cycl[3.2.2]azine (**21**, 0.004 g, 27%) showing identical melting point and spectral characteristics with those of sample obtained from the formylation of 2,5,7-trimethyl-6-azaindolizine (**5**).

Thioformylation of 2,7-dimethyl-6-azaindolizine (**2**, 0.250 g) was carried out by treatment of **2** with dimethylformamide (2 ml) and phosphoryl chloride (0.35 g) at room temperature. The reaction mixture was poured into a 2 *M* aqueous sodium hydrogen sulfide[7] solution (30 ml) and extracted with chloroform. Evaporation of the chloroform followed by column chromatography using benzene and recrystallization from benzene–cyclohexane (1:5) gave **2,7-dimethyl-3-thioformyl-6-azaindolizine** (**8**, 0.190 g, 58%) as red needles: mp 175–176°; λ_{max} *439*, 433 (infl), 420 (infl), 370, 308, 300 (infl), 253 (infl), 238 (infl), *227* nm (log ϵ 4.20, 4.15, 3.98, 3.65, 3.76, 3.72, 3.91, 4.02, 4.20, respectively); ir 870, 980, 1135, 1258, 1318, 1510, 1610 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}N_2S$: C, 63.1; H, 5.3; N, 14.7. Found: C, 63.4; H, 5.4; N, 15.0.

Reduction of aldehydes **7** and **10** to give, respectively, **2,3,7-trimethyl-6-azaindolizine** (**3**) and **2,3,5,7-tetramethyl-6-azaindolizine** (**6**) was carried out with lithium aluminum hydride–aluminum chloride in ether by a procedure similar to that reported in a previous paper.[20] 3-Formyl-2,7-dimethyl-6-azaindolizine (**7**, 0.5 g) gave a brown oil (0.21 g). This oil after TLC afforded as the main band 2,3,7-trimethyl-6-azaindolizine (**3**, 0.01 g, 2%) which showed identical spectral characteristics with the sample obtained from the Chichibabin reaction between 4,6-dimethylpyrimidine and 3-bromo-2-butanone.

3-Formyl-2,5,7-trimethyl-6-azaindolizine (**10**, 0.20 g) after TLC gave 2,3,5,7-tetramethyl-6-azaindolizine (**6**, 0.05, 27%) as needles: mp 64–67°; λ_{max} 358 (br), 295, 284, 277 (infl), *240* nm (log ϵ 3.15, 3.82, 3.83, 3.71, 4.39, respectively); ir 868, 1287, 1363, 1436, 1530, 1630 cm^{-1}. Calcd mass for $C_{11}H_{14}N_2$: 174.1156. Found: M^+ (base peak) 174.1157.

2,6-Dimethyl-5-azacycl[3.2.2]azine (22) from 3-Formyl-2,7-dimethyl-6-azaindolizine (**10**). A mixture of 3-formyl-2,7-dimethyl-6-azaindolizine (**10**, 0.05 g) and potassium hydroxide (2.0 g) were quickly fused in a sealed, evacuated tube. Immediately a yellow vapor formed and droplets of a yellow-brown liquid condensed. After cooling, the contents of the tube were extracted with ether, the ether evaporated, and the residue after TLC gave as an intense yellow band 2,6-dimethyl-5-azacycl[3.2.2]azine (**22**, 0.012 g, 27%) which showed identical melting point and spectral characteristics with those of the sample obtained after hydrolysis and decarboxylation of the product from the 1,3-dipolar addition reaction between 2,7-dimethyl-6-azaindolizine and dimethyl acetylenedicarboxylate.

Methylene-1,1′-(2,2′,3,3′,7,7′-hexamethyl)di-6-azaindolizine (**18**). Addition of 40% aqueous formaldehyde (2.0 ml) to a solution of 2,3,7-trimethyl-6-azaindolizine (**3**, 0.8 g, 5 mmol) in ethanol (3 ml) gave on gentle reflux for 15 min a cloudy solution from which yellow needles of the symmetrical di-6-azaindolizylmethane (**18**, 0.73 g, 88%) precipitated. Recrystallization from ethyl acetate gave the compound **18**: mp 238–240° dec; λ_{max} 376, 299, 287, 277 (infl), *243* nm (log ϵ 3.22, 3.91, 3.91, 3.83, 4.53, respectively); ir 850, 1120, 1175, 1240, 1350, 1420, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (6 H, 2- and 2′-Me), 2.32 (6 H, 3- and 3′-Me), 2.39 (6 H, 7- and 7′-Me), 3.97 (2 H, bridge methylene), 6.68 (2 H, H-8 and H-8′), 8.44 (2 H, H-5 and H-5′).

Anal. Calcd for $C_{21}H_{24}N_4$: C, 75.9; H, 7.3; N, 16.8. Found: C, 76.0; H, 7.5; N, 17.1.

Acknowledgment. The authors wish to thank Drs. Murray, Youngson, and Watson for helpful suggestions, Mr. N. Faulkes for the ^1H NMR spectra, and the SED for a research studentship to C.S.

Registry No.—**1**, 57139-15-8; **2**, 57108-98-2; **3**, 57108-99-3; **4**, 57109-00-9; **5**, 57109-01-0; **6**, 57109-02-1; **7**, 57109-03-2; **8**, 57109-04-3; **9**, 57109-05-4; **10**, 57109-06-5; **11**, 57109-07-6; **12**, 57109-08-7; **13**, 57109-09-8; **16**, 13219-97-1; **16** *p*-nitrophenylhydrazone, 57109-10-1; **17**, 1500-94-3; **18**, 57109-11-2; **19**, 57109-12-3; **20**, 57109-13-4; **21**, 57109-14-5; **22**, 57109-15-6; **23**, 57109-16-7; **24**, 57109-17-8; 4,6-dimethylpyrimidine, 1558-17-4; bromoacetone, 598-31-2; 3-bromo-2-butanone, 814-75-5; 2,4,6-trimethylpyrimidine, 22114-27-8; phenacyl bromide, 70-11-1; acetylacetone, 123-54-6; 3,4-dicarbomethoxy-2,6-dimethyl-5-azacycl[3.2.2]azine, 57109-18-9.

