orbital stabilization has been suggested by Paquette[12] for the solvolysis of **5**.

Experimental Section

The infrared spectra were recorded on a Beckman IR-5 instrument. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer, using TMS as an internal standard and deuteriochloroform as solvent. Melting and boiling points are not corrected. Gas chromatographic analysis were performed on an F & M Model 400 unit, using a hydrogen flame detector and Disc integrator.

Preparation of 4-Methyl-*cis*-3a,4,7,7a-tetrahydrophthalan (1).—The known *cis*-3-methyl-4-cyclohexene-*cis*-*cis*-1,2-dicarboxylic acid anhydride[13] (60 g) was dissolved in 600 ml of anhydrous ether and this was added to a refluxing solution prepared from 15.2 g of lithium aluminum hydride in 600 ml of anhydrous ether. After hydrolyzing the reaction mixture, the ethereal layer was separated, dried, and distilled [116–124° (0.5 mm)] to yield 33.0 g (59%) of a crude diol. The diol (21 g) was immediately dissolved in 40 ml of dry pyridine and heated to reflux while 38 g of *p*-toluenesulfonyl chloride in 40 ml of pyridine were added. The reaction mixture was refluxed for 12 hr, cooled, and poured over an ice–sulfuric acid mixture. The product was extracted with pentane and distilled to yield 14 g (73%) of a water-clear liquid, bp 44–48° (0.2 mm). The infrared spectrum exhibited the characteristic ether linkage of tetrahydrofuran derivatives at 9.2 μ (1087 cm^{-1}).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.14.

Hydration of 1 by Hydroboration.—Sodium borohydride (1.43 g) was added to a solution containing 3.5 g of **1** and 15 ml of anhydrous THF. The reaction mixture was placed under a nitrogen atmosphere at 0° and BF_3 etherate (9.3 g, 0.056 mol) was slowly added. After hydrolysis of the boron complex, the reaction mixture was warmed to room temperature. After about 12 hr, the mixture was extracted with ether to yield a crude alcohol mixture. This was immediately subjected to Jones oxidation, giving the liquid ketones **2** and **3**, bp 76–82° (10 mm). These could be separated on a 6 ft × 6 mm glass column packed with 20M Carbowax on 30/60 firebrick or by column chromatography utilizing a 30 × 60 mm water-cooled column packed with silica gel (14 g silica gel G, 30 ml of H_2O, activated for 45 min) and eluted with solvent [chloroform–ether–pentane (55:28:17)]. The identity of **3** was established by deuterium exchange. No distinguishing features could be noted in the infrared spectrum. The nmr spectra of the ketones were consistent with the assigned structures. The 2,4-dinitrophenylhydrazones of **2** (mp 164–165°) and **3** (mp 176–177°) were prepared.

Anal. Calcd for $C_{15}H_{18}N_4O_5$ (the 2,4-dinitrophenylhydrazone of **2**): C, 53.89; H, 5.43. Found: C, 53.81; H, 5.31. Calcd for $C_{15}H_{18}N_4O_5$ (the 2,4-dinitrophenylhydrazone of **3**): C, 53.89; H, 5.43. Found: C, 53.92; H, 5.55.

Hydration of 1 by Disiamylborane.—The disiamylborane was prepared and used according to the procedure of Brown.[14] Products were worked up and after Jones oxidation the ketones were subjected to analytical glc.

Hydration of 1 by Oxymercuration–Demercuration.—Utilizing the procedure of Brown,[15] the alkene **1** was converted to the alcohol mixture and after Jones oxidation the ketones were analyzed.

Hydrations of 3-Methylcyclohexene.—These reactions were performed as discussed for **1**.

Registry No.—**1**, 31684-77-2; **2**, 31684-78-3; **2** 2,4-DNPH, 31684-79-4; **3**, 31684-80-7; **3** 2,4-DNPH, 31731-95-0; 1-methylcyclohexene, 591-49-1; 3-methylcyclohexene, 591-48-0.

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[14] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, Chapter 13.

[15] H. C. Brown and P. J. Gaoghengan, Jr., *J. Org. Chem.*, **35**, 1844 (1970).

Epoxidation. III. The Relative Reactivities of Some Representative Olefins with Peroxybenzimidic Acid[1]

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We recently reported[3] that the stereochemistry of epoxidation of conformationally biased methylenecyclohexanes with peroxybenzimidic acid (formed *in situ* from benzonitrile and alkaline hydrogen peroxide[4]) differed significantly from the results obtained with a variety of peracids, and these results have been confirmed in an independent study by Sykes.[5] We earlier suggested that the observed difference in stereochemistry resulted from the greater reactivity of the peroxybenzimidic acid. In order to test this hypothesis we have examined the relative reactivities of some representative olefins with peroxybenzimidic acid utilizing the competition technique. The results of these studies are summarized in Table I along with some comparative data for peracid epoxidation[6] and methylenation.[7]

In addition, 4-vinylcyclohexene and *d*-limonene were epoxidized with 0.1 equiv of *m*-chlorperbenzoic acid and 0.1 equiv of peroxybenzimidic acid and the results of these experiments are summarized in Figures 1 and 2.

