is the endo side for the *exo*-4,7-methano-1*H*-indene molecule. The *endo*-4,7-methano-1*H*-indene system, on the other hand, suffers attack from the exo side. This indicates that the reactions of these molecules are very stereospecific.

Experimental Section

Melting points were determined with an electrothermal apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian EM-360A spectrometer. IR spectra were recorded with a Perkin-Elmer 735B spectrophotometer. Elemental analyses were carried out by Galbraith Enterprises, Inc.

***endo*-1-Hydroxy-3a,4,7,7a-tetrahydro-*exo*-4,7-methano-1*H*-indene (3).** This compound was prepared by using *exo*-dicyclopentadiene[7] and SeO_2 and the procedure of Woodward and Katz:[2] bp 70–73 °C (0.1 torr); IR (neat) 3200 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 6.22 (m, 2 H, H-2 and H-3), 5.8 (m, 2 H, H-5 and H-6), 4.3 (dd, 1 H, H–C–OH), 3.3 (s, 1 H, OH), 2.6–2.0 (m, 6 H, H-3a, H-4, H-7, H-7a, 2H-8). Anal. Calcd for $C_{10}H_{12}O$: C, 81.03; H, 8.18. Found: C, 81.22; H, 8.31.

***endo*-1-Hydroxy-2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1*H*-indene (1).** A solution of **3** (30 g, 0.2 mol) in 150 mL of ethanol was subjected to hydrogen (3 atm) in a Parr hydrogenator with a 5% Pd/C catalyst. Removal of the catalyst by filtration and distillation gave **1**: 26 g (0.16 mol 84% yield); bp 78–80 °C (0.1 torr); IR (neat) 3150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.65 (m, 1 H, H–C–OH), 3.3 (s, 1 H, OH), 2.25–0.85 (m, 12 H, alkyl H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.88; H, 10.61. Found: C, 78.92; H, 10.55.

***endo*-1-Hydroxy-2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1*H*-indene-*2,3,5,6-d*$_4$ (5).** By use of the procedure reported for **1**, **3** (3 g, 0.02 mol) was reduced with deuterium to yield **5**. Mass spectral analysis indicated that four deuteriums had been incorporated into the molecule to greater than 98%: NMR ($CDCl_3$) δ 3.70 (dd J = 2, 9 Hz, 1 H H–C–OH), 3.25 (s, 1 H, OH), 2.30–0.80 (m, 8 H, alkyl H).

2,3,3a,4,5,6,7,7a-Octahydro-*exo*-4,7-methano-1*H*-inden-1-one (6). The procedure of Ratcliffe[6] was used to prepare **6**: yield 93%; bp 58–60 °C (0.3 torr); IR (neat) 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.55–0.95 (m, 14 H). Anal. Calcd for $C_{10}H_{14}O$: C, 79.94; H, 9.41. Found: C, 79.77; H, 9.26.

***exo*-1-Hydroxy-2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1*H*-indene (2).** To a solution of **6** (10 g, 0.06 mol) in 100 mL of ethanol cooled to 0 °C was added $NaBH_4$ (2.0 g, 0.05 mol). Stirring for 1 h and refluxing for 2 h followed. Water (20 mL) was added, and the solution was stirred at 50 °C for 30 min. After extraction with hexane followed by drying over Na_2SO_4, **6** was isolated by distillation: yield 8.7 g (0.55 mol, 88%); mp 63.5 °C; IR (neat) 3250 cm^{-1}; NMR ($CDCl_3$) δ 3.70 (s, 1 H, OH), 3.80 (dd, J = 5, 6 Hz, 1 H, H–C–OH), 2.4–1.1 (m, 14 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.88; H, 10.61. Found C, 78.84; H, 10.75.

Registry No. 1, 10271-46-2; 2, 10271-47-3; 3, 24529-79-1; 5, 80532-99-6; 6, 17364-68-0.

(7) G. L. Nelson and C. L. Kuo, *Synthesis*, 105 (1975).

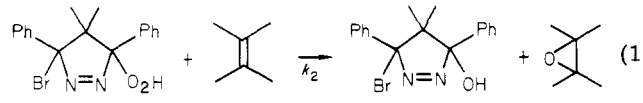
Epoxidation of Alkenes by 3-Bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole

Alfons L. Baumstark* and Robert S. Pilcher

Laboratory for MBS, Department of Chemistry, Georgia State University, Atlanta, Georgia 30303

Received October 23, 1981

Epoxidation of alkenes by alkyl hydroperoxides usually requires the presence of a catalyst.[1] A number of peroxides (triphenylsilyl hydroperoxide,[2] 2-hydroperoxy-hexafluoro-2-propanol,[3] and α-substituted hydroperoxides[4]) have been shown to epoxidize alkenes. Recently, 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole (**1**) was shown[5] to undergo reaction with 2,3-dimethyl-2-butene to yield **2** and tetramethyloxirane in good yield under mild conditions (reaction 1).



