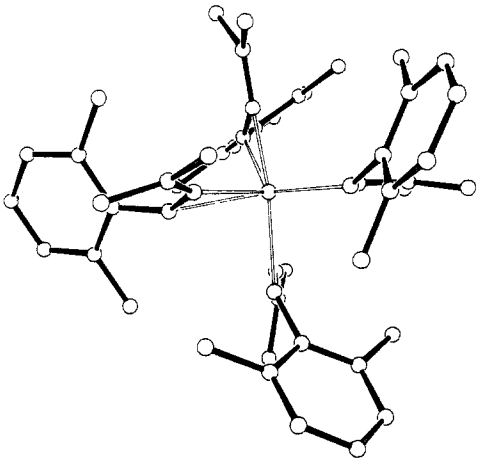

Figure 1. Ball-and-stick diagram of the $Mo(\eta^2\text{-}Me_2NCN\text{-}2,6\text{-}Me_2C_6H_3)_4$ molecule showing the alignment of the four η^2-NC ligands. Viewed down the z axis the NCN units are aligned in a pairwise manner along xz and yz planes.

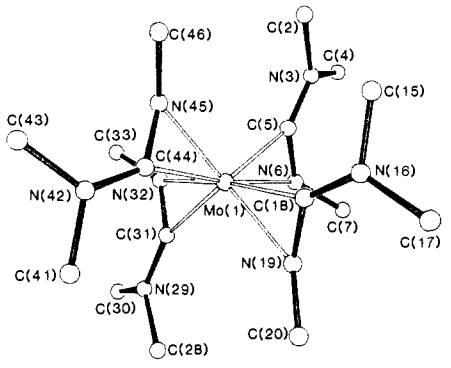

Figure 2. View of the central $Mo(\eta^2\text{-}C(NC_2)NC)_4$ moiety showing the atom number scheme. Pertinent distances (Å): for short Mo–C and Mo–N, Mo–C(18) = 2.032 (3), Mo–N(19) = 2.205 (2), Mo–C(44) = 2.024 (3), Mo–N(45) = 2.181 (2), η^2-(C–N) = 1.336 (7) (av); for long Mo–C and Mo–N, Mo–C(5) = 2.111 (3), Mo–N(6) = 2.278, Mo–C(31) = 2.116 (3), Mo–N(32) = 2.294 (2), η^2-(C–N) = 1.297 (3) (av) and Me_2N–CNAr = 1.335 (6) (av).

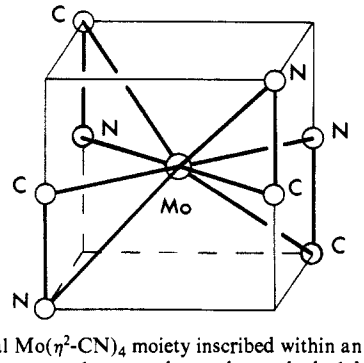

Figure 3. Central $Mo(\eta^2\text{-}CN)_4$ moiety inscribed within an idealized cube showing the cis-square-planar and pseudotetrahedral MoC_2N_2 units.

molecular motions allow the attainment of idealized C_2 symmetry. The observed restricted rotations about Me_2N–C and N–C aryl bonds presumably reflect electronic and steric factors, respectively.

Finally we note it is interesting to describe the distorted dodecahedral $Mo(\eta^2\text{-}CN)_4$ unit in terms of its relationship to an idealized metal-centered cube, MX_8, from which so many eight-coordinate structures are derived.[10] The present structure involves the fusing of a planar *cis*-MC_2N_2 unit within a MC_2N_2 tetrahedron as shown in Figure 3. The short Mo–C distances are mutually cis and trans to the long Mo–N distances. To our knowledge there are no related structures of $M(\eta^2\text{-}XY)_4$ compounds.

Further studies are in progress.[11]

Supplementary Material Available: Ball-and-stick diagram giving the atom number scheme, tables of isotropic and anisotropic thermal parameters, and complete listings of bond distances and bond angles (6 pages). Ordering information is given on any current masthead page.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry, A Comprehensive Text*; 4th ed.; Wiley: New York, 1980; p 53. Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179 and references cited therein.

(11) We thank the National Science Foundation and the Wrubel Computing Center for support.

