1-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (IV).—To a solution of 0.450 g. (0.008 mole) of potassium hydroxide in 5 ml. of methanol was added a solution of 1.670 g. (0.007 mole) of *trans*-2-bromo-1-methyl-1-tetralol (I) in 6 ml. of methanol. A precipitate appeared in about 5 min. The reaction mixture was stirred for 2.25 hr. The clear methanolic solution was decanted and the solid was washed with anhydrous ether. The combined organic layer was concentrated under reduced pressure to give a solid material. Two crystallizations of the solid material from pentane gave 0.89 g. (80%) of the epoxide IV, m.p. 34–36°. The infrared spectrum of the compound indicated the loss of a hydroxyl group.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 81.74; H, 7.25.

1-Methyl-2-tetralone (II).—The reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene in ether[10] gave a 31.5% yield of 1-methyl-2-tetralone (II): b.p. 125° (10 mm.), n^{24}_{D} 1.5595; lit.[10] b.p. 105–107° (3 mm.), n^{23}_{D} 1.5495. The infrared spectrum of the compound showed a maximum at 1710 cm.$^{-1}$ which was attributed to an unconjugated carbonyl group. This compound gave a negative iodoform test, and its semicarbazone melted at 193–193.5° dec. (lit.[10] m.p. 194° dec.).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 82.99; H, 6.55.

Rearrangement of 1-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (IV) with Sulfuric Acid.—This reaction was carried out according to the procedure reported for the rearrangement of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene with sulfuric acid.[4] The reaction mixture was heated at reflux temperature for 6 hr. The semicarbazone (m.p. 192–193° dec.) of the crude product showed no melting point depression when mixed with a sample of semicarbazone of 1-methyl-2-tetralone (II) obtained from the reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene (III).

Rearrangement of *trans*-2-Bromo-1-methyl-1-tetralol (I). A. With Phenylmagnesium Bromide.—A Grignard solution prepared from 1.20 g. (0.047 g.-atom) of magnesium and 6.5 ml. (7.38 g., 0.047 mole) of bromobenzene in 45 ml. of dry ether was added rapidly to a solution of 11.4 g. (0.047 mole) of *trans*-2-bromo-1-methyl-1-tetralol (I) in 40 ml. of dry benzene. The reaction mixture was heated under nitrogen at the reflux temperature for 6 hr. before it was decomposed on 250 g. of ice covered with 10 ml. of concentrated hydrochloric acid. The product was extracted with ether, washed with 5% sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. The yield of 1-methyl-2-tetralone which distilled at 125° (10 mm.) was 2.31 g. (40%), n^{24}_{D} 1.5615. The infrared spectrum of the product was similar to that of the 1-methyl-2-tetralone obtained from the reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene, both showing a strong maximum at 1710 cm.$^{-1}$ (C=O). The semicarbazone (m.p. 192–193° dec.) did not depress the melting point of a sample of semicarbazone of the ketonic product (II) obtained from the perbenzoic acid reaction. In addition, this compound did not give a positive iodoform test.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 82.46; H, 7.64.

B. With Silver Tosylate.—A solution of 11.8 g. (0.042 mole) of silver tosylate in 55 ml. of acetonitrile was added in the dark dropwise to a stirred solution of 10.0 g. (0.41 mole) of *trans*-2-bromo-1-methyl-1-tetralol in 45 ml. of acetonitrile. The reaction mixture was stirred at room temperature for 12 hr. After the removal of solid silver bromide by filtration, the reaction mixture was poured into 200 ml. of water. The product was extracted with ether, washed with 5% sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. Two products were obtained upon distillation. The yield of 1-methylnaphthalene (VI), the major product, which distilled at 64–65° (0.3 mm.) was 2.4 g. (42%): n^{20}_{D} 1.616.; lit.[10] b.p. 110° (12 mm.), n^{20}_{D} 1.618. The infrared analysis of the compound showed no significant absorption except those which were characteristic of C–H stretching. This compound also gave an absorption spectrum in the ultraviolet region identical with that obtained from an authentic sample of freshly distilled 1-methylnaphthalene. The permanganate oxidation of the compound following usual procedures gave 1-naphthoic acid, m.p. 160–161° (lit.[21] m.p. 160–161°).

