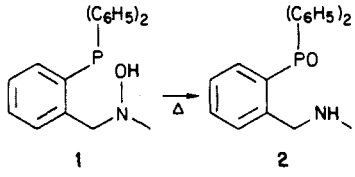
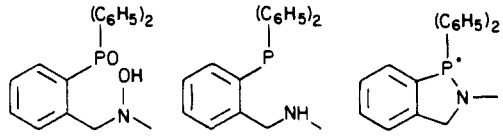
wish to report the use of this approach to a evaluate the geometry of a formal displacement at oxygen.

The conversion of **1** to **2**, in which an oxygen is transferred from nitrogen to phosphorus, proceeds in toluene at 100 °C in 1 h in 95% yield.[5] The disappearance of **1** and the appearance of **2** are kinetically first order in **1** with a rate constant of $k = 5.0\ (\pm 0.6) \times 10^{-2}\ min^{-1}$ over a 5-fold concentration range. If the reaction proceeded by an S_N2 pathway, with phosphorus acting as a nucleophile and a geometrical requirement of a bond angle of 180° between the entering and leaving groups in the transition state, the reaction would be expected to be second order and to involve **3** and **4**.[6] Independently prepared **3** and **4** provide **2** at a rate



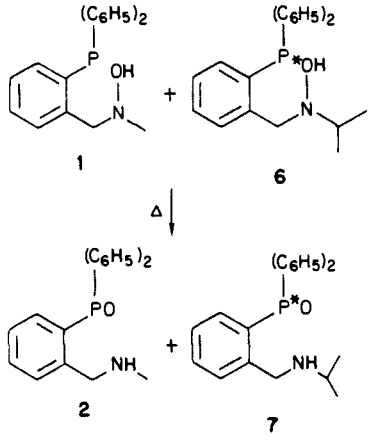
1 **2**



3 **4** **5**

that is much slower than the rate of formation of **2** from **1**. Accordingly this formal nucleophilic substitution at oxygen does not proceed by a classic S_N2 process.

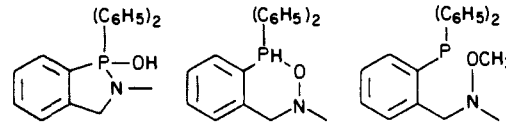
A free radical chain reaction with an adventitous initiator and reaction via **5** could be kinetically first order.[7] To test this possibility, which would involve intermolecular transfer of oxygen, a double-labeling experiment was carried out. A 49:51 ratio of unlabeled **1** and **6** bearing 44% (±4) ^{18}O gives **2** which is unlabeled and **7** which has 42% (±4) ^{18}O. The rate of reaction of **6** is within



1 **6** **2** **7**

25% that of **1** in this mixture. By the labeling criterion, the oxygen transfer from nitrogen to phosphorus is intramolecular and the radical chain reaction is not operative.

Mechanisms for oxygen transfer which meet the bond angle requirement for the intramolecular transfer are biphilic addition between the nitrogen and oxygen to provide **8**[8] or addition of oxygen and hydrogen to phosphorus to give **9**.[9,10] The latter is favored because **10** is inert upon heating in toluene at 100 °C even in the presence of acetic acid.



8 **9** **10**

The present work shows that the mechanistic analogy of backside displacement for nucleophilic substitution at carbon cannot be extended to displacement by phosphenes at oxygen. The present evidence suggests that, in fact, this formal displacement by phosphorus on oxygen is initiated by addition of oxygen and hydrogen to the phosphorus. Further tests using this general approach to provide previously unavailable information about the reaction geometry at nonstereogenic atoms are under way.

Acknowledgment. We are grateful to Dr. W. G. Bentrude, Dr. S. G. Mills, and D. R. Chrisope for discussions and to the National Institute of Health and National Science Foundation for support.

(4) Beak, P.; Basha, A.; Kokko, B. *J. Am. Chem. Soc.* **1984**, *106*, 1511.