Stereochemical and Mechanistic Studies of the "Suicide" Event in Biomimetic P-450 Olefin Epoxidation

James P. Collman,* Philip D. Hampton, and John I. Brauman

Department of Chemistry, Stanford University Stanford, California 94305

Received July 8, 1986

Both cytochrome P-450 and metalloporphyrin model systems have been reported to exhibit stereospecific olefin epoxidation[1,3c] and to undergo the "suicide" porphyrin N-alkylation reaction with 1-olefins.[2,3] In this paper we report that in the previously studied model system N-alkylation[2a] is both stereospecific (syn), as observed[3c] for P-450 itself, and is olefin structure dependent. In addition, we have observed that even terminal olefins which are active toward epoxidation, styrenes and 1,1-disubstituted olefins, undergo this "suicide" event. The partitioning between epoxidation and N-alkylation is highly dependent on olefin structure but independent of olefin concentration, catalyst concentration, and the presence of a competing olefin. Unlike the natural system, where the suicide event destroys catalytic activity, the *N*-alkylporphyrins in this model system retain catalytic activity, albeit a greatly reduced activity.

Using[4] Fe(TDCP)Cl under heterogenous conditions with the oxygen atom donor pentafluoroiodosylbenzene (PFIB), we found that a variety of 1-olefins produce green pigments (Soret at 446 nm), characteristic of N-alkylation, as observed by Traylor[2a] and Mansuy.[2b] In addition, we find that methylenecyclohexane, isobutylene, styrene, 2,6-dimethylstyrene, and 3-methyl-1-butyne also yield green pigments. We have isolated the *N*-alkylporphyrins for several of these.[5,6] To our knowledge, the 1,1-disubstituted olefins and styrenes have never before been reported to produce *N*-alkylporphyrins in either P-450 or model systems. Just as in

(1) (a) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343. (b) Collman, J. P.; Kodadek, T.; Brauman, J. I. *Ibid.* **1986**, *108*, 2588 and references therein.

(2) (a) Mashiko, T. M.; Dolphin, D.; Nakano, T.; Traylor, T. G. *J. Am. Chem. Soc.* **1985**, *107*, 3735. (b) Mansuy, D.; Devocelle, L.; Artaud, J.; Battioni, J. *Nouv. J. Chim.* **1985**, *9*, 711.

(3) (a) Loosemore, M. J.; Wogan, G. N.; Walsh, C. *J. Biol. Chem.* **1981**, *256*, 8705. (b) Ortiz de Montellano, P. R.; Mico, B. A. *Arch. Biochem. Biophys.* **1981**, *206*, 43. (c) Ortiz de Montellano, P. R.; Mangold, B. L. K.; Wheeler, C.; Kunze, K. L.; Reich, N. O. *J. Biol. Chem.* **1983**, *258*, 4208.

(4) TDCP: 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphine dianion.

(5) 21-(2-Hydroxy-3-methylbutyl)-23-H-TDCP: calcd M^+ 976, found 976. ^1H NMR ($CDCl_3$) δ 8.66 (s, β-pyrrolic, 2 H), 8.29–8.40 (m, β-pyrrolic, 4 H), 7.63–7.91 (m, β-pyrrolic, 2 H; phenyl, 12 H), 0.2–0.3 (m, $NCH_AH_BCH_X(OH)$, 1 H), –0.57 (d, CH_XOH, J = 5.7 Hz, 1 H), –1.1 to –1.0 (m, $CH(OH)CH(CH_3)_2$, 1 H), –1.19 (d, $CH(CH_3)_2$, J = 6.6 Hz, 3 H), –2.00 (d, $CH(CH_3)_2$, J = 6.3 Hz, 3 H), –2.2 to –2.1 (br s, NH, 1 H), –4.19 (d of d, $NCH_AH_BCH_X(OH)$, J_{BX} = 11, J_{AB} = 15 Hz, 1 H), –4.42 (d of d, $NCH_AH_BCH_X(OH)$, J_{AX} = 2, J_{AB} = 15 Hz, 1 H); UV max 428 (Soret), 486 sh, 521, 555, 607, 666 (weak).

(6) 21-(2-Hydroxy-2-methyl-1-propyl)-23-H-TDCP: calcd M^+ 962, found 962. ^1H NMR ($CDCl_3$) δ 8.67 (s, β-pyrrolic, 2 H), 8.32 (br s, β-pyrrolic, 4 H), 7.91–7.56 (m, β-pyrrolic, 2 H, phenyl, 12 H), –0.85 (br s, $C(CH_3)_2OH$, 7 H), –2.14 (s, NH, 1 H), –3.98 (s, NCH_2, 2 H). 21-[(1-Hydroxycyclohexyl)methyl]-23-H-TDCP: calcd M^+ 1002, found 1002. 21-(α-Hydroxy-2,6-dimethylstyryl)-23-H-TDCP: calcd M^+ 1038, found 1038.