Anal. Calcd. for $C_{11}H_{10}$: C, 92.96; H, 7.04. Found: C, 93.18; H, 6.83.

The minor product of this reaction, which was first isolated by rapid distillation, b.p. 80–120° (0.3 mm.), was a solid at room temperature. Repeated extraction of this crude solid material with boiling pentane followed by cooling the pentane solution in a bath kept at $-5°$ overnight led to the isolation of a white crystalline product. Recrystallization of this material from cyclohexane yielded 40 mg. (0.06%) of a solid, 1-methyl-1-hydroxy-1,4-dihydronaphthalene, m.p. 108–110°. The infrared spectrum of the compound showed two characteristic absorption maxima, one at 3650 (O–H) and the other at 1635 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 82.72; H, 6.57.

Attempted Preparation of *cis*-2-Bromo-1-methyl-1-tetralol.—Preparations of *cis*-2-bromo-1-methyl-1-tetralol by the addition of methylmagnesium bromide or methyllithium[22] to 2-bromo-1-tetralone without first isolating the alcoholic salt were unsucessful. Each experimental run gave a crude oil which contained an appreciable amount of ketonic impurities. It was impossible to purify the products by distillation. The Grignard reactions were conducted at 0 and 35°; the reactions employing methyllithium were conducted at -35, -20, 0, 25, and 35°.

---

[21] N. A. Lange, Ed., "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 599.

[22] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1932).

The Rates of Epoxidation of *cis*-Δ^4-Tetrahydrophthalic Anhydride and of Related *endo*-Methylene Derivatives

ALLAN P. GRAY AND DONALD E. HEITMEIER

Neisler Laboratories, Inc., Decatur, Illinois

Received November 16, 1964

Second-order rate constants for epoxidation with *m*-chloroperbenzoic acid in chloroform have been found to increase in the order: bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (II) < the *exo* isomer III < the corresponding *endo*-N-phenethylimide IV < the *exo*-N-phenethylimide V ≪ *cis*-Δ^4-tetrahydrophthalic anhydride (I). Field and steric effects satisfactorily account for the results.

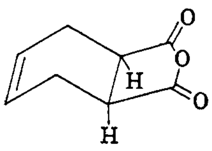
An earlier report from these laboratories[1] showed quite conclusively that the β-epoxy[2] derivative forms as the apparently exclusive product of the peracid epoxidation of *cis*-Δ^4-tetrahydrophthalic anhydride (I) and as the predominant product of the epoxidation of derived N-substituted imides. This unexpected result[3] was tentatively rationalized in terms of the "equatorial half-boat" conformation as shown for I, which would offer steric hindrance to α approach of the

---

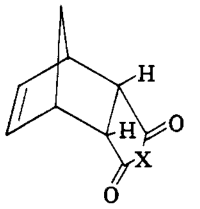
[1] A. P. Gray, D. E. Heitmeier, and H. Kraus, *J. Am. Chem. Soc.*, **84**, 89 (1962).

[2] β according to the steroid convention; that is with the epoxy oxygen and the anhydride ring on the same side of the cyclohexane nucleus.

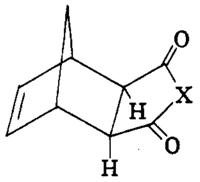
[3] *Cf.* H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959); N. S. Crossley, A. C. Darby, H. B. Henbest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Letters*, 398 (1961).



I



II, X = O
IV, X = $NCH_2CH_2C_6H_5$



III, X = O
V, X = $NCH_2CH_2C_6H_5$

peracid and thus favor β attack. One can, however, argue just as plausibly that equilibration of the "axial" and "equatorial" conformers would proceed much more rapidly than the epoxidation and that the stereochemical course of the reaction need not indicate the ground-state conformation, but only that the equatorial form reacted faster than the axial.[4] As an approach to learning more about these not mutually exclusive alternatives, we thought it would be instructive to evaluate the rates of epoxidation of the *endo* (II and IV) and *exo* (III and V) *endo*-methylene derivatives, which can formally be considered as rigidly fixed relatives of, respectively, the axial and equatorial conformations of I.