1 2 (1)

Few quantitative kinetic studies are available on the epoxidation of alkenes by reactive hydroperoxides. **1** has structural similarities with flavin 4a-hydroperoxides, α-peroxy esters, and peracids. An understanding of the chemical properties of **1** should provide insight into the factors required to effect oxygen-atom-transfer chemistry. We report a study of the reaction of **1** with a series of substituted alkenes to produce the corresponding oxiranes in moderate yields.

Results

Addition of an excess of alkene to **1** in $CDCl_3$ at 34 °C resulted in the formation of **2** and the corresponding oxiranes in moderate to high yields. Tetrasubstituted alkenes were found to be more reactive than trisubstituted alkenes. Disubstituted alkenes were found to be unreactive[6] or only marginally reactive in the epoxidation reaction. Product yields were found to be dependent upon the concentration of the alkene. Addition of 1 equiv of alkene to **1** in $CDCl_3$ produced only low yields of the oxiranes (55% for the best case) due to competition with the normal[7] thermal decomposition of **1**. Product yields were determined, relative to an internal standard, by NMR spectroscopy. Oxirane yields for a 3–5-fold excess of alkene were found to be in the range of 40–80% for tri- and tetrasubstituted alkenes (see Table I). Experiments with a larger excess of alkene (see Table II) produced oxirane yields of between 72% and 94% for tetra- and trisubstituted alkenes. The yield of **2** was found to be within the experimental error of the yield of oxirane in all cases. **2** was isolated by careful crystallization from $CDCl_3$/pentane. The oxirane yields were

Table I. Oxirane Yields for the Reaction of 1 in $CDCl_3$ at 34 °C with Alkenes

alkene	[alkene], M	[alkene]/[1]$_0$	% yield of oxirane[b]
2,3-dimethyl-2-butene	0.38	4	84
1,2-dimethylcyclohexene	0.29	3	72
2-methyl-2-butene	0.49	5	59
1-methylcyclohexene	0.51	5	40
cyclopentene	0.53	5	19

[a] [1]$_0$ ≈ 0.090 to 0.10 M. [b] Relative to internal standard (anisole). The yield of **2** was within the experimental error of the yield of epoxide in all cases.

(1) (a) Swern, D. "Organic Peroxides"; Wiley-Interscience: New York, 1971; Vol II, pp 83–86. (b) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 752.

(2) Rebek, J.; McCready, R. *Tetrahedron Lett.* **1979**, 4337.
(3) Heggs, R. P.; Ganem, B. *J. Am. Chem. Soc.* **1979**, *101*, 2484.
(4) (a) Rebek, J., Jr.; McCready, R.; Wolak, R. *J. Chem. Soc., Chem. Commun.* **1980**, 705. (b) Rebek, J., Jr.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602.
(5) Baumstark, A. L.; Chrisope, D. R.; Landis, M. E. *J. Org. Chem.* **1981**, *46*, 1964.
(6) No epoxidation products were detected in the reaction of **1** with a 20-fold excess of *cis*- or *trans*-3-hexene. **1** underwent normal thermal decomposition although at a greatly reduced rate.
(7) Landis, M. E.; Lindsey, R. L.; Watson, W. H.; Zabel, V. *J. Org. Chem.* **1980**, *45*, 525.

0022-3263/82/1947-1141$01.25/0

Table II. Second-Order Rate Constants for the Reaction of Alkenes with 1[a] in $CDCl_3$ at 34 °C

entry	alkene	[alkene], M	% yield of epoxide	$10^4 k_2$, M^{-1} s^{-1}	rel reactivity
1	2,3-dimethyl-2-butene	0.33-0.75	94	31.3 ± 2.3	11.4
2	1,2-dimethylcyclohexene	0.29-0.31	85	20.5 ± 1.5	7.45
3	2-methyl-2-butene	0.64-1.12	79	2.75 ± 0.15	1.00
4	1-methylcyclohexene	0.80-1.69	72	2.10 ± 0.27	0.764
5	cyclopentene	2.23-3.64	41	0.32 ± 0.02	0.116

[a] $[1]_0 \approx 0.040$-0.10 M.

