ^1H NMR spectrum indicated that isomer **4** had two more aliphatic protons than **1**.[10] Finally, the ^{13}C NMR spectrum of **4**[14] exhibited 24 distinct absorptions,

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[1] Dreyfus Teacher–Scholar 1979–1984.

[2] Keller, L. S. Ph.D. Thesis, Yale University, New Haven, CT, 1970.

[3] Kapicak, L. A.; Battiste, M. A. *J. Chem. Soc., Chem. Commun.* **1973**, 930–931.

[4] Otsubo, T.; Mizogami, S.; Osaka, N.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1841–1849.

[5] This reaction also takes place when solid **1** is heated in a sealed, evacuated tube.

[6] The material did not exhibit a distinct melting point; however, accurate microanalysis was obtained on material recrystallized from EtOAc.[7]

[7] Anal. Calcd for $C_{22}H_{18}O_2$ (**3**): C, 84.05; H, 5.77. Found: C, 83.87; H, 5.94.

[8] Compare with the ultraviolet spectrum of **1**: $\lambda_{max}$$CHCl_3$ (ϵ) 250 nm (1616), 260 (1722), 268.5 (1824), 275.5 (1875), 282.5 (1773).

[9] These protons must be anti to the two ether bridges if the mechanism described in Scheme II is valid. This stereochemistry is supported by NMR data in the following: Feiser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599–1606.

[10] Compare with the ^1H NMR spectrum of **1** ($CDCl_3$): δ 6.82 (AA'BB', 8 H), 6.41 (s, 4 H), 2.52 (AA'BB', 8 H).

[11] Compare with the ^{13}C NMR spectrum of **1** ($CDCl_3$; δ 157.8, 141.7, 122.6, 117.1, 91.5, 27.4) where six absorptions appear for 24 carbon atoms.

[12] Anal. Calcd for $C_{24}H_{20}O_2$ (**4**): C, 84.68; H, 5.92. Found: C, 84.50; H, 5.95.

[13] The dibromide was prepared (77% yield) by treating **4** with 1 equiv of Br_2/CCl_4 and characterized by microanalysis and spectroscopic methods.

[14] ^{13}C NMR ($CDCl_3$) δ 146.2, 145.1, 144.5, 139.1, 134.5, 134.0, 131.2, 127.2, 126.9, 126.3, 126.2, 124.6, 118.3, 118.1, 98.04, 98.00, 97.4, 95.6, 72.9, 71.6, 39.3, 38.0, 34.5, 29.2.

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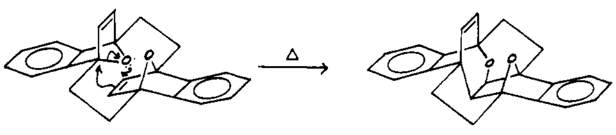
Scheme III



1 4

verifying the absence of symmetry. The structure that is most compatible with the above data is **4**.[15]

The formation of polycyclic diethers **3** and **4** must take place via two distinct pathways, both of which are probably facilitated by large nonbonded intracavity interactions and both of which give rise to products with reduced intramolecular interactions. Loss of acetylene from **1** by a retro-Diels–Alder reaction would substantially reduce the oxygen–oxygen interaction and give rise to intermediate **5** (see Scheme II). Further loss of acetylene (to give **2**) would compete unfavorably with an intramolecular Diels–Alder reaction in **5** because of the proximity of the dienic and dienophilic moieties and the reactivity of the isobenzofuranoid system toward Diels–Alder reactions. Internal trapping would further reduce the intracavity interaction in **5** and give the relatively unstrained diether **3**. The unusually low temperature at which the loss of acetylene takes place[16] argues for the substantial amount of strain released upon forming **5**, in which one of the oxygen atoms forms part of the planar isobenzofuranoid system.

Attempted trapping of **5** with external dienophiles produces **3** and **4**.[17] Though this result does not initially support the intermediacy of **5** (and perhaps suggests a concerted pathway for **1** → **3**[18]), there are at least three reasons why external dienophiles would not compete favorably for the isobenzofuranoid moiety. First, the diene and dienophilic portions in **5** are geometrically disposed to give **3** by a favored intramolecular Diels–Alder reaction.[19] Second, the formation of **3** would be essentially irreversible since there is comparatively little strain associated with it. Third, addition of an external dienophile would be a more difficult process because it would reinstate the original intracavity nonbonded interactions of the oxygen atoms, as in **1**.

Both **3** and **4** are stable under the reaction conditions. Diether **4** is therefore not the precursor of **3**, and its formation must take place via a pathway distinct from **3**. In this instance, the close contact between the oxygen atoms and the proximate olefinic units allows for the release of strain by the migration of one of the oxygen atoms to an olefinic carbon (see Scheme III), generating the dissymmetry in **4** and reducing the intracavity interactions originally present in **1**. Since **4** is the major product of the thermolysis of **1**, release of strain by this pathway is quite important despite the unusual nature of the reaction between ether and olefin groups.

Whether or not molecular oxygen can be extruded from **1**, or a derivative thereof, is of interest. Further investigations concerning the unusual migration of the oxygen atom in **1**, as well as the chemistry caused by the severity of nonbonded interactions in similar systems, are currently in progress.

Acknowledgment. We thank the NSF (CHE-79 10295) and NIH (Biomedical Research Support Grant RR 07044) for support of this work.

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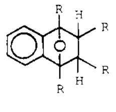
[15] A crystal structure determination is being carried out on the bromide to confirm this assignment.

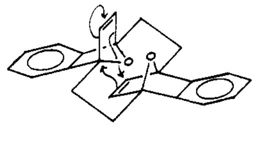
[16] To our knowledge the loss of acetylene to give isobenzofuranoid systems is unknown. Normally, ethylenic units are lost from dihydroprecursors such as i to give isobenzofurans but this loss generally takes place at low pressure and at temperatures greater than 600 °C. See: Wiersum, U. E.; Mijs, W. J. *J. Chem. Soc., Chem. Commun.* **1972**, 347–348.



i

[17] Compound **1** was heated with neat dimethylacetylenedicarboxylate or in xylene with a 2-fold excess of the dienophile.

[18] Because of the geometry of **1**, a concerted loss of acetylene with concomitant cyclization to form **3** can be envisioned (see ii).



ii

[19] For similar intramolecular Diels–Alder reactions, where the diene and dienophile are in comparable orientations, see: (a) Cram, D. J.; Montgomery, C. S.; Knox, G. R. *J. Am. Chem. Soc.* **1966**, *88*, 515–525. (b) Wasserman, H. H.; Keehn, P. M. *Ibid.* **1966**, *88*, 4522. (c) Wasserman, H. H.; Keehn, P. M. *Tetrahedron Lett.* **1969**, 3227.

New EXAFS Models for the Iron Sites of the Iron Molybdenum Cofactor of Nitrogenase: The $[(p\text{-}CH_3C_6H_4S)_2FeS_2FeS_2MoS_2]^{3-}$ Trianion and the $[(C_6H_5O)_2FeS_2MoS_2]^{2-}$ Dianion

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The FeMo cofactor[1] from the MoFe protein of the enzyme nitrogenase is known to contain a novel Mo–Fe–S cluster.[2,3] Two types of related structural unit are now well characterized: those containing the $MoFe_3S_4$ cubane core,[4,5] and those containing the "linear" MoS_2Fe core.[6-10] Several of these synthetic Mo–Fe–S

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