The required compounds were obtained unexceptionally as indicated in the Experimental section. Roughly quantitative epoxidation rate studies were carried out using *m*-chloroperbenzoic acid (selected as a convenient, easily handled epoxidizing agent)[5] in chloroform solution at 25°. Except for the oxidation of I, which proceeded too rapidly for accurate measure by the technique employed and for which only an approximate rate constant could be calculated, the reactions showed good second-order kinetics over practically their entire course and good second-order rate constants were obtained. Mean values of these are listed in Table I.

TABLE I

RATES OF EPOXIDATION[a]

Compd.	$k \times 10^4$, l./mole-sec.	Relative rates
I	50[b]	80
II	0.61	1
III	1.97	3.2
IV	4.6	7.5
V	11.3	18.5

[a] With *m*-chloroperbenzoic acid in chloroform at 25°. [b] This value only approximate.

Inspection of the data reveals that I is epoxidized at a considerably greater rate, from about 25 to 80 times greater, than are its *exo* (III) and *endo* (II) bicyclic anhydride counterparts. Nonetheless, it seems most significant that, with both the anhydride and imide pairs of stereoisomers, the *exo* isomer reacts more rapidly, more than 3 times as fast in the case of the anhydrides and close to 2.5 times as fast in the case of the imides. Of further interest is the fact that the imides are epoxidized at rates 5.8 (V *vs.* III) and 7.5 (IV *vs.* II) greater than their corresponding anhydrides.

The finding that the *exo* isomers are more rapidly epoxidized than their *endo* analogs lends quite firm support to the idea that the equatorial conformer of I reacts faster than does the axial, but does not conflict with the possibility that the former may indeed be the predominant conformation. However, since the bicyclic anhydrides[6] and imides[7a] afford the *exo* epoxide derivatives to all appearances exclusively, the observed relative rates of epoxidation of the *exo vs. endo* isomers should be noted to be just opposite to what might have been predicted on the basis of the work of Henbest and his associates.[3] These authors' observation that cycloalkenes with single polar substituents, *e.g.*, cyano or carbalkoxy, were preferentially epoxidized from the side *trans* (or α) to the substituent led them to propose that dipole–dipole interaction between the polar group and the polarized transition state for epoxidation operated to slow *cis* and thus to favor *trans* attack by the peracid. If such an interaction prevailed here, the *endo* rather than the *exo* derivatives should have undergone the more rapid epoxidation.[7b] Explanation of the present results would clearly seem to lie in a field effect of the anhydride and imide carbonyl groups wherein these polarized groups provide an electron-deficient center acting across space to deactivate the double bond to electrophilic attack from either direction. Deactivation would, however, be more pronounced in the *endo* (and axial) isomers, in which the electron-deficient center would be situated much closer to the double bond, than in the *exo* (and equatorial) analogs.[4,8] The fact that the imides undergo epoxidation at more rapid rates than the anhydrides furnishes strong additional support for the intervention of field effects. Inasmuch as the carbonyl groups of an imide function are less strongly polarized than those of an anhydride, the carbonyl carbon atoms of the imide derivatives bear less of a positive charge and thereby provide a weaker electron-deficient center with a smaller deactivating influence on the double bond.

Henbest's suggestion[9] that the observed β-epoxidation of I might be explained in terms of "intermediate addition of the peroxyacid to one of the carbonyl groups" would not appear tenable since, if this were so, one would expect its *endo*-*endo*-methylene relative II to behave similarly, react faster than the *exo* isomer III, and, moreover, yield the *endo* rather than the actu-

---

[4] This possibility had originally suggested itself to us on the basis of evidence from some unpublished work, but had been discounted. It was revived in a discussion with Dr. Theodore Cohen. We thank Dr. Cohen and Dr. Ernest Wenkert for briefly discussing the problem with us.