References and Notes

(1) A. Chichibabin, *Ber.*, **60**, 1607 (1927).
(2) V. Boekelheide and S. Kertelj, *J. Org. Chem.*, **28**, 3212 (1963).
(3) M. Fraser, S. McKenzie, and D. Reid, *J. Chem. Soc. B*, 44 (1966).
(4) M. Fraser, *J. Org. Chem.*, **36**, 3087 (1971).
(5) This is most conveniently carried out by adding a small drop of deuteriotrifluoroacetic acid to the 6-azaindolizine in $CDCl_3$ solution, whereupon exchange occurs at C-3 and to a limited extent at C-1. A further drop of acid was generally sufficient to complete the exchange at C-3 and considerably diminish the intensity of the H-1 signal.
(6) E. Ochiai and M. Yanai, *J. Pharm. Soc. Jpn.*, **59**, 18, 97 (1939).
(7) S. Mackenzie and D. Reid, *J. Chem. Soc. C*, 145 (1970).
(8) The widths of the H-5 and formyl proton signals were temperature dependent and the peri shifts observed consistent with those cited in ref 7.
(9) J. Taylor and D. Wibberley, *J. Chem. Soc. C*, 2693 (1968).
(10) Both C-3 and C-1 have been calculated to be the sites of highest electron density for the 6-azaindolizine system: V. Glasso, G. Alti, and A. Bigotto, *Theor. Chim. Acta*, **9**, 222 (1968); E. Kleinpeter, R. Borsdorf, G. Fischer, and H. Hofmann, *J. Prakt. Chem.*, **314**, 515 (1972).
(11) O. Fuentes and W. Paudler, *J. Org. Chem.*, **40**, 1210 (1975).
(12) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 284.
(13) The C-5 position is calculated to be the site of greatest electron deficiency for the 6-azaindolizine system; see ref 10.
(14) S. Klutchko, H. Hansen, and R. Meltzer, *J. Org. Chem.*, **30**, 3454 (1965).
(15) J. Streith and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 1157 (1970).
(16) R. Guy and R. Jones, *Aust. J. Chem.*, **19**, 107 (1966).
(17) V. Sprio and E. Ajello, *Ann. Chim. (Rome)*, **56**, 858 (1966).
(18) A. Hantzsch, *Ber.*, **23**, 1474 (1890).
(19) R. Cunningham, D. Farquhar, W. Gibson, and D. Leaver, *J. Chem. Soc. C*, 239 (1969).
(20) M. Fraser, *J. Org. Chem.*, **37**, 3027 (1972).

Stereospecific Epoxidation of Dihydrophthalates

S. A. Cerefice* and E. K. Fields

Amoco Chemicals Corporation, Naperville, Illinois 60540

Received June 16, 1975

Carboxylate groups exert specific syn-directing effects on the epoxidation of adjacent double bonds in the absence of steric or conformational effects. Peracid epoxidation of dimethyl *trans*-1,2-dihydrophthalate is stereospecific and gives a 90:9.5:0.5 mixture of diepoxides **2**, **3**, and **4** in 95–98% yields. Epoxidation converts monoepoxide **5** to diepoxide **2** in 100% selectivity, and dimethyl 1,4-dihydrophthalate to a 75:25 mixture of the cis and trans monoepoxides. Cis diepoxide **4** is obtained by thermal rearrangement of endo peroxide **11**. Irradiation of **11** in cyclohexane gives a mixture of **4** and unsaturated diol **12**. Both catalytic hydrogenation and lithium aluminum hydride reduction of diepoxide **2** are regiospecific and give alcohols **13** and **14**.

Epoxidation[1] and photooxygenation[2] are valuable for stereospecific introduction of oxygen into olefins. The stereochemistry of epoxidations and of ring opening reactions of epoxides has been extensively studied.[3] There is considerable interest in syntheses and reactions of cyclohexadiene diepoxides[4–6] and in 1,4-endo peroxides (1,4-epidioxide compounds)[7] as precursors to cis diepoxides by thermal[8] or photochemical rearrangements.[9] Recently, iso-

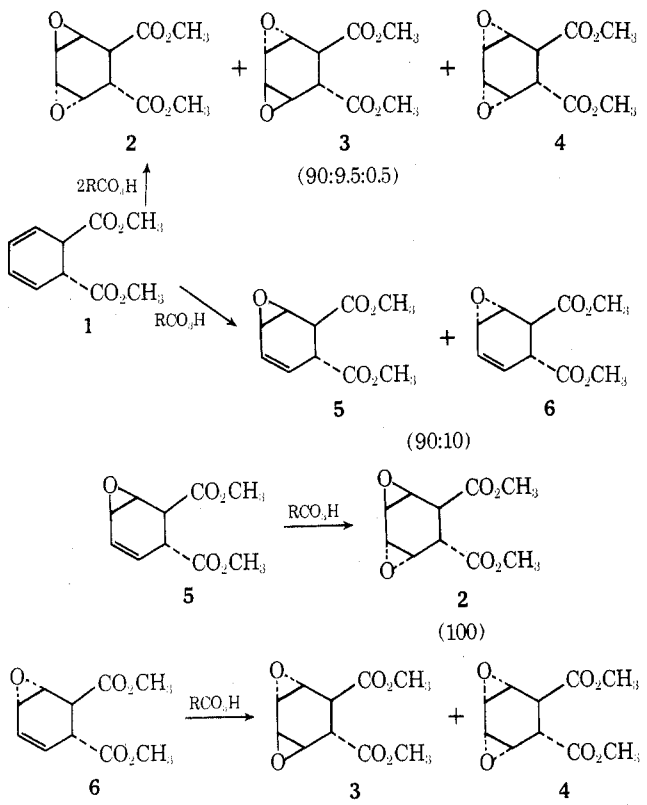
meric di- and triepoxides of benzene and annulenes have been reported.[10]

The stereospecific syn-directing effects of allylic alcohols in epoxidations were first described by Henbest[11] and Albrecht[12] in 1957. Much has been published since on the stereochemistry of epoxidation and directive effects of polar substituents. For studying the latter, substituted 1,3-cyclohexadiene is a good system; it is nearly flat and has no steric or conformational interferences. We have been studying the chemistry or dihydrophthalic acid derivatives[13] and here report our results on stereospecific epoxidations of the dihydrophthalates, regiospecific reductions of the epoxides, and the preparation, rearrangement, and reductions of 1,2-dihydrophthalate endo peroxides.