(5) The reaction can be directly followed by ^1H NMR. The yield is based on that observation. The product was isolated in 75% yield from a reaction in refluxing dioxane. The reactants and products are fully characterized by analytical and spectral properties.

(6) Kirby, A. J.; Warren, S. G. *The Organic Chemistry of Phosphorus*; Elsevier: New York, 1967; pp 63-94. Smith, D. J. H. *Compr. Org. Chem.* **1979**, *2*. These authors provide a large number of examples of deoxygenations by phosphorus reagents and the reasonable rationale that many of these reactions are nucleophilic attacks on oxygen.

(7) Additions of alkoxy radicals to phosphines are well-established; Bentrude, W. G.; Moriyama, M.; Mueller, H. D.; Sopchik, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 6053 and references cited therein. A recent attempt to observe a radical displacement on oxygen in a 5-exo-trig reaction showed this processes was not operative: Kraus, G. A.; Landgrebe, K. *Tetrahedron* **1985**, *19*, 4039.

(8) Reactions of peroxides with phosphines are formulated as biphilic insertions by phosphorus into the oxygen-oxygen bond to provide dialoxyphopholanes: Lloyd, J. R.; Lowther, N.; Hall, C. D. *J Chem. Soc., Perkin Trans. 2*, **1985**, 245. Clennan, E. L.; Heah, P. C. *J. Org. Chem.* **1981**, *46*, 4105. Baumstark, A. L.; McCloskey, C. J.; Williams, T. E.; Chrisope, D. R. *J. Org. Chem.* **1980**, *45*, 3593. Denney, D. B.; Denney, D. Z.; Hall, C. D.; Marsi, K. L. *J. Am. Chem. Soc.* **1972**, *94*, 245 and references cited therein. Retention at phosphorus is observed in such reactions: Wozniak, L.; Kowalski, J.; Chojnowski, J. *Tetrahedron Lett.* **1985**, 4965.

(9) Brazier, J. F.; Houalla, D.; Loenig, M.; Wolf, R. *Top. Phosphorus Chem.* **1976**, *8*, 99.

(10) Cadogan and Mackie (Cadogan, J. I. G.; Mackie, R. K. *Chem. Soc. Rev.* **1974**, *3*, 87) cite Emerson and Rees (Emerson, T. R.; Rees, C. W. *J. Chem. Soc.* **1964**, 2319) for a mechanism of deoxygenation of amine oxides which involves nucleophilic addition of oxygen to phosphorous.

Asymmetric Total Synthesis of (+)-Pentalenene via Chiral Sulfinylallyl Anions. Hydrolytic Ring Closure of Enol Thioether Ketones

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As part of our continued studies to apply asymmetric induction reactions involving chiral sulfinylallyl anions with enones,[1] the synthesis of the family of sesquiterpenes pentalenene,[2] pentalenic acid,[3] and pentalenolactone[4] was undertaken. (+)-Pentalenene (**1**) was isolated[2] from the less oxidized metabolites in the mycelia

(1) Hua, D. H.; Sinai-Zingde, G.; Venkataraman, S. *J. Am. Chem. Soc.* **1985**, *107*, 4088. The diastereospecific addition reactions of carbanions derived from allylic sulfoxides and allylic phosphine oxides: (b) Binns, M. R.; Haynes, R. K.; Katsifis, A. A.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, *26*, 1565. (c) Binns, M. R.; Chai, O. L.; Haynes, R. K.; Katsifis, A. A.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, *26*, 1569. The 1,4-addition of carbanion of phenyl allyl sulfoxide and cyclopentenones: (d) Vasil'eva, L. L.; Mel'nikova, V. I.; Gainullina, E. T.; Pivnitskii, K. K. *J. Org. Chem. USSR* **1983**, *19*, 835. (e) Vasil'eva, L. L.; Mel'nikova, V. I.; Pivnitskii, K. K. *Zh. Org. Khim* **1984**, *20*, 690 and references cited therein.

(2) Seto, H.; Yonehara, H. *J. Antibiot.* **1980**, *33*, 92.