[5] Subsequent to the completion of this work N. H. Schwartz and J. H. Blumbergs [*J. Org. Chem.*, **29**, 1976 (1964)] reported on rate studies utilizing this peracid.

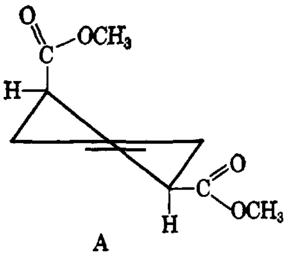
[6] J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 4341 (1958).

[7] (a) Unpublished work from these laboratories. (b) We have pointed out[1] that one basic distinguishing feature between the compounds of Henbest, *et al.*, and ours, notably between methyl 3-cyclohexenecarboxylate and I, resides in the predominant conformation of the unsaturated ring.

[8] Such an explanation has been invoked by H. Kwart and L. J. Miller [*J. Am. Chem. Soc.*, **83**, 4552 (1961)] to account for similar effects observed in the addition of the electrophilic reagent, 2,4-dinitrobenzenesulfenyl chloride, to bicycloheptene derivatives. G. I. Poos and J. D. Rosenau [*J. Org. Chem.*, **28**, 665 (1963)] were able to explain the observed directions of epoxidation of *exo*- and *endo*-imidobicycloheptene derivatives having an additional exocyclic double bond in like fashion.

[9] H. B. Henbest, *Proc. Chem. Soc.*, 164 (1963).

ally obtained *exo* epoxide product. The fact that I is epoxidized much more rapidly than either II or III would seem most reasonably accounted for in terms of steric hindrance to approach of the peracid offered by the *endo*-methylene group present in the latter derivatives, although other, more subtle, effects could certainly play a role. Henbest's finding[9] that dimethyl *cis*-Δ^4-cyclohexene-1,2-dicarboxylic acid (A) does indeed provide the α-epoxide as would be predicted from his work does not seem to us to introduce any theoretical conflict. As already indicated,[1] the cyclohexene ring of a compound such as A, without the anhydride ring fused thereto, would not be in a half-boat conformation as is most probable for I, but in a half-chair with one carbomethoxy group axial and the other equatorial. One would expect the peracid to approach a molecule in this conformation from the side opposite the axial carbomethoxy group and thus produce the α-epoxide derivative.



A

Experimental[10]

Materials.—*cis*-Δ^4-Tetrahydrophthalic anhydride (I) (Matheson), bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (II) (Eastman, White Label), 40% peracetic acid, and *m*-chloroperbenzoic acid (FMC Corp.) were commercially available. Bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride (III), m.p. 141–143°, was prepared as described in the literature.[11]

Preparation of Imides. N-Phenethylbicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboximide (IV).—A stirred mixture of 246 g. (1.5 moles) of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride, 188 g. (1.55 moles) of β-phenethylamine, and 1700 ml. of dry toluene was heated under reflux with azeotropic removal of water. A quantitative yield (28 ml.) of water was collected in 3 hr. The cooled toluene solution, diluted with hexane, deposited 117 g. of crystals that melted at 81–82°. Concentration of the mother liquor and recrystallization of the residue from isopropyl alcohol gave an additional 244.5 g. of product, m.p. 81–82° (total yield, 90%), m.p. 82–83° after further recrystallization.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.39; H, 6.41. Found: C, 76.48; H, 6.49.

N-Phenethylbicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboximide (V).—In similar fashion, treatment of 82.1 g. (0.5 mole) of bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride with 63.0 g. (0.52 mole) of β-phenethylamine in 575 ml. of boiling toluene gave, after recrystallization from isopropyl alcohol, 124.8 g. (94%) of V, m.p. 92–94°.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.39; H, 6.41; N, 5.24. Found: C, 75.98; H, 6.53; N, 5.36.