Results

Epoxidation of dimethyl *trans*-1,2-dihydrophthalate (1) with excess *m*-chloroperbenzoic acid in chloroform gave 95–98% yields of a 90:9.5:0.5 mixture of all three possible diepoxides **2**, **3**, and **4** and 2–5% dimethyl phthalate (Scheme I). The ratio of products showed little dependence

Scheme I

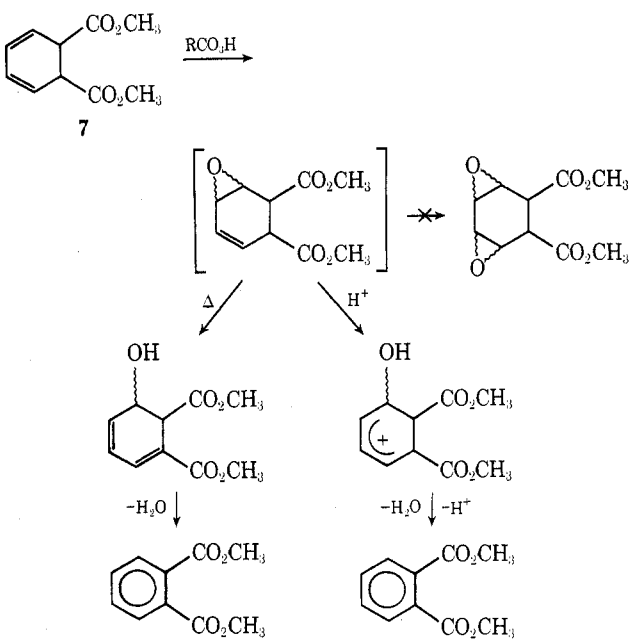


on solvent, temperature, or peracid. Diepoxide **2** was formed with 87–93% selectivity in methylene chloride, chloroform, or benzene at 20–80° using perbenzoic, *m*-chloroperbenzoic, or peracetic acid buffered with sodium carbonate. Alkaline hydrogen peroxide in methanol converted 1 to dimethyl phthalate and dimethyl 1,4-dihydrophthalate (8).

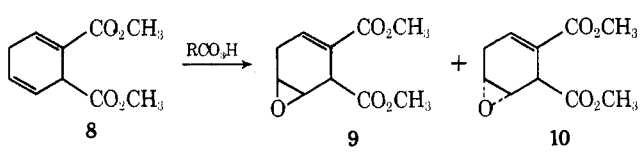
Reaction of 1 with 1 equiv of *m*-chloroperbenzoic acid gave high yields of a 9:1 mixture of monoepoxides **5** and **6** plus 2–5% dimethyl phthalate. Further reaction of the monoepoxides with peracid gave the same mixture of diepoxides **2**, **3**, and **4** obtained directly from 1. Monoepoxides **5** and **6** are particularly reactive as they are allylic ethers and contain tertiary hydrogens activated by carbomethoxy groups. In the presence of acid or base, or on attempted chromatography over silica gel or alumina, they are rapidly converted to dimethyl phthalate. An isomerically pure sample of cis monoepoxide **5** was obtained by diazomethane esterification of the corresponding diacid, which is the exclusive product from peracid monoepoxidation of *trans*-1,2-dihydrophthalic acid.[14] Epoxidation of cis monoepoxide **5** was 100% stereospecific; **2** was the only diepoxide formed. To account for the 0.5% yield of cis diepoxide **4**, trans monoepoxide **6** must be converted to diepoxides **3** and **4** in a ratio of 95:5.

Reaction of dimethyl *cis*-1,2-dihydrophthalate (7) with *m*-chloroperbenzoic acid, under conditions that gave high yields of diepoxides from *trans*-1,2-dihydrophthalate (1), led exclusively to formation of dimethyl phthalate (Scheme II).

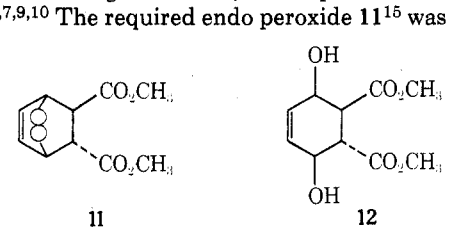
Scheme II



Reaction of dimethyl 1,4-dihydrophthalate (8) with 1 or more equiv of *m*-chloroperbenzoic acid in refluxing chloroform gave 95% of monoepoxides and 5% of dimethyl phthalate. Epoxidation of 8 was less stereospecific than epoxidation of 1; a 75:25 mixture of cis and trans epoxides **9** and **10** was formed. The homoallylic monoepoxides **9** and **10** were more stable than monoepoxides **5** and **6**; they could be chromatographed on silica gel, but were converted to dimethyl phthalate on alumina.



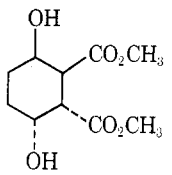
As cis diepoxide **4** was obtained in such low yield (0.5%) by direct epoxidation of diene 1, we studied an alternative route, the rearrangement of 1,4-endo peroxides to cis diepoxides.[2,7,9,10] The required endo peroxide **11**[15] was prepared



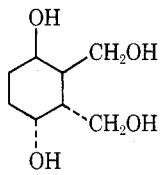
in 98% yield by reaction of 1 in acetone with singlet oxygen generated photochemically using rose bengal as the sensi-

tizer. In refluxing xylene **11** was converted to cis diepoxide **4** (35% yield) and dimethyl 3-hydroxyphthalate. The endo peroxide was also isomerized to cis diepoxide **4** photochemically by irradiation in methanol or cyclohexane solution. In cyclohexane, unsaturated diol **12** was formed (15% yield) in addition to **4** (6% yield) by trapping of the intermediate diradical[9] by solvent in competition with intramolecular addition of the dioxygen diradical to the double bond (Scheme IV).

Catalytic hydrogenation of diepoxide **2** in methanol using palladium on carbon catalyst gave a mixture of diols from which a single crystalline diol **13** was isolated in 70% yield. Lithium aluminum hydride reduction of **13** afforded



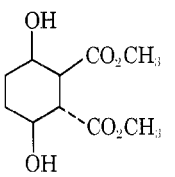
13



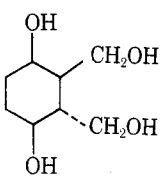
14

tetraol **14** in high yield. Reduction of **2** with lithium aluminum hydride in tetrahydrofuran gave the same stereoisomer **14**, isolated in 54% yield, and overreduced products (diols and hydrocarbons).

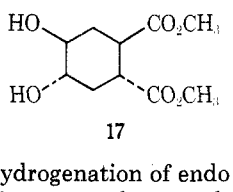
Isomeric diols **15** and **17** and a tetraol **16** were needed to aid in the characterization and assignment of stereochemistry to the major product from epoxidation of **1** and its reduction products. We prepared **15**[15] in 80% yield by catalytic hydrogenation of endo peroxide **11** in methanol over a palladium on carbon catalyst. Lithium aluminum hydride reduction of **15** in tetrahydrofuran gave tetraol **16**.