(3) Seto, H.; Sasaki, T.; Uzawa, J.; Takeuchi, S.; Yonehara, H. *Tetrahedron Lett.* **1978**, 4411.

(4) (a) Martin, G.; Slomp, G.; Mizsak, S.; Duchamp, D. J.; Chidester, C. G. *Tetrahedron Lett.* **1970**, 4901. (b) Duchamp, D. J.; Chidester, C. G. *Acta Crystallogr., Sect. B* **1972**, *B28*, 173. (c) Seto, H.; Sasaki, T.; Yonehara, H.; Uzawa, J. *Tetrahedron Lett.* **1978**, 923. (d) Seto, H.; Sasaki, T.; Uzawa, J.; Takeuchi, S.; Yonehara, H. *Tetrahedron Lett.* **1978**, 4411. (e) Aizawa, S.; Akutsu, H.; Satomi, T.; Kawabata, S.; Sasaki, K. *J. Antibiot.* **1978**, *31*, 729. (f) Cane, D. E.; Rossi, T. *Tetrahedron Lett.* **1979**, 2973.

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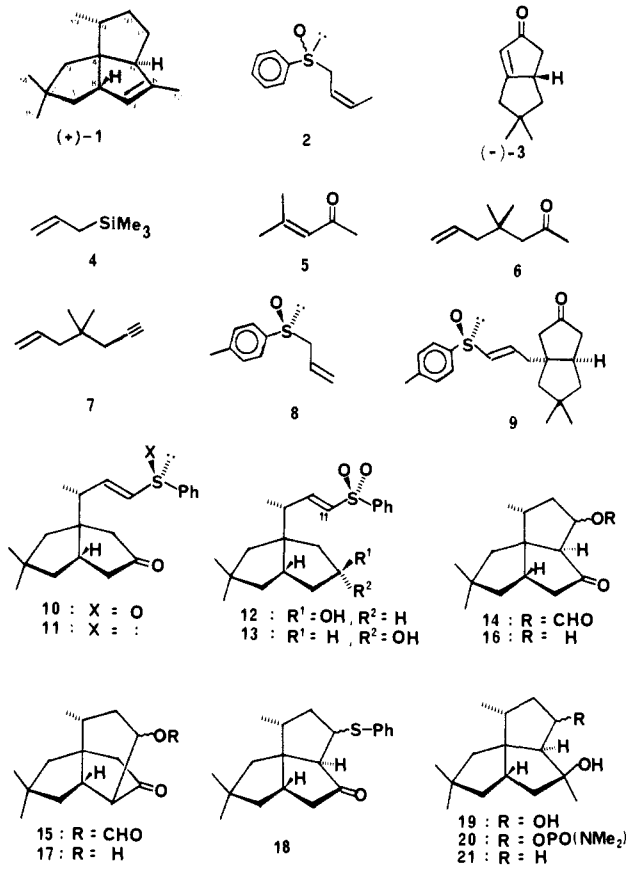
of the *S. griseochromogenes* organism which also produced pentalenolactones and pentalenic acid. The antibiotic properties of pentalenolactone[4,5] (an agent which is active against Gram-positive/negative bacteria and fungi and which inhibits the enzyme glyceraldehyde-3-phosphate dehydrogenase) and the antitumor activity of deoxypentalenylglucuron[6] have prompted widespread synthetic efforts.[7] Although the total synthesis of (±)-pentalenene [(±)-**1**)] has been reported,[7a] the absolute configuration of (+)-**1** remained unknown.[2] We report here an efficient asymmetric total synthesis of (+)-**1**, starting with racemic *cis*-crotyl phenyl sulfoxide (**2**) and (−)-(*S*)-7,7-dimethylbicyclo[3.3.0]-2-octen-3-one [(−)-**3**], and establish its absolute configuration.