Preparation of Epoxides. N-Phenethyl-*exo*-5,6-epoxybicyclo-[2.2.1]heptane-*endo*-2,3-dicarboximide (VI).—To a stirred solution of 168.6 g. (0.63 mole) of IV in 750 ml. of chloroform was added, dropwise at room temperature, a solution of 110 ml. of 40% peracetic acid (0.75 mole). The temperature was maintained between 26 and 30° by the intermittent application of an ice bath. After the initial, mildly exothermic reaction had subsided the mixture was stirred for 48 hr. The reaction mixture was then washed with water and cold 5% sodium hydroxide solution until a peroxide test was negative. The chloroform layer was dried and concentrated to dryness to leave a colorless oil that solidified on cooling. The crude solid was crystallized from benzene to give 148.8 g. (83%) of VI, m.p. 134–136°. The infrared spectrum showed absorption at 1700 and 1770 (five-membered-ring imide) and at 850 cm.$^{-1}$ (bicycloheptane epoxide)[8,12]; OH and NH absorption bands were absent.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05. Found: C, 72.07; H, 6.00.

A mixture melting point of VI with the epoxide isolated (80% yield) from the corresponding *m*-chloroperbenzoic acid rate study was not depressed.

N-Phenethyl-*exo*-5,6-epoxybicyclo[2.2.1]heptane-*exo*-2,3-dicarboximide (VII).—A solution of 105 g. (0.4 mole) of V in 400 ml. of chloroform was epoxidized with 65 ml. of 40% peracetic acid (0.44 mole) containing 3.7 g. of sodium acetate trihydrate which was added to neutralize the 1% sulfuric acid present. The reaction was run and worked up as described for VI to give, after recrystallization from acetone–pentane, 94.9 g. (85%) of product, m.p. 108–110°. The analytical sample, recrystallized from isopropyl alcohol, had m.p. 112–113°. The infrared spectrum had bands at 1700 and 1775 (imide) and at 847 cm.$^{-1}$ (epoxide)[8,12]; OH and NH absorptions were absent.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.50; H, 5.90; N, 4.94.

A mixture melting point of VII with the epoxide isolated (75% yield) from the corresponding *m*-chloroperbenzoic acid rate study was not depressed.

The epoxides of *cis*-Δ^4-tetrahydrophthalic anhydride,[1,13] bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride,[6] and bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride[6] have previously been described.

Rates of Epoxidation.—*m*-Chloroperbenzoic acid (82.4% by iodometric assay) was used in the rate studies. Runs were made in duplicate. A 20 mole % excess of the peracid was added all at once at zero time to a stirred solution of 0.1 mole of the olefin substrate in dry chloroform (solution volume adjusted to 500 ml.) contained in a flask which was surrounded by a large water reservoir maintained at 25 ± 0.2°. Stirring was continued and at appropriate intervals 1.00-ml. samples were withdrawn by pipet and the amount of unconsumed *m*-chloroperbenzoic acid remaining was determined by iodometric titration. Values from duplicate runs differed by no more than ±2% at one-half the completion time. Averaged results are given in Table II.

TABLE II

Time, hr.	Compd. I	II	III	IV	V
	m-Chloroperbenzoic acid used, mole				
0.5	0.070	0.002	0.008	0.018	0.036
1	0.087	0.004	0.014	0.039	0.054
2	0.097	0.009	0.027	0.046	0.069
3	...	0.013	0.035	0.056	0.079
4	...	0.018	0.043	0.062	0.084
5	...	0.021	0.048	0.070	0.088
6	...	0.025	0.054	0.074	0.090
7	...	0.028	0.057	0.078	0.092
8	...	...	0.059	0.082	0.094
12	...	0.041	...	...	...
24	...	0.059	0.083	...	...

Acknowledgment.—The authors thank Mr. R. Garver for skillful technical assistance and Mr. D. F. Cortright and Miss M. Unroe for the infrared spectra.

---

(10) Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Melting points are corrected for stem exposure. Infrared spectra were determined in chloroform with a Beckman IR-5 infrared spectrophotometer.

(11) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

(12) M. P. Kunstmann, D. S. Tarbell, and R. L. Autrey, *ibid.*, **84**, 4115 (1962), and references cited therein.

(13) J. E. Gill and J. Munro, *J. Chem. Soc.*, 4630 (1952).