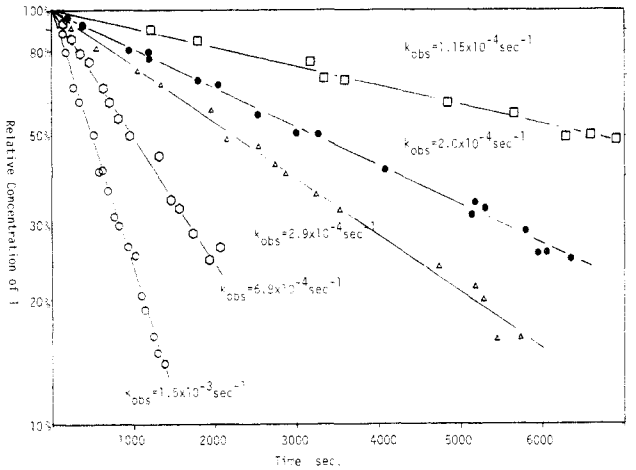


Figure 1. Pseudo-first-order plots for the reaction of 1 with alkenes: ○, [2,3-dimethyl-2-butene]$_0$ = 0.47 M; ○, [1,2-dimethylcyclohexene]$_0$ = 0.31 M; △, [2-methyl-2-butene]$_0$ = 1.03 M; ●, [1-methylcyclohexene]$_0$ = 0.80 M; □, [cyclopentene]$_0$ = 3.64 M. [1]$_0$ = 0.06 M for the runs shown.

checked by gas chromatography. The oxiranes were identified by comparison of spectral data with those of authentic samples.

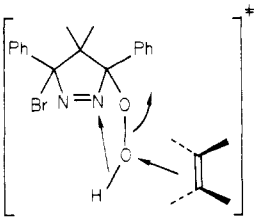
The kinetics of the epoxidation reaction was investigated. The reaction was found to be first order with respect to both alkene and 1. The disappearance of 1 vs. time was monitored by NMR spectroscopy under pseudo-first-order conditions. The rate of formation of epoxide and of 2 were found to be identical with the rate of disappearance of 1. Typical pseudo-first-order results of the plots of [1] vs. time are shown in Figure 1. The second-order rate constants calculated from the pseudo-first-order plots are listed in Table II.

Discussion

A comparison of the reactivity of 1 toward epoxidation of alkenes with those of other α-substituted hydroperoxides is hampered by the lack of quantitative kinetic data for the systems under similar conditions. Qualitatively, the reactivity of 1 toward an alkene appears comparable to that of 2-hydroperoxyhexafluoro-2-propanol[3] and is at least 1 order of magnitude greater than that of α-peroxy esters and nitriles.[4] The reaction of 1 with 2-methyl-2-butene in $CDCl_3$ at 34 °C was found to be approximately 2 orders of magnitude slower than the reaction of peracetic acid[8] with 2-methyl-2-butene in acetic acid at 26 °C.

Compound 1 is more efficient at epoxidation of 2,3-dimethyl-2-butene than the postulated carbonyl oxide intermediates in the decomposition of furan endoperoxides.[9] However, an intermediate in the thermolysis of isobenzofuran endoperoxide has been reported[10] to epoxidize

Scheme I



norbornene. Thus, a comparison of the reactivity of 1 toward epoxidation with those of "carbonyl oxide" intermediates is not possible at present.

The relative reactivity series for the reaction of 1 with alkenes (see Table II) shows the selectivity of the epoxidation reaction to be surprisingly similar to those reported for acetic acid epoxiations[8] and epoxidation by an intermediate formed in the metal ion catalyzed oxygenation of azibenzil.[11] This suggests that the mechanism for the epoxidation of alkenes by 1 might be similar to that suggested for peroxy ketals.[4b] Intramolecular hydrogen bonding to the nitrogen atom in 1 could account for the increased reactivity compared to that of α-peroxy esters and nitriles (Scheme I). The position of approach shown in Scheme I is essentially identical with that suggested for peracid epoxidations.[12]

Several reactive hydroperoxides have been suggested[3,4,5] as models for flavin 4a-hydroperoxides.[13] Recently, we have shown[14] that the reactions of 1 with tertiary amines and sulfides to produce 2 and the corresponding amine oxides and sulfoxides are comparable in rate and yield with those of flavin 4a-hydroperoxides.[15] The similarity of the relative reactivity of 1 toward epoxidation to that of peracids and the similarity of oxygen transfer from 1 to amines or sulfides to that from flavin 4a-hydroperoxides[15] indicate that the earlier prediction of olefin epoxidation by flavin 4a-hydroperoxides by Rebek[4b] should be feasible.