Racemic enone **3** was easily prepared in a three-stage reaction sequence: (i) 1,4-addition reaction of allyltrimethylsilane (**4**) with mesityl oxide (**5**)–$TiCl_4$ in CH_2Cl_2[8] to provide 4,4-dimethyl-6-hepten-2-one (**6**) (87% yield); (ii) formation of the enol phosphate of ketone **6** by treatment with LDA–$ClPO(OEt)_2$–THF, followed by in situ dehydrophosphonation with 2 equiv of LDA[9] to provide 4,4-dimethyl-6-hepten-1-yne (**7**) (61% yield); and (iii) intramolecular cyclization of α,σ-enyne **7** with 1 equiv of $Co_2(CO)_8$ in heptane (6 mL/g) and CO atmosphere in a sealed tube at 120 °C for 3 days (58% yield).[10] Kinetically selective resolution of **3** was effected by treating (*S*)-allyl *p*-tolyl sulfoxide (**8**)[1] with 1 equiv of LDA in THF at −78 °C for 1 h, adding 2 equiv of racemic **3** in THF at −78 °C, and maintaining the mixture for 30 min; adduct **9** (80% yield) and (−)-(*S*)-**3** [45% yield; $[\alpha]^{25}_D = -141°$ (*c* 0.14, $CHCl_3$)] were obtained.[11] Addition of the sulfinylallyl anion, derived from the reaction of 2 equiv of racemic *cis*-crotyl phenyl sulfoxide (**2**)[12] with 2 equiv of LDA in THF at −78 °C, to 1 equiv of (−)-(*S*)-**3** in THF at −78 °C and maintaining the mixture for 45 min afforded 91% yield of sulfoxide **10**[13] (82% optionally pure). Its optical purity was determined by ^1H NMR spectra of the Mosher derivatives[14] of alcohols **12** and **13**, these alcohols being obtained from **10** by reduction with $NaBH_4$–MeOH at −20 °C for 20 min followed by oxidation with *m*-chloroperbenzoic acid–CH_2Cl_2 at 0 °C (95% overall yield; **12**:**13** = 73:27) and separation by low-pressure liquid chromatography.

The difficulty of hydrolizing vinyl sulfides possessing an α-CH to the corresponding aldehydes with $HgCl_2$ or under strongly acidic conditions has been reported.[15] We found that vinyl sulfide **11**,



obtained from the reduction of sulfoxide **10** with Zn–AcOH at room temperature for 24 h (95% yield), underwent hydrolysis followed by rapid intramolecular cyclization with the ϵ enol moiety when treated with 88% HCO_2H–CF_3CO_2H (70–0.1 mL/g) at 60 °C for 24 h to give 60% of formate **14**, 8% of isomer **15**,[16] 4% of alcohol **16**, 2% of isomeric alcohol **17**, 15% of sulfide **18**, and benzenethiol. Formate **14** was transformed into alcohol **16** by treatment with 1 equiv of K_2CO_3–MeOH at room temperature for 15 min (100% yield); addition of 4 equiv of MeMgBr to **16** in ether (40 mL/g) at 0 °C provided 70% yield of **19** (30% recovery of alcohol **16**). Finally, (+)-pentalenene [(+)-**1**][17] was obtained by the sequence (i) phosphorylation of **19** with 1.2 equiv of *N,N,N',N'*-tetramethyldiamidophosphorochloridate–3 equiv of Et_3N–2 equiv 4-(dimethylamino)pyridine in toluene (5 mL/g) at 60 °C for 10 h (96% yield of **20**), (ii) deoxyphosphorylation[18] of **20** with 10 equiv of lithium–4 equiv *t*-BuOH in $EtNH_2$–THF at 0 °C for 30 min (97% yield of **21**), and (iii) dehydration of **21** with 0.5 equiv of BF_3–ether in CH_2Cl_2 (100 mL/g) at room temperature for 45 min [99% yield of (+)-**1**]. The spectral properties (IR, ^1H and ^{13}C NMR, and mass) of (+)-**1** were identical with those of authentic material.[19] Sulfide **18** was also transformed into alcohol **21** by the sequence (i) desulfurization with Raney nickel (W-2)–EtOH and (ii) addition of 2 equiv of MeMgBr–ether (82% overall yield).