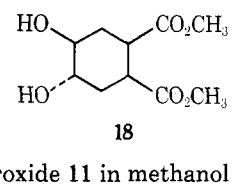
15



16



17



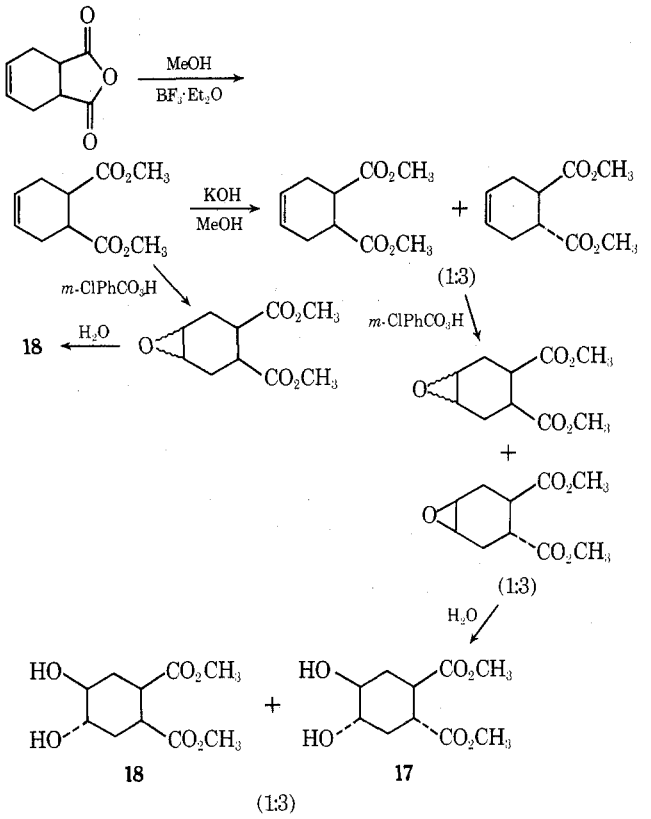
18

The syntheses of 4,5-dihydroxyhexahydrophthalates **17** and **18** are outlined in Scheme III. Epoxidation of dimethyl *cis*-1,2,3,6-tetrahydrophthalate gave a mixture of monoepoxides that was converted by aqueous hydrolysis to the trans 4,5-diol (**18**) of *cis*-tetrahydrophthalate,[16] which is a noncrystallizable viscous oil. Epimerization of dimethyl *cis*-1,2,3,6-tetrahydrophthalate in methanolic potassium hydroxide gave a 3:1 mixture of *trans*- and *cis*-1,2,3,6-tetrahydrophthalates which was converted to a 3:1 mixture of **17** and **18** by epoxidation and hydrolysis. The trans 4,5-diol (**17**) of *trans*-tetrahydrophthalate is crystalline, and was isolated from the mixture by crystallization from benzene.

Discussion

Diepoxide **4**, formed in 0.5% yield from bisepoxidation of **1**, was identified by comparison with diepoxide obtained by thermal rearrangement of endo peroxide **11**. Assignment of stereochemistry to the major diepoxide of **1** as that indicated by **2** rather than **3** was based on the following evidence: it was reduced to **13** and **14**, the diaxial alcohols expected from trans-coplanar epoxide ring opening of **2**, and not **24**, the diol expected from reduction of **3**; and it was identical with the dimethyl ester of 3α,8β-dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylic acid (the diacid corresponding to structure **2**), obtained by peracid epoxidation of *trans*-1,2-dihydrophthalic acid.[14] The product formed in 9.5% yield was isomeric with diepoxides **2** and **4** and, therefore, must have structure **3**.

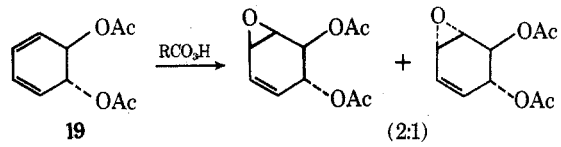
Scheme III



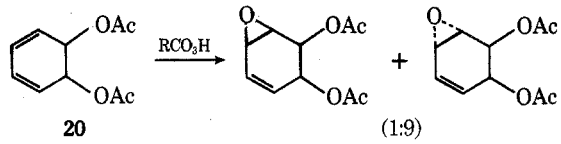
The stereochemistry of epoxidations is determined by the ease of approach of the peracid to the more stable conformer of a substituted olefin. In the absence of directing effects from polar substituents, epoxidation would take place from the less hindered side to give trans epoxides. As **1** is nearly planar, there should be no steric or conformational preferences for epoxidation syn or anti to the carboxylate substituents. It is surprising, therefore, that epoxidation of **1** proceeded in 90% stereospecificity to monoepoxide **5**, and to diepoxide **2**. We propose that a carboxylate group exerts a syn-directive effect on the stereochemistry of peracid epoxidations and that, in the absence of steric effects, syn epoxidation will predominate to give epoxide cis to the carboxylate (cis epoxide).

Although much has been published on the stereochemistry of epoxidations and the syn directive effects of allylic alcohols,[1] little is known about directive effects of carboxylate substituents. The stereospecific directive effect of allylic hydroxyl groups is due to stabilization of the transition state leading to cis epoxides by hydrogen bonding to the peracid.[11,12,17] This interaction is more effective when the directing group is in the pseudoequatorial position.[18,19] Where no such hydrogen bonding is possible, as for allylic ethers, trans epoxides are formed. Epoxide substituents do not show syn directive effects, so epoxidation of epoxycyclohexenes gives mainly trans diepoxides.[4,5,10] Epoxidation of allylic acetates is not very stereospecific, but generally gives more of the cis epoxides than expected on the basis of steric interactions alone.[18] Carboxylate and acetate substituents show specific directing effects on the stereochemistry of the mechanistically closely related Simmons–Smith cyclopropanation reaction, but are not as effective as hydrox-

yl groups.[20] A free carboxylic acid is a more effective syn directing group than a carboxylate ester, as peracid epoxidation of *trans*-1,2-dihydrophthalic acid gave only the cis monoepoxide.[14] An ester is a better syn-directing group than acetate. Epoxidation of *trans*-5,6-diacetoxycyclohexa-1,3-diene (**19**) gave a 2:1 mixture of cis and trans monoepoxides,[17] compared to a 9:1 mixture of **5** and **6** from the corresponding dicarboxylate **1**. Cis diacetate **20** gave 90% trans monoepoxide;[21] apparently the steric influence of the pseudoaxial acetate in **20** overcomes any directive effect of the acetate group.