Experimental Section

All solvents were of reagent grade. 3-Bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole (1) was prepared according to the published procedure[7] (**Caution**! Danger of explosion!) and recrystallized at −30 °C from methylene chloride/petroleum ether before use. 1 was stored as the solid in approximately 0.5-g quantities at −30 °C. The alkenes (99%+ pure) were available commercially and were used without further purification. Melting points were recorded on a Thomas-Hoover (Uni-melt) capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian 360L spectrometer.

(8) (a) Reference 1a, pp 355–475. (b) Swern, D. *Chem. Rev.* **1945**, *45*, 1949.
(9) Adams, W.; Rodriquez, A. *J. Am. Chem. Soc.* **1980**, *102*, 404.
(10) Saito, I.; Nakata, A.; Matsuurn, T. *Tetrahedron Lett.* **1981**, 1697.
(11) Ryang, H.-S.; Foote, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 2129.
(12) (a) Bach, R. D., Willis, C. L.; Domagala, J. M. In "Applications of Molecular Orbital Theory in Organic Chemistry"; Csimada, I. G., Ed.; Elsevier: Amsterdam, 1977; pp 221–229. (b) Sharpless, K. B.; Verkoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63–74. (c) Reference 1b pp 750–751 and references therein.
(13) (a) Hamilton, G. A. *Prog. Bioorg. Chem.* **1971**, *1*, 83–157. (b) Massey, V.; Hemmerich, P. *Enzymes* **1976**, *12*, 191–252. (c) Bruice, T. C. *Prog. Bioorg. Chem.* **1976**, *4*, 1–87.
(14) Baumstark, A. L.; Chrisope, D. R. *Tetrahedron Lett.* **1981**, 4591.
(15) (a) Ball, S.; Bruice, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 6498. (b) Ball, S.; Bruice, T. C. *Ibid.* **1979**, *101*, 4017.

IR spectra were recorded on a Perkin-Elmer 700 spectrometer. VPC studies were carried out on a Varian 920 preparative gas chromatograph by using a 6 ft × 0.25 in. SE-30 on Chromosorb P column.

Kinetic Studies. The following general procedure was employed. Compound 1 (20 mg, 0.055 mmol) was added, as the solid, to 500 μL of $CDCl_3$ (Merck; no Me_4Si) containing 1 μL of *cis*-3-hexene[6] in a new 5-mm NMR tube. Anisole (5 μL) was added as an internal standard. The NMR spectrum was recorded, and the signals were electronically integrated. The desired amount of alkene was added, via syringe, to the solution at 34 °C and mixed by inverting the tube. Runs were carried out with 1-fold, 3–4-fold, and 7–10-fold excesses of each alkene relative to 1. Runs with a 15–20-fold excess of alkene to 1 were carried out for the less reactive alkenes. The signals were recorded and integrated vs. time. The rates of appearance of 2 and oxirane were checked and found to correspond to the rate of disappearance of 1. Final product yields of 2 and oxirane were determined relative to the internal standard. For example, the yields of 2 and oxirane were 55% and 60% for the reaction of 1 with 1 equiv of 2,3-dimethyl-2-butene but increased to 90% and 94%, respectively, for a reaction with a 7-fold excess of the alkene. Pseudo-first-order plots of the relative concentration of 1 were linear for at least 2 half-lives. The second-order rate constants were determined by dividing the observed pseudo-first-order rate constants by the initial alkene concentrations. A 2-fold variation in the concentration of 1 in the presence of a large excess of alkene did not affect the observed pseudo-first-order rate constant. A 3-fold variation in the alkene concentration resulted in a 3-fold variation in k_{obsd} while the calculated second-order rate constants were within experimental error of each other (±10%).

Product Studies. Compound 2 (mp 93–94 °C) was isolated (crystallization at −20 °C) from the reaction mixtures in ~30% yield by partial removal of the solvent at reduced pressure followed by addition of pentane. The structural proof for 2 has been reported.[5] The NMR spectra of the completed reaction mixtures showed the epoxides to be present in all cases. The yield of epoxide for each reaction was confirmed by gas chromatography. The epoxides from the 2,3-dimethyl-2-butene and the cyclopentene cases were isolated by preparative gas chromatographic techniques and proven to be identical with authentic samples by comparison of spectral data. Authentic samples of the oxiranes were prepared by the reaction of the corresponding alkenes with 1 equiv of *m*-chloroperbenzoic acid.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the NIH (Grant RR 09201).