It is clear from these results that peroxybenzimidic acid is a far less selective reagent for the epoxidation of double bonds than are peracids. Although the reaction of peracids with alkenes is very markedly accelerated by the presence of electron-donating alkyl groups and a trisubstituted double bond is epoxidized approximately 275–300 times as fast as a monosubstituted double bond, the relative rates are greatly attenuated with peroxybenzimidic acid and the trisubstituted double bond is only five times as reactive as a monosubstituted olefin. As in peracid oxidations,[6] however, the cis isomer of a cis–trans pair is oxidized more rapidly. In contrast to a number of other addition reactions,[7] cyclopentene is oxidized less readily than both cyclohexene and cycloheptene.

This study indicates that peroxybenzimidic acid is a relatively indiscriminate reagent and is not the reagent of choice for selective epoxidation of polyunsaturated substrates. The data are consistent with a transition

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[1] For part II, see R. G. Carlson and R. Ardon, *J. Org. Chem.*, **36**, 216 (1971).

[2] Alfred P. Sloan Foundation Research Fellow, 1970–1972.

[3] R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967).

[4] G. B. Payne, *Tetrahedron*, **18**, 763 (1962), and references cited therein.

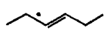
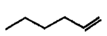
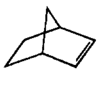
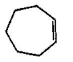
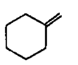
[5] J. D. Ballantine and P. J. Sykes, *J. Chem. Soc. C*, 731 (1970).

[6] D. Swern, *J. Amer. Chem. Soc.*, **69**, 1692 (1947).

[7] B. Rickborn and J. H. Chan, *J. Org. Chem.*, **32**, 3576 (1967).

Table I

Relative Rates of Epoxidation and Methylenation of Some Representative Olefins (Cyclohexene = 1.00)

Olefin	Registry no.	PhC-(=NH)-O$_2$H	CH$_3$-CO$_3$H	ICH$_2$ZnI
	563-79-1	3.5		1.29^{a}
	513-35-9	2.1	7.95^{b}	2.18^{a}
	13269-52-8	0.9	$1.00^{c,d}$	0.42^{a}
	7642-09-3	1.3	$1.00^{c,d}$	0.83^{a}
	592-41-6	0.4	0.039^{b}	0.36^{a}
	498-66-8	3.8	1.2^{e}	1.70^{f}
	628-92-2	2.03	1.36^{c}	1.18^{f}
	142-29-0	0.92	1.43^{b}	1.60^{f}
	1192-37-6	1.46		3.84^{f}

[a] E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.*, **86**, 1337 (1964). [b] J. Boeseken and J. Stuurman, *Recl. Trav. Chim. Pays-Bas*, **56**, 1034 (1937). [c] J. Boeseken and C. J. Hanegraaff, *ibid.*, **61**, 69 (1942). [d] The cis and trans isomers were not determined separately. [e] Value for perlauric acid in chloroform: K. D. Bingham, G. D. Meakins and G. H. Whitham, *Chem. Commun.*, 445 (1966). [f] Reference 7.

state that is reached somewhat earlier along the reaction coordinate than the corresponding transition state for peracid epoxidation.[3]

Experimental Section

Competition Experiments.—A solution of equimolar amounts of the appropriate olefin and cyclohexene in methanol was treated with 0.05 equiv of toluene (internal standard), benzonitrile, hydrogen peroxide, and potassium bicarbonate. The resulting solution was stirred overnight and analyzed by vapor phase chromatography on an F & M 700 gas chromatograph. The detector had been previously calibrated by preparing working curves from solutions containing varying amounts of toluene, cyclohexene oxide, and an authentic sample of the appropriate epoxide. All values reported in Table I are averages of two or more runs. Authentic samples of each epoxide were prepared by epoxidation of the appropriate olefin with *m*-chloroperbenzoic acid in methylene chloride.

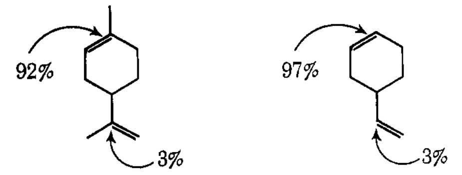


Figure 1.—Site of attack by *m*-chloroperbenzoic acid in methylene chloride in epoxidation of limonene and 4-vinylcyclohexene.

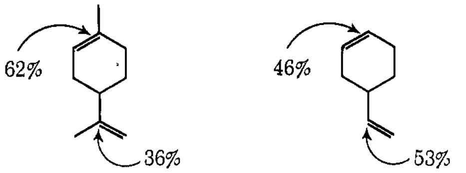


Figure 2.—Site of attack by peroxybenzimidic acid in epoxidation of limonene and 4-vinylcyclohexene.