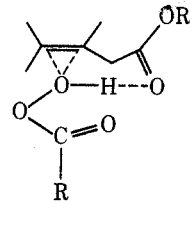


19 (2:1)

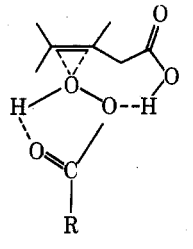


20 (1:9)

The high degree of stereochemical control found for allylic carboxylates may be due to stabilization of the transition state (possibly **21** and/or **22** for carboxylic acids) leading to syn epoxidations when the carboxylate is pseudoequatorial and there are no interfering steric or conformational effects. The relative order of effectiveness for syn-directing allylic substituents is $-OH \gg -CO_2H > -CO_2R \gg -O_2CR$.



21

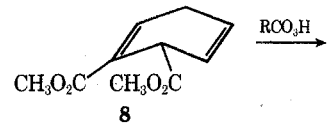


22

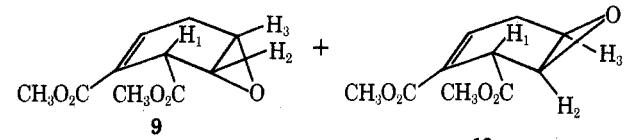
Monoepoxides **5** and **6** could not be separated and isolated in a pure state, owing to their tendency to aromatize to dimethyl phthalate by loss of water. They were characterized as a mixture of 90% **5** and 10% **6** by peracid conversion to a 90:9.5:0.5 mixture of **2**, **3**, and **4**. Epoxidation of **5**, obtained isomerically pure by esterification of the diacid,[14] was 100% stereospecific to **2**, owing to a combination of the syn directive effect of the allylic pseudoequatorial carboxylate and the steric effect of the adjacent epoxide group. In epoxidation of **6** there is a competition between the carboxylate directing effect to give **4**, and the epoxide steric effect to give **3**. The latter dominated almost completely, as the ratio of **3** to **4** was 95:5 (Scheme I).

We were not able to isolate epoxides of dimethyl *cis*-1,2-dihydrophthalate (**7**). Reaction of **7** with peracid gave dimethyl phthalate, presumably by acid-catalyzed or thermal isomerization or an intermediate monoepoxide and dehydration (Scheme II). Epoxidation of the monoepoxide is expected to be very slow, as approach of peroxy acid from either side of the double bond is sterically hindered by the epoxide or pseudoaxial carboxylate.

Epoxidation of dimethyl 1,4-dihydrophthalate (**8**) gave only monoepoxides, as the double bond conjugated to the carboxylate is deactivated toward attack by electrophilic peracid reagent. The reaction was less stereospecific and gave a 75:25 mixture of cis and trans epoxides **9** and **10**, due to the conformational effects in 1,4-cyclohexadienes. In the more stable flattened-boat conformation of **8**, the pseudoequatorial carboxylate would direct syn epoxidation to the more sterically crowded inside face. Thus, attack of peracid from the unhindered side, leading to trans epoxide, is expected to be more important than in the absence of this conformational effect.[4,22,23]



8

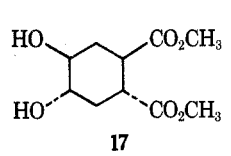


9 **10**

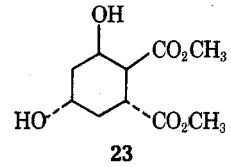
Assignment of stereochemistry to **9** and **10** was made by comparison of their NMR spectra. Multiplets assigned to H_1 at δ 3.25, H_2 (H_3) at 4.10, and H_3 (H_2) at 3.48 in the major product were shifted 0.10–0.15 ppm higher in the minor product, whereas the other ring hydrogens had the same chemical shifts in both isomers. Inspection of models of each isomer showed that in structure **10** H_1, H_2, and H_3 are closer to the oxirane oxygen or the carboxylate group than in structure **9**. As the deshielding anisotropic effects of these substituents are expected to increase the chemical shifts of adjacent hydrogens, the higher chemical shifts found for H_1, H_2, and H_3 in the minor product show that it is the trans epoxide **10**, and that the major product is **9**.

The structures of diols **15**, **17**, and **18** and tetraol **16** were unambiguously determined by their methods of synthesis. Both catalytic hydrogenation and lithium aluminum hydride reductions of **2** were regiospecific and gave products with the same stereochemistry; tetraol obtained by hydride reduction of **2** was identical with the product from hydrogenation of **2** followed by hydride reduction.

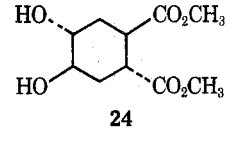
The hydrogenation product of **2** was assigned structure **13**, rather than the other possible isomers **17** or **23**, and the



17



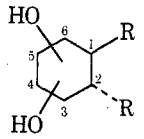
23



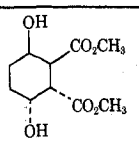
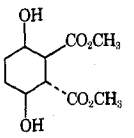
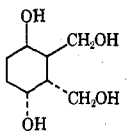
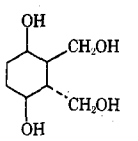
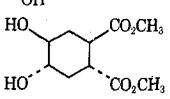
24

hydride reduction product was characterized as **14**, based on the following evidence. Diol **17** was prepared by an independent synthesis and was different than the hydrogenation product. The hydrogenation product gave a negative periodate test for *vic*-glycols, as did the 1,4-diol **15**. Structure **24**, the product expected from reduction of diepoxide **3**, was ruled out because it is expected to give a positive periodate test,[24] as did the 1,2-diols **17** and **18**. The NMR spectra of **13** and **14** are consistent with the proposed structures, are similar to the spectra of stereoisomers **15** and **16**, and are different from **17** and spectra expected for structure **23**. NMR spectral data and assignments for compounds **13**, **14**, **15**, **16**, and **17** are shown in Table I. Structure **13** is identical with **15**, and **14** is identical with **16**, except for the stereochemistry at C_3. H_3 and H_6 have the same chemical shifts in **13** (δ 4.40) as H_6 in **15** (δ 4.40); H_3 and H_6 have the same chemical shifts in **14** (δ 4.14) as H_6 in

Table I
NMR Spectra[a] of Substituted Cyclohexane Diols of General Structure



(R = CH_2OH or CO_2CH_3)