In summary, the utility of the asymmetric induction reaction of chiral sulfinylallyl anions and enones has thus been extended to another skeletal class. The method leading to the total synthesis

(5) Koe, B. K.; Sobin, B. A.; Celmer, W. D. *Antibiot. Annu.* **1956/1957**, 672.

(6) Takahashi, S.; Takeuchi, M.; Arai, M.; Seto, H.; Otake, N. *J. Antibiot.* **1983**, 226.

(7) (±)-Pentalenene: (a) Annis, G. D.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4505. (b) Mehta, G.; Rao, K. S. *J. Chem. Soc., Chem. Commun.* **1985**, 1484. (c) Crimmins, M. T.; Deloach, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 800. (±)-Pentalenolactone. (d) Danishefsky, S.; Hirama, M.; Gombatz, K.; Harayama, T.; Berman, E.; Schuda, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 6536; **1979**, *101*, 7020. (e) Parsons, W.; Schlessinger, R. H.; Quesada, M. L. *Ibid.* **1980**, *102*, 889. (f) Paquette, L. A.; Annis, G. D.; Schostarez, H. *J. Am. Chem. Soc.* **1982**, *104*, 6646. (g) Cane, D. E.; Thomas, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 5295. (h) Ohtsuka, T.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1983**, 3851. (i) Taber, D. F.; Schuchardt, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5289. (±)-Pentalenic acid. (j) Sakai, K.; Ohtsuka, T.; Misumi, S.; Shirahama, H.; Matsumoto, T. *Chem. Lett.* **1981**, 355.

(8) Sakurai, H.; Hosomi, K.; Hayashi, J. *Org. Synth.* **1984**, *62*, 86.

(9) Negishi, E.-I.; King, A. O.; Klima, W. L.; Patterson, W.; Silveira, A., Jr. *J. Org. Chem.* **1980**, *45*, 2526.

(10) (a) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. (b) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, 4851. This cyclization reaction has been repeated many times, and the yields are consistent.

(11) The absolute configuration of **3** is assigned as *S* configuration according to our previous study.[1a] The relative stereochemistry at C-8, C-4, and sulfur of the 1,4-adduct of the carbanion derived from *p*-tolyl allyl sulfoxide with 2-([(*tert*-butyldimethylsilyl)oxy]methyl)-7,7-dimethylbicyclo[3.3.0]-2-octen-3-one has been proven by X-ray diffraction. This work will be published elsewhere.

(12) Sulfoxide **2** was prepared from sodium benzenethiolate and *cis*-1-chloro-2-butene followed by oxidation with MCPBA in CH_2Cl_2.

(13) All enantiomers are being depicted with absolute stereochemistry as indicated. All new compounds displayed satisfactory ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), UV, IR, and low-resolution mass spectra (both EI and CI) and satisfactory elemental analysis or high-resolution MS.

(14) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. The C-11 H's of the diastereomers of the Mosher's derivatives of **12** and **13** have different chemical shifts.

(15) Mura, A. J., Jr.; Majetich, G.; Grieco, P. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4437.

(16) The structure of **15** was proven by hydrolysis with 1 equiv of K_2CO_3–MeOH at room temperature for 15 min to alcohol **17** followed by oxidation with pyridinium chlorochromate–CH_2Cl_2 to the corresponding diketone (C-6, C-11). ^1H NMR spectrum of this diketone shows four doublets of δ 2.60 (J = 20 Hz, C-5 H) and 2.18 (J = 20 Hz, C-5 H) and 1.83 (J = 14 Hz, C-3 H) and 1.50 (J = 14 Hz, C-3 H). This cyclization reaction has also been tested in other compounds and showed similar results and will be published in a full paper.

(17) $[\alpha]^{25}_D$ +32° (*c* 0.06, CH_2Cl_2) [lit.[2] +11.8° (*c* 6.8, $CHCl_3$)].

(18) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.