0002-7863/86/1508-7861$01.50/0

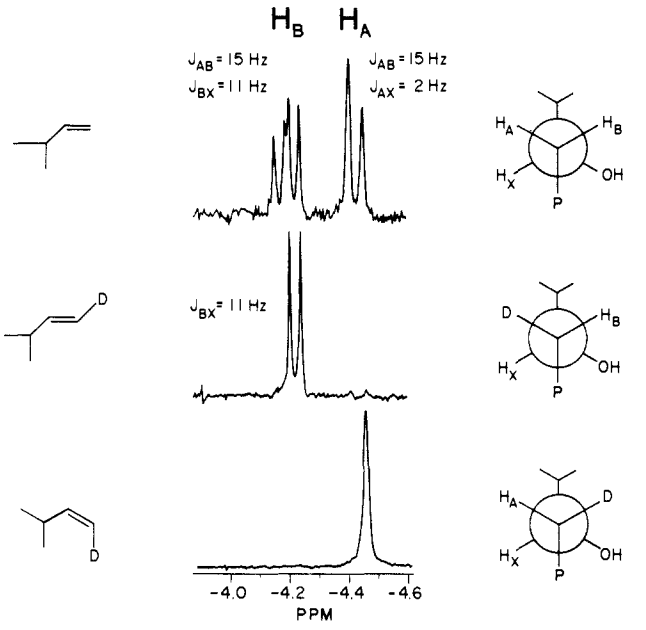

Figure 1. High-field ^1H NMR of *N*-alkylporphyrins from 3-methyl-1-butene and its *E*- and *Z*-1-deuterio isomers.

the biological system, epoxides do not form green pigments under our catalytic conditions.

The *N*-alkylporphyrin isolated from 3-methyl-1-butene has a ^1H NMR ($CDCl_3$) similar to that previously reported[2b] with a high-field pair of doublets for the methylene attached to the pyrrolic nitrogen (Figure 1). When the *E*- and *Z*-1-deuterio olefins are used, only one doublet is observed, indicative of a stereospecific reaction. The actual stereochemistry of addition was determined from the coupling constants, assuming a conformation with the bulky isopropyl group and the porphyrin trans (Figure 1). The anti coupling constant for the *E*-1-deuterio olefin requires that the N-alkylation must result from a syn addition of oxygen and nitrogen to the olefin. The *N*-alkylporphyrin from the *Z*-1-deuterio olefin confirms this stereospecificity (Figure 1). The same stereochemistry has been reported for P-450, using an indirect method.[4c] Analysis of recovered olefin showed no loss of stereochemistry, and the epoxide indicated a stereospecific syn addition.

Olefin partition numbers (moles of epoxide produced per mole of catalyst N-alkylated) were measured[7] and found to be highly structure dependent: 1-decene, 100; methylene cyclohexane, 800; styrene, 10 000. These values resemble those observed for P-450 (200–230) with allylisopropylacetamide.[3a,b] The partition number for 1-decene is independent of both catalyst and olefin concentration. In addition, the presence of a competing olefin, cyclooctene, at a 1:10 and 1:2 (cyclooctene/1-decene) ratio while decreasing both epoxidation and N-alkylation rates does not affect the partition number for 1-decene. Such observations are consistent with (but do not require) the presence of a common intermediate that can partition between N-alkylation and epoxidation. That 1,1-disubstituted olefins and styrenes yield *N*-alkylporphyrins in this model system and not in the biological system may be due to a steric effect or simply due to the greater stability of this catalyst and the large partition numbers for these olefins.

Several pathways have been proposed for olefin epoxidation and N-alkylation: formation of an olefin–oxo π-complex,[9] an acyclic cation or radical,[3c,2b] an electron-transfer species followed by collapse to a radical or cation,[8] a metallacarbene,[9] or a metallacycle.[1a,2b] We have proposed a metallacyclic intermediate for olefin epoxidation[1a] and phenylacetaldehyde formation[1b] and believe a metallacycle could be involved in porphyrin N-alkylation. The observed regiospecificity of the N-alkylation and the dependence on olefin structure are easily explained by preference for one regioisomer of a putative metallacycle. We are continuing to explore the mechanism of these reactions.