Registry No. 1, 76847-41-1; 2, 76847-42-2; 2,3-dimethyl-2-butene, 563-79-1; 1,2-dimethylcyclohexene, 1674-10-8; 2-methyl-2-butene, 513-35-9; 1-methylcyclohexene, 591-49-1; cyclopentene, 142-29-0.

Polymeric Inclusion Compound Derived from β-Cyclodextrin

Ken Hirotsu* and Taiichi Higuchi

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Kahee Fujita,* Tadashi Ueda, Akihiro Shinoda, and Taiji Imoto

Faculty of Pharmaceutical Sciences, Kyushu University, Higashi-ku, Fukuoka 812, Japan

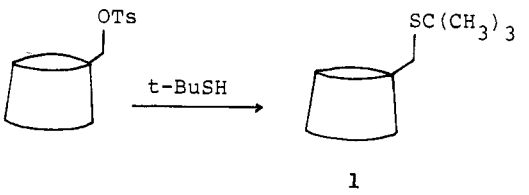
Iwao Tabushi*

Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan

Received November 20, 1981

Cyclodextrins have received much attention as relatively low molecular weight models for biological macromolecules.[1] This interest has been enhanced by their specific chemical modifications, giving more desirable mimics of enzymes.[2] However, the structures of modified cyclodextrins, even simple monosubstituted cyclodextrins, have never been studied although cyclodextrins[3,4] and their inclusion complexes[5-8] with various guest molecules have been extensively studied by X-ray analysis. Moreover, there is no direct evidence concerning the existence of

Scheme I



1

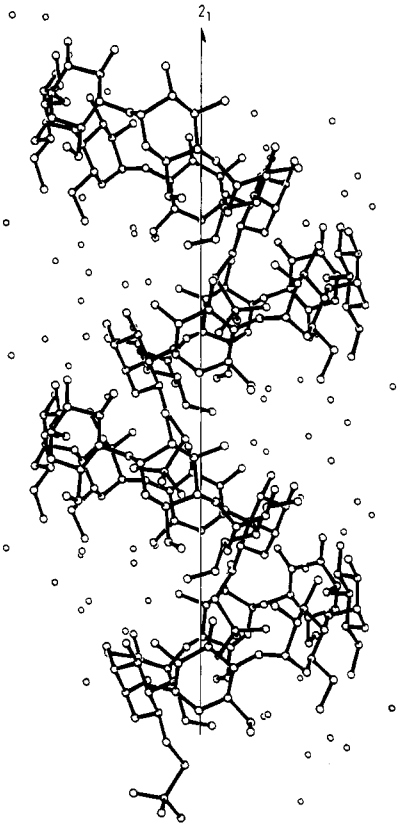


Figure 1. Drawing of a novel helical polymer penetrated by the 2_1 screw axis which is parallel to the *c* axis and shown by a long straight line. The *t*-BuS group is intermolecularly included in the hydrophobic cavity of the macrocycle. Water oxygen atoms are represented by smaller circles.

(1) (a) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry". Springer-Verlag: West Berlin and Heidelberg, 1978. (b) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344–362.

(2) (a) Tabushi, I.; Kuroda, Y.; Mochizuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152–1153. (b) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *J. Am. Chem. Soc.* **1979**, *101*, 4759–4760. (c) Breslow, R.; Hammond, M.; Lauer, M. *J. Am. Chem. Soc.* **1980**, *102*, 421–422. (d) Breslow, R.; Bovy, P.; Hersh, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 2115–2117. (e) Fujita, K.; Ueda, T.; Shinoda, A.; Imoto, T.; Tabushi, I.; Toh, N.; Koga, T. *Bioorg. Chem.*, in press.

(3) Manor, P. C.; Saenger, W. *J. Am. Chem. Soc.* **1974**, *96*, 3630–3639.

(4) Lindner, K.; Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 694–695.

(5) Harata, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2782–2786.

(6) Noltemeyer, M.; Saenger, W. *J. Am. Chem. Soc.* **1980**, *102*, 2710–2722.

(7) Stezowski, J. J.; Jogun, K. H.; Eckle, E.; Bartels, K. *Nature (London)* **1978**, *274*, 617–619.

(8) Harding, M. M.; Maclennan, J. M.; Paton, R. M. *Nature (London)* **1978**, *274*, 621–623.

0022-3263/82/1947-1143$01.25/0