Epoxidation of *d*-Limonene. A. With *m*-Chloroperbenzoic Acid.—To a solution of 2.00 g (14.6 mmol) of *d*-limonene in 75 ml of dry methylene chloride at 0° was added 3.15 g (14.6 mmol) of 80% *m*-chloroperbenzoic acid in 60 ml of methylene chloride over a period of 30 min. After the solution was stirred for 1 hr, the excess peracid was destroyed with 5 ml of 10% sodium sulfite solution and the methylene chloride solution was washed carefully with 100 ml of saturated sodium bicarbonate solution, the organic layer separated, and the aqueous layer was washed twice with methylene chloride. The organic layers were combined, washed with brine, dried, evaporated, and distilled to afford 1.28 g (58%) of product, bp 87-90° (15 mm) [lit.[8] bp 92-94° (20 mm)]. Vpc analysis[9] indicated the presence of 12% unreacted *d*-limonene, 87% 1,2-oxide,[10] and 0.5% 8,9-oxide. The 1,2-oxide was collected by preparative vpc and exhibited ir absorption at 3090 (vinyl H), 2985, 2945, 2870, 1645 (double bond), 1440, 1340, 1115, 887 (>C=CH$_2$), 838, and 668 cm^{-1} and nmr absorption at δ 4.67 (2 H, broad, >C=CH$_2$), 2.75-2.92 (1 H, epoxy CH), 1.68 (3 H, J = 1.0 Hz, >C=CCH$_3$), 1.3-2.3 (7 H, m), and 1.25 (3 H, s, epoxy CCH$_3$).

B. With Hydrogen Peroxide-Benzonitrile.—A solution of 0.1 g (0.74 mmol) of *d*-limonene, 8 mg (0.074 mmol) of 30% hydrogen peroxide, 9 mg (0.074 mmol) of benzonitrile, 0.5 ml of methanol, and 25 mg of potassium bicarbonate was stirred at room temperature for 4 days. The mixture was diluted with water and extracted three times with pentane, and the combined pentane layers were washed with water and brine. The crude product obtained after distillation of the pentane was analyzed by vpc[9] and found to consist of 61% 1,2-oxide, 37% 8,9-oxide, and 2% diepoxide of undetermined stereochemistry. A sample of the 8,9-oxide[11] collected by preparative vpc exhibited ir absorption at 3050, 3020, 2980, 2920, 1440, 1345, 1150, 1109, 1070, 1045, 915, and 903 cm^{-1} and nmr absorption at δ 5.37 (1 H, broad s, >C=CH), 2.35-2.60 (2 H, dd, epoxy CH$_2$), 1.3-2.2 (10 H, m), 1.63 (3 H, s, >C=CCH$_3$), and 1.20 (3 H, s, epoxy CCH$_3$).

Epoxidation of 4-Vinylcyclohexene. A. With *m*-Chloroperbenzoic Acid.—Epoxidation of a 1.00-g (9.7 mmol) sample of 4-vinylcyclohexene with 1.95 g (9 mmol) of 80% *m*-chloroperbenzoic acid by the above procedure afforded 1.03 g (93%) of crude product. Vpc analysis[9] indicated the presence of 10% unreacted starting material, 88% 1,2-oxide,[12] and 2% 7,8-oxide. A sample of the 1,2-oxide collected by preparative vpc exhibited ir absorption at 3050, 3010, 2860, 1650, 1440, 1340, 1260, 992, 915, 871, 852, and 660 cm^{-1} and nmr absorption at δ 4.75-6.00 (3 H, m, CH=CH$_2$), 3.01 (2 H, m, epoxy CH), and 1.2-2.4 (7 H, m).

The previously uncharacterized 7,8-oxide exhibited ir absorption at 3050, 3010, 2990, 2945, 2855, 1655, 1480, 1455, 1440, 1360, 1250, 1192, 1141, 1044, 940, 932, 920, 878, 854, and 654 cm^{-1} and nmr absorption at δ 5.65 (2 H, br s, CH=CH), 2.3-2.5 (1 H, dd, J = 5.2, 2.7 Hz, epoxy CH), 2.5-2.85 (2 H, m, epoxy CH$_2$), and unresolved absorption in the region 1.2-2.3 (7 H).

B. With Hydrogen Peroxide-Benzonitrile.—Epoxidation of 0.1 g of 4-vinylcyclohexene using the same procedure as was used for *d*-limonene gave a crude product which was shown by vpc[9] to consist of 46% 1,2-oxide, 53% 7,8-oxide, and 1% diepoxide.

Registry No.—Peroxybenzimidic acid, 20996-66-1; *m*-chloroperbenzoic acid, 937-14-4; *d*-limonene, 5989-27-5; 4-vinylcyclohexene, 100-40-3; *d*-limonene 1,2-oxide, 10008-60-3; *d*-limonene 8,9-oxide, 31684-93-2; 4-vinylcyclohexene 1,2-oxide, 106-86-5; 4-vinylcyclohexene 7,8-oxide, 5116-65-4.

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[8] E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **31**, 1937 (1966).

[9] A 10 ft × 0.25 in. column packed with 10% Carbowax 20M and 10% sodium hydroxide on 60-80 mesh Chromosorb W was employed for this analysis.

[10] J. Richer and G. Perrault, *Can. J. Chem.*, **43**, 18 (1965).

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[12] F. C. Frostick, Jr., B. Phillips, and P. S. Starcher, *J. Amer. Chem. Soc.*, **81**, 3350 (1959).