Acknowledgment. We thank Jeffrey P. Fitzgerald, Scott A. Raybuck, and Thomas J. Kodadek for advice and technical assistance and acknowledge support from the Bioorganic, Biomedical Mass Spectroscopy Resource (A. L. Burlingame, Director), supported by NIH Division of Research Resources Grant RR01614, the National Institutes of Health (NIH GM17880), and the National Science Foundation (NSF CHE83-18512).

(7) To determine partition numbers, aliquots of a mixture (20 mL) of olefin (0.1–2 M), PFIB (0.2–0.6 mmol), alkane standard (0.01–0.5 mmol), and Fe(TDCP)Cl (3–12 μmol) in CH_2Cl_2 at 17 °C were taken and excess oxidant was quenched with PPh_3. The disappearance of Fe(TDCP)Cl (416 nm Soret) and formation of *N*-alkylporphyrin (446 nm Soret) was isosbestic (four points) and first order in Fe(TDCP)Cl. Epoxide formation was followed by GC. Since the *N*-alkylporphyrins have a catalytic activity an order of magnitude lower than Fe(TDCP)Cl, the partition numbers were measured by determining the ratio of epoxide to total catalyst when formation of the *N*-alkylporphyrin was essentially complete. The actual partition numbers were found to be (within 15%) 1-decene, 130; methylene cyclohexane, 830; and styrene, 12 000 by our best estimate considering the catalytic activity of the *N*-alkyl porphyrin. Similar partition numbers were obtained alternatively by measuring either the epoxide formation at half-conversion (one half-life) or the ratio of initial rates for both processes.

(8) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782.

(9) Groves, J. T. 41st Northwest Regional Meeting of the American Chemical Society, ACS, Portland OR, June 16–18, 1986.

Organic Synthesis Using Carbon Monoxide. Regiospecific Cobalt-Mediated Synthesis of 2*H*-Pyran-2-ones

William P. Henry and Russell P. Hughes*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received July 28, 1986

(η^3-Oxocyclobutenyl)(tricarbonyl)cobalt complexes **1** can be prepared in good yields by the reaction of readily available cyclopropenyl cations with the $[Co(CO)_4]^-$ anion.[1] This ring-expansion reaction incorporates one molecule of CO originally present on the metal into the oxocyclobutenyl framework. Excellent regioselectivity is obtained with unsymmetrically substituted cations, the unique substituent R on the cyclopropenyl ring invariably appearing adjacent to the ketone in the oxocyclobutenyl product.[1] We now report that reaction of these oxocyclobutenyl complexes with carbon or hydride nucleophiles under an atmosphere of CO results in conversion to the important 2*H*-pyran-2-one skeleton,[2] with regeneration of the $[Co(CO)_4]^-$ anion. A key step in the mechanism is shown to involve transfer of an acyl or formyl ligand from cobalt to the oxocyclobutenyl ring.

Reaction of the oxocyclobutenyl complex **1a**[1] with methyllithium (THF, −78 °C) under a CO atmosphere followed by warming to room temperature affords a solution whose IR spectrum contains a single band at 1887 cm^{-1}, indicating clean formation of the $[Co(CO)_4]^-$ anion.[3] Chromatographic workup affords the known[4] pyrone **2a**, identified by comparison of its spectral properties with

(1) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846–4859.

(2) The pyrone skeleton is an important component of human leukocyte elastase inhibitors: Spencer, W. B.; Copp, L. J.; Pfister, J. R. *J. Med. Chem.* **1985**, *28*, 1828–1832. Groutas, W. C.; Stanga, M. A.; Brubaker, M. J.; Huang, T. L.; Moi, M. K.; Carroll, R. T. *Ibid.* **1985**, *28*, 1106–1109. For a review of the synthesis and chemistry of 2*H*-pyran-2-ones, see: Staunton, J. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, **1979**; Chapter 18.2.

(3) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403–6406. In the absence of CO the IR spectrum of the solution is more complicated, although the organic product (vide infra) is still formed.

(4) For other syntheses of **2a,b**, see: Hayasi, Y.; Nozaki, H. *Tetrahedron* **1971**, *27*, 3085–3093. For **2e**, see: Ishibe, N.; Masui, J. *J. Am. Chem. Soc.* **1974**, *96*, 1152–1158.

0002-7863/86/1508-7862$01.50/0