cedure A above) yielded pure **1b** (250 mg) along with ca. 400 mg of 2-phenoxybenzoic acid.

In a separate, control experiment, 0.76 g of TCNQ (3.72 mmol), 0.88 g of sodium 2-phenoxybenzoate (1 equiv), 0.20 g of authentic phenyl salicylate (0.25 equiv), and 200 mL of acetone were mixed as above and stirred at 25 °C for 137 h. During that time, aliquots from the reaction were periodically removed, concentrated, and spotted on TLC (5:1 hexane/ethyl acetate). Phenyl salicylate was easily detected throughout the course of the reaction as a strongly UV-active spot, R_f 0.56, alongside an authentic sample. At the end of the reaction, pure phenyl salicylate was isolated from the crude reaction mixture by flash chromatography followed by preparative TLC (26.5 mg, 13% recovery).

Acetone/THF Mixture as Solvent for the Sodium Benzoate Reaction. To a slurry of TCNQ (2.04 g, 10 mmol) and sodium benzoate (1.44 g, 10 mmol) in 125 mL of acetone (dried over calcium chloride) was added 125 mL of THF (freshly distilled). This mixture was protected from light and stirred at 25 °C for 67 h. The mixture was then filtered and concentrated in vacuo. The resulting solid was extracted with hot methylene chloride. After concentration, that extract was inspected by TLC (94:3:3 chloroform/methanol/acetic acid). A spot corresponding to **1b** was clearly present. No spot corresponding to **6b** could be seen (authenic **6b** obtained exactly according to ref 6 was spotted alongside the extract for reference). Compound **1b** was then isolated from the extract by flash chromatography as described in method A above to give 190 mg of **1b**.

The methylene chloride insoluble part of the reaction mixture was extracted with hot ethyl acetate to give, after concentration, a black powder. No **6a** could be seen in the NMR and IR spectra of that powder (authentic **6a** was obtained by deprotonation of **6b** with sodium hydroxide).

Acknowledgment. We are grateful to Dr. Charlotte S. Russell for providing an authentic sample of dimer **2**. We also thank Professor Ernest Wenkert for suggesting the tetrabutylammonium fluoride reaction. Helpful discussions with Dr. Robert J. Crawford are acknowledged.

Registry No. 1b, 80515-70-4; sodium benzoate, 532-32-1; 7,7,8,8-tetracyanoquinodimethane, 1518-16-7; acetone, 67-64-1; *p*-phenylenedimalononitrile, 18643-56-6; tetrabutylammonium fluoride, 429-41-4; sodium 2-phenoxybenzoate, 5138-68-1; phenyl salicylate, 118-55-8.

Stereospecific Syntheses of *endo*- and *exo*-1-Hydroxy-2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1*H*-indene

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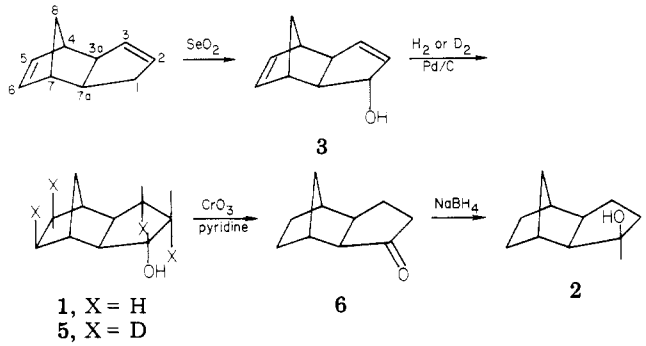
Received July 7, 1981

The dicyclopentadiene molecule and its hydrogenated derivatives are the basic structures for a variety of compounds from pesticides to jet fuels. The metabolism of these compounds tends to proceed via hydroxylation at the C_1 carbon. Although there have been numerous reports on the preparation of the hydroxylated derivatives of *endo*-dicyclopentadiene,[1] this paper reports the first preparation of the 1-hydroxy derivatives of the *exo*-dicyclopentadiene molecule.

exo-Dicyclopentadiene was treated with selenium dioxide (SeO_2) by using the allylic hydroxylation procedure of Woodward and Katz[2] to give *endo*-1-hydroxy-3a,4,7,7a-tetrahydro-*exo*-4,7-methano-1*H*-indene (**3**). The IR showed a broad band at 3200 cm^{-1}. The stereochemistry of **3** was established by noting that the carbinol proton in the ^1H NMR appeared as a doublet of doublets with J = 2 and 3 Hz. The small coupling constant indicated an anti arrangement for H_1 and H_{7a}[3]. A Dreiding model of **3** predicts a dihedral angle of approximately 120° if H_1 and H_{7a} are anti, which would lead to a coupling constant of 1-3 Hz[4]. Since H_{7a} is endo, H_1 must be exo, and the OH group must be endo. It is noteworthy that the major product of SeO_2 oxidation of *endo*-dicyclopentadiene is *exo*-1-hydroxy-3a,4,7,7a-tetrahydro-*endo*-4,7-methano-1*H*-indene (**4**).[2] In the cases of both *endo*- and *exo*-dicyclopentadiene the large SeO_2 molecule approaches the allylic group from the least hindered side to give exclusively the requisite alcohol.

Scheme I



Catalytic reduction of **3** over 5% palladium on charcoal yielded **1**. The ^1H NMR spectrum showed the absence of peaks in the 5.5-6.5-ppm range, indicating that the reduction of the olefinic groups was complete.

Catalytic reduction of **3** with deuterium on Pd/C yielded 1-*2,3,5,6-d*$_4$ (**5**). It was assumed that the deuterium added exo to the 5,6-positions.[5] Examination of ^1H NMR showed that proton H_1 was still a doublet of doublets but now with J = 2 and 9 Hz. This indicated that since H_1 and H_{7a} were anti, H_1 and H_2 were eclipsed. For H_1 and H_2 to be approximately eclipsed required that the deuteriums approached from the endo side.

By use of a modification of the Sarrett reaction,[6] **3** was oxidized to 2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1-indenone (**6**). The IR showed a strong band at 1685 cm^{-1} (C=O) and absence of a band in the 3200-cm^{-1} (OH) region. The ^1H NMR showed only a multiplet at δ 0.95-2.55.

Sodium borohydride ($NaBH_4$) reduction of **6** gave **2**. The IR spectrum showed a strong band at 3250 cm^{-1}. The ^1H NMR showed peak at 3.70 ppm, which was assigned to the proton H_1. The large coupling constants of J = 8 and 10 Hz for the carbinol hydrogen indicated that the OH group must be exo so that H_1 is approximately eclipsed by H_2. A coupling between H_1 and H_2 anti is small (J = 1 Hz) and could be seen only by changing the NMR sweep width. There was no trace by GLC of any **1** being formed by the $NaBH_4$ reduction. Thus, BH_4^- like SeO_2 and H_2 all approach from the least sterically hindered side which

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(5) Deuterium has been shown to add exo to the 5,6-positions of *endo*-dicyclopentadiene.[3a] Addition to the norborene molecule always occurs from the exo side unless the exo side is blocked by substituents in the 7-position (J. March, "Advanced Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1977, p 680).
(6) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35** 4000 (1970).

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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.

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

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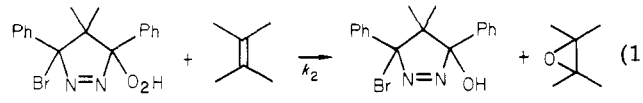
Received October 23, 1981

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.

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