Compd		H_1	H_2	H_3	H_4	H_5	H_6	CH_2OH	CO_2CH_3
	(13)	3.12 s	3.12 s	4.40 s	1.80 m	1.80 m	4.40 s		3.70 s
	(15)	2.94 s	2.88 d[b]	~3.7[b]	1.80 m	1.80 m	4.40 s		3.70 s, 3.73 s
	(14)	1.85 m	1.85 m	4.14 s	1.75 m	1.75 m	4.14 s	3.66 m	
	(16)	(1.4–2.0 m)		3.6–4.0 m	(1.4–2.0 m)		4.18 s	2.6–4.0 m	
	(17)	3.00 m	3.00 m	1.94 m	3.85 s	3.85 s	1.94 m		3.72 s

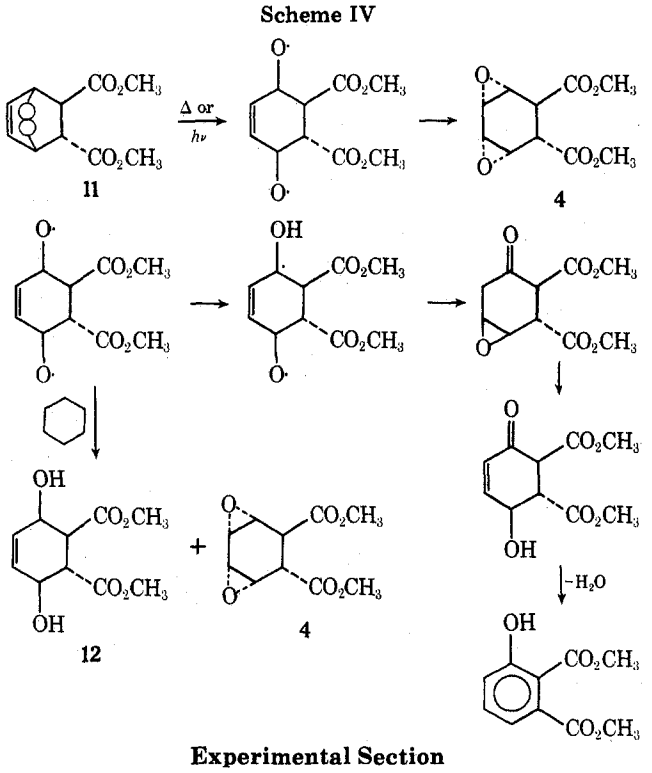
[a] All spectra were run in D_2O; chemical shifts (δ, 100 MHz) were measured in parts per million from TSP (sodium 3-trimethylsilylpropionate-d_4). [b] H_2 is a doublet, $J_{H_2-H_3}$ = 9 Hz; H_3 is partially buried under the methyl ester peak at 3.70.

16 (δ 4.18). The cis coupling constants between H_1 and H_6 in all four structures and between H_2 and H_3 in 13 and 14 are expected to be small,[14] and the observed couplings are less than 1 Hz.

Hydride reductions of substituted cyclohexene oxides are generally quite regiospecific. The stereochemistry is determined by trans-coplanar (diaxial) attack of hydride on the more stable conformer, and in conformationally rigid systems the axial alcohol is formed.[3,25] Tetraol 14 is the product expected from diaxial opening of both epoxide groups and reduction of the esters in 2. Catalytic hydrogenation gave the diaxial diol 13, which is the stereoisomer predicted by approach of the diepoxide from its less hindered side to the hydrogenated metal surface.

Cis diepoxides are not formed to any appreciable extent by direct epoxidation of dienes. Thermal[8] or photochemical[9] rearrangements of endo peroxides, readily available by Diels–Alder reactions of conjugated dienes and singlet oxygen,[2] produce cis diepoxides stereospecifically. Some endo peroxides are so prone to undergo this transformation that they cannot be isolated at room temperature;[10] others are stable at 200°.[26] Endo peroxide 11 was thermally stable at 100°, and required higher temperatures to effect isomerization. The same products are obtained and the same mechanism is proposed for thermal as for photochemical rearrangements of endo peroxides.[9] Isolation of 12 from irradiation of a cyclohexane solution of 11 (Scheme IV) is good evidence for the proposed dioxygen diradical intermediate. Common side products in these isomerizations are β,γ-epoxy ketones or products derived from these by a 1,2-hydride shift in the diradical and ring closure. The formation of dimethyl 3-hydroxyphthalate can be explained in this way.

Scheme IV



Experimental Section

NMR spectra were recorded on a Joel H-100 spectrometer and are reported in parts per million (δ) downfield from internal Me_4Si or TSP (for D_2O solvent). Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. GC analyses were obtained on a Hewlett-Packard Model 5750 gas chromograph attached to a Varian Aerograph Model 477 digital integrator, using a 15 ft ×

0.125 in. column packed with 10% OV 210 (methyl silicone with 50% trifluoropropyl groups) on Chromosorb W (80/100). Melting points are uncorrected.

Dimethyl 3α,8β-Dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylate (2). A solution of 6.30 g (32 mmol) of 1[13] and 13.50 g (66.5 mmol) of 85% *m*-chloroperbenzoic acid in 250 ml of $CHCl_3$ was refluxed for 4 hr. The solution was extracted with 5% $NaHCO_3$ (4 × 200 ml) and H_2O (200 ml). The $CHCl_3$ solution was dried, filtered, and evaporated to dryness under reduced pressure to give 7.30 g of a 90:9.5:0.5 mixture of **2**, **3**, and **4** (98%) and dimethyl phthalate (2%). The product mixture was dissolved in 20 ml of warm CCl_4; 10 ml of hexane was added and the solution was cooled to 0° and filtered. **2**, 4.75 g, was obtained as a white, crystalline solid, mp 96–100°. A second recrystallization from carbon tetrachloride–hexane (5:1) raised the melting point to 104–105°: ir (Nujol) 1737, 1440, 1300, 1280, 1250, 1235, 1190, 1180, 1020, 987, 895, 768, 750 cm^{-1}; NMR ($CDCl_3$) δ 3.40 (s, 2 H), 3.52 (s, 4 H), 3.80 (s, 6 H); *m/e* (M^+) 228.0643 (calcd, 228.0634).

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.6; H, 5.3. Found: C, 52.5; H, 5.1.