(19) The IR, NMR (^1H, ^{13}C), and mass spectra of **1** were provided by Professor Haruo Seto of the University of Tokyo.

of (+)-pentalenene [(+)-1] is stereocontrolled, short, and effective and should be applicable to the constructions of isocomene,[20] silphinene,[21] senoxydene,[22] pentalenic acid, and pentalenolactone. The hydrolytic ring closure reaction of vinyl sulfide and ketones seems to be general and should prove to be a valuable new reaction tool in other syntheses. Utilization with more highly oxidized members of the sesquiterpene is being explored.

Acknowledgment. We thank the NSF and Kansas State University for a grant for the purchase of the Bruker WM-400 NMR spectrometer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8419265) for generous financial support. We are indebted to Professor Haruo Seto for providing the spectral data and Gurudas Sinai-Zingde and Ibraheem Badejo for technical assistance.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compound **1-3**, **10**, **11**, and **14-21** (21 pages). Ordering information is given on any current masthead page.

(20) (a) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 456. (b) Bohlmann, F.; LeVan, N.; Pickhardt, J. *Chem. Ber.* **1977**, *110*, 3777. (c) Zalkow, L. H.; Harris, R. N., III; Burke, N. I. *J. Nat. Prod.* **1979**, *42*, 96.
(21) Bohlmann, F.; Jakupovic, J. *Phytochemistry* **1980**, *19*, 259.
(22) Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 1747.

Hydrogen-Deuterium Exchange during Propylene Epoxidation by Cytochrome P-450

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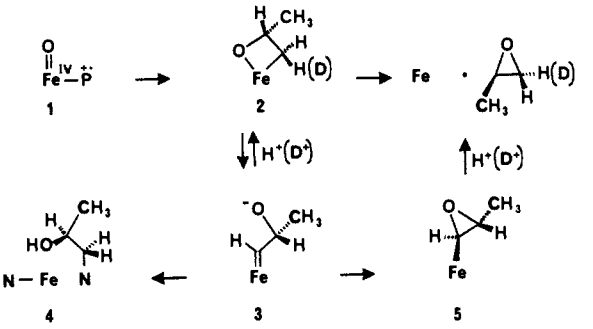
The nature of the "active oxygen species" and the mechanism of the oxygen-transfer event in the catalytic cycle of cytochrome P-450[1] have been the subject of extensive investigation and speculation. A powerful approach to the study of such elusive intermediates has been the use of substrate molecules designed to reveal the chemistry of the ultimate oxidant. We have previously demonstrated that epimerization[2] and allylic rearrangement[3] occur during the aliphatic hydroxylation by cytochrome P-450. We report here that the epoxidation of *trans*-1-deuteriopropylene by a reconstituted cytochrome P-450 system proceeds with significant loss of the deuterium label. Further, the epoxidation of propylene by this enzymic system in D_2O affords predominantly *trans*-1-deuteriopropylene oxide.

In a typical experiment cytochrome $P\text{-}450_{LM2}$ (5 nmol), cytochrome P-450 reductase (10 nmol), and dilauroyl-GCP (150-220 μL of a 1 mg/mL solution) were mixed and then diluted with 0.5 mL of phosphate buffer (pH 7.4) and 0.5 mL of water in a manner identical with that which we have previously described.[3,4] NADPH (250 μL of a 10 mg/mL solution) was added from a bent side neck and the mixture was cooled to 4 °C. After removal of air on a vacuum line, propylene (1.9-2.2 mmol) or *trans*-1-deuteriopropylene (0.9-1.0 mmol, 70% d_1) was admitted to the reaction vessel and the mixture was allowed to equilibrate for 15-30 min. After propylene was removed to 0.5 atm and replaced with oxygen, the mixture was allowed to stand at 4 °C overnight. After removal of oxygen from the frozen reaction mixture, volatile products were transferred to a cold trap. Unreacted propylene was removed from the reaction products by distillation, and propylene oxide was either condensed into a sample bulb or isolated from the product fraction by preparative gas chromatography on a 20% Carbowax column. The amount of propylene oxide was determined manometrically at this point. Simultaneous, quantitative analysis of propylene oxide, *trans*-1-deuteriopropylene oxide, *cis*-1-deuteriopropylene oxide, and unreacted propene was carried out by microwave spectroscopy as we have previously described.[5] Blank samples were determined before and after each run to assure that the vacuum line, gas chromatograph, and microwave cavity were free of contamination.

Scheme I



Typical data for a series of propylene oxidations presented as intensity ratios for five prominent mirowave transitions are shown in Table I. Product yields and isotopomer distributions are presented in Table II. Remarkably, the epoxidation of *trans*-1-deuteriopropylene afforded 95% propylene-d_0 oxide. This apparent deuterium exchange was confirmed by the runs performed with unlabeled propylene in D_2O which gave greater than 80% *trans*-1-deuteriopropylene oxide. Thus, *the epoxidation of propylene with this reconstituted cytochrome P-450 system proceeded with a concomitant, stereospecific hydrogen/deuterium exchange from the aqueous milieu.*

Electrophoretically homogeneous cytochrome P-450 alone catalyzed the epoxidation of propylene with iodosylbenzene to give an isotopomer ratio indistinguishable from that of the starting propylene. Further, the incubation of propylene oxide with the fully reconstituted P-450 system in D_2O for 3 days caused no more than 10% exchange. The epoxidation of *trans*-1-deuteriopropylene with Fe(TPP)Cl or Mn(TPP)Cl and iodosylbenzene in wet methylene chloride gave products consistent with complete retention of configuration with the iron porphyrin and significant trans-cis rearrangement with the manganese porphyrin but with no H-D exchange. Similar results have been obtained for these synthetic porphyrin catalysts with other substrates.[6]

A number of mechanisms have been suggested for the substrate oxygenation catalyzed by cytochrome P-450.[1] No simple oxygen-transfer process would have predicted the stereospecific exchange of a carbon-bound hydrogen observed here, however. Two processes that do allow for the observed results are shown in Scheme I. We have described the preparation and characterization of an oxoiron(IV) porphyrin cation radical species (**1**) which is capable of epoxidizing olefins at low temperature.[7] Such a

†Current address: Department of Chemistry, Princeton University, Princeton, NJ 08544.
(1) (a) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315. (b) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9-16. (c) Groves, J. T. *Adv. Inorg. Biochem.* **1979**, *1*, 119-145.
(2) (a) Groves, J. T.; McClusky, G. A.; White, R. E.; Coon, M. J. *Biochem. Biophys., Res. Commun.* **1978**, *81*, 154-160. (b) Gelb, M. H.; Heimbrook, D. C.; Mälkönen, P.; Sligar, S. G. *Biochemistry* **1982**, *21*, 370-377.
(3) (a) Groves, J. T.; Subramanian, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 2177-2181. (b) Groves, J. T.; Akinbote, O. F.; Avaria, G. E. In *Microsomes, Drug Oxidations and Chemical Carcinogens*; Coon, M. J., et al., Eds.; Academic Press: New York, 1980; Vol. 1, pp 253-261.
(4) (a) Haugen, D. R.; Coon, M. J. *J. Biol. Chem.* **1976**, $_2$5, 7929-7939. (b) Coon, M. J.; van der Hoeven, T. A.; Dahl, S. B.; Haugen, D. A. *Methods Enzymol.* **1978**, *52*, 109-117.
(5) (a) Larrabee, A. L.; Kuczkowski, R. L. *J. Catal.* **1978**, *52*, 72-80. (b) Imachi, M.; Egashira, M.; Kuczkowski, R. L.; Cant, N. W. *J. Catal.* **1981**, *70*, 177-181. (c) Imachi, M.; Kuczkowski, R. L. *J. Mol. Struct.* **1982**, *96*, 55-60. (d) Lide, D. R., Jr.; Christensen, J. *J. Chem. Phys.* **1961**, *35*, 1374. (e) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868.
(6) (a) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (b) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786.
(7) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2885.

0002-7863/86/1508-3837$01.50/0