Dimethyl 3β,8α-Dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylate (3). Recrystallization of the mother liquors from above, *containing a 70:28:2 ratio of* **2**, **3**, *and* **4**, *from* CCl_4–hexane (2:1) gave a second crop of **2** (96% pure) and filtrates that consisted of 48% **2**, 49% **3**, and 3% **4**. Solvent was removed and the residue was recrystallized from acetone to give a 90:10 mixture of **3** and **2**. Pure **3** was obtained by recrystallization of this enriched mixture from CCl_4–hexane (2:1): mp 139.0–139.5°; ir (Nujol) 1742, 1725, 1435, 1270, 1245, 1015, 1005, 900, 875, 840, 765, 725, 690 cm^{-1}; NMR ($CDCl_3$) δ 3.50 (m, 2 H), 3.64 (m, 2 H), 3.82 (s, 8 H); *m/e* (M^+) 228.0625 (calcd, 228.0634).

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.6; H, 5.3. Found: C, 52.4; H, 5.3.

Dimethyl 3α,8α-Dioxatricyclo[5.1.0.0^{2,4}]octane-5α,6β-dicarboxylate (4). Removal of most of the diepoxides **2** and **3** from the products obtained by epoxidation of **1** left a viscous oil that contained about 20% of diepoxide **4**, which was identified in this mixture by GC and NMR by comparison with spectra of diepoxide isolated by thermal rearrangement of **11**.

4 by Thermal Rearrangement of Endo Peroxide 11. A solution of 2.40 g of **11** in 50 ml of *p*-xylene was refluxed for 20 hr. The solution was decanted from a small amount of an insoluble gum and the xylene was distilled at reduced pressure, leaving a yellow, viscous oil (2.20 g). NMR and GC analysis of the product mixture showed that it contained 35 wt % of **4**. Fractions containing a total of 0.58 g (25%) of **4** were obtained by column chromatography of the crude products over silica gel, using benzene as eluent. Recrystallization from Et_2O at −78° gave 0.48 g of **4** as a crystalline solid, mp 76–78°. **4** was further purified by recrystallization from CCl_4: mp 79–80°; ir (Nujol) 1735 (shoulders at 1745 and 1725), 1470, 1440, 1300, 1280, 1265, 1245, 1230, 1170, 1150, 1020, 960, 945, 920, 865, 785, 770, 735 cm^{-1}; NMR ($CDCl_3$) δ 3.20 (m, 1 H), 3.24 (m, 2 H), 3.40 (m, 1 H), 3.50 (m, 2 H), 3.76 (s, 6 H); *m/e* 229 (P + 1).

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.6; H, 5.3. Found: C, 52.4; H, 5.1.

Elution of the silica gel column, containing the products from thermal reaction of **11**, with $CHCl_3$ gave 1.20 g (about 50%) of a gummy solid, that was mainly dimethyl 3-hydroxyphthalate:[27] ir (Nujol) 3400, 1715, 1600, 1575, 1325–1200, 1125, 1065, 885, 880, 800, 785, 765, 710 cm^{-1}; NMR ($CDCl_3$) δ 7.74 (m, 1 H), 7.3–6.8 (m, 3 H), 3.92 (s, 3 H), 3.86 (s, 3 H); *m/e* 210.

Dimethyl 7β-Oxabicyclo[4.1.0]hept-4-ene-2β,3α-dicarboxylate (5). Monoepoxide **5** was prepared by esterification with diazomethane of the corresponding diacid, obtained by monoepoxidation of *trans*-1,2-dihydrophthalic acid[13] according to the procedure described by Berchtold.[14] It was pure by GC: ir (film) 1737, 1435, 1305, 1275, 1195, 1165, 1020, 980, 860, 755 cm^{-1}; NMR ($CDCl_3$) δ 3.14 (m, 1 H), 3.40 (m, 1 H), 3.55 (m, 1 H), 3.72 (m, 4 H), 3.80 (s, 3 H), 6.00 (m, 2 H).

Dimethyl 7β- and 7α-Oxabicyclo[4.1.0]hept-4-ene-2β,3α-dicarboxylates (5 and 6) by Epoxidation of 1. A solution of 4.85 g (24.7 mmol) of **1** and 5.20 g (25.6 mmol) of 85% *m*-chloroperbenzoic acid in 200 ml of $CHCl_3$ was refluxed for 2 hr. The reaction product was worked up as described above. A yellow oil (5.20 g) was obtained that contained 3% of dimethyl phthalate (by NMR) and 4% of **2** (by GC). The ir and NMR spectra of the product mixture were similar to those of pure **5**. Chromatography over alumina, silica gel, or Florisil converted **5** and **6** to dimethyl phthalate. Relative composition could not be determined by GC as the monoepoxides partially decomposed to dimethyl phthalate and unidentified products: *m/e* (on mixture of **5** and **6**) 212 (76), 210 (1.6), 196 (7.3), 194 (14). The composition of **5** and **6** was shown to be 90:10 by reaction of the mixture with 1 equiv of *m*-chloroperobenzoic acid to give 90% **2** (from **5**), 9.5% **3**, and 0.5% **4** (from **6**).

Dimethyl 7β- and 7α-Oxabicyclo[4.1.0]hept-3-ene-2β,3-dicarboxylates (9 and 10). A solution of 4.60 g (23.4 mmol) of 8[13] and 5.30 g (26.2 mmol) of 85% *m*-chloroperbenzoic acid in 100 ml of chloroform was refluxed for 6 hr. A viscous oil (4.90 g, 98% yield) was obtained that consisted of **9** (69%), **10** (23%), dimethyl phthalate (4%), and unidentified products (~4%). The monoepoxides were purified and partially separated by chromatography over silica gel. Preparative GC afforded pure samples of **9** and **10**.

9: ir (film) 1736, 1720 (shoulder), 1662, 1435, 1365, 1312, 1265, 1200, 1174, 1125, 1095, 1055, 1035, 1015, 950, 825, 807, 760, 735 cm^{-1}; NMR ($CDCl_3$) δ 2.74 (m, 2 H), 3.25 (m, 1 H), 3.48 (m, 1 H), 3.72 (s, 6 H), 4.10 (m, 1 H), 6.80 (m, 1 H); *m/e* 212.

Anal. (M^+) Calcd for $C_{10}H_{12}O_5$: 212.06847. Found: 212.06735.

10: ir (film) 1740, 1717, 1660, 1435, 1360, 1300, 1262, 1225, 1198, 1170, 1035, 1025, 785, 760 cm^{-1}; NMR ($CDCl_3$) δ 2.74 (m, 2 H), 3.36 (m, 1 H), 3.64 (m, 1 H), 3.72 (s, 3 H), 3.76 (s, 3 H), 4.20 (m, 1 H), 6.80 (m, 1 H); *m/e* 212.

Anal. (M^+) Calcd for $C_{10}H_{12}O_5$: 212.06847. Found: 212.06735.

Dimethyl 7,8-Dioxabicyclo[2.2.2]oct-2-ene-*trans*-5,6-dicarboxylate (11).[15] A solution of 2.00 g (10.2 mmol) of **1** in 550 ml of acetone containing 50 mg of rose bengal was irradiated through a Pyrex filter by a Hanovia 450-W medium-pressure mercury immersion lamp at 22° for 30 min. A stream of oxygen was bubbled through the solution at a rate of 150 ml/min during the irradiation. Acetone was removed under reduced pressure. The residue was dissolved in Et_2O and filtered. Removal of solvent left 2.28 g (98%) of **11** as a pale yellow, viscous oil. The product was purified by chromatography in benzene over silica gel. Pure **11** (1.58 g) was obtained: ir (film) 1737, 1440, 1375, 1325, 1290, 1265, 1240, 1210, 1180, 1055, 980, 940, 875, 760, 705 cm^{-1}; NMR (CCl_4) δ 2.95 (m, 1 H), 3.63 (s, 3 H), 3.74 (s, 3 H), 3.78 (m, 1 H), 4.93 (m, 2 H), 6.54 (m, 2 H); MS *m/e* (rel intensity) 228 (2.6), 197 (6.9), 196 (12.1), 169 (2.1), 164 (12.1), 137 (100.0), 136 (20.2).

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.6; H, 5.3. Found: C, 52.7; H, 5.1.

Dimethyl 1β,4β-Dihydroxycyclohex-5-ene-2β,3α-dicarboxylate (12). A solution of 1.02 g of **11** in 500 ml of cyclohexane was irradiated as above. The solvent was removed under vacuum. The residue was taken up in benzene and filtered to give 0.15 g (15%) of **12**. Examination of the mother liquor by NMR showed the presence of about 6% **4**. Recrystallization of **12** from acetone–benzene (1:1) gave a pure product: mp 160.5–161.5°; ir (Nujol) 3275, 1740, 1725, 1440, 1335, 1225, 1200, 1187, 1135, 1070, 1050, 1030, 970, 950, 900, 880, 820, 790, 755 cm^{-1}; NMR (D_2O) δ 3.0 (m, 2 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 4.20 (m, 1 H), 4.55 (m, 1 H), 5.92 (s, 2 H); MS *m/e* (rel intensity) 230 (1.9), 198 (4.0), 154 (9.7), 152 (9.5), 136 (100), 122 (10.4).

Irradiation of a solution of **11** (1.0 g) in methanol (550 ml) as above gave a 10% yield of **4** (by NMR and GC). None of **12** was obtained.

Dimethyl 1β,4α-Dihydroxycyclohexane-2β,3α-dicarboxylate (13). **1** (2.0 g) in 100 ml of methanol was hydrogenated in a rocking autoclave using 0.50 g of 5% Pd/C, under a pressure of 500 psi of hydrogen at 23° for 17 hr. After filtering, removing solvent at reduced pressure, and recrystallizing from benzene, we obtained 1.39 g (68%) of **13**: mp 134–135° (after two recrystallizations from benzene); ir (Nujol) 3550, 3500, 3450 (shoulder), 1735, 1718, 1440, 1315, 1300, 1240, 1220, 1190, 1175, 1167, 1115, 1050, 1035, 1000, 967, 900 cm^{-1}; NMR (Table I); MS *m/e* (rel intensity) 233 (1.3), 232 (0.0), 214 (3.7), 145 (100.0), 113 (90.0).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.7; H, 7.0. Found: C, 51.6; H, 7.0.

1β,4α-Dihydroxy-2β,3α-bis(hydroxymethyl)cyclohexane (14). A solution of 1.19 g (5.13 mmol) of **13** in 10 ml of THF was added slowly to a stirred suspension of 1.10 g (29.0 mmol) of lithium aluminum hydride in 25 ml of THF at 10–20° under nitrogen. The mixture was stirred at 10° for 30 min, then refluxed for 2 hr. To the cooled reaction mixture, 1 ml of water was added with rapid stirring, followed by 1 ml of 15% sodium hydroxide and 3 ml of water. The solids were filtered and washed with THF (300 ml). The solution was dried, filtered, and evaporated to dryness under vacuum to give 0.81 g (90%) of **14**. Two recrystallizations from acetone gave a pure product: mp 132–133°; ir (Nujol) 3400–3200, 1420, 1360, 1288, 1200, 1185, 1100, 1075, 1015, 980, 940, 905, 865, 820 cm^{-1}; NMR (Table I); MS *m/e* (rel intensity) 177 (1.0), 176 (0.3), 158 (0.5), 140 (18.0), 110 (20.0) 85 (62.0), 79 (25.0), 54 (100.0).

Anal. Calcd for $C_8H_{16}O_4$: C, 54.5; H, 9.2. Found: C, 54.4; H, 9.0.

14 by Hydride Reduction of 1. A solution of 4.42 g (19.4 mmol) of **1** in 30 ml of THF was added to a stirred suspension of 4.00 g

(105 mmol) of lithium aluminum hydride in 100 ml of THF. The mixture was refluxed for 2 hr and the products were isolated as above. Recrystallization of the crude products from acetone gave 1.85 g (54%) of **14**, which was identical with the product from hydride reduction of **13**.

Dimethyl 1β,4β-Dihydroxycyclohexane-2β,3α-dicarboxylate (15).[15] 11 (0.98 g) dissolved in 100 ml of methanol was hydrogenated in a rocking autoclave using 0.50 g of 5% Pd/C under a 500 psi pressure of hydrogen at 23° for 17 hr. The catalyst was removed and the solvent evaporated under vacuum. Recrystallization of the residue from benzene gave 0.75 g (80%) of **15**: mp 131°; ir (Nujol) 3300, 1743, 1720, 1485, 1435, 1377, 1365, 1260, 1217, 1200, 1180, 1165, 1130, 1070, 1050, 1030, 1015, 987, 950, 930, 880, 775 cm^{-1}; NMR (Table I); MS *m/e* (rel intensity) 233 (0.1), 214 (0.1), 155 (7.0), 146 (29.6), 145 (85.2), 114 (66.2), 113 (100.0).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.7; H, 7.0. Found: C, 51.8; H, 6.9.

1β,4β-Dihydroxy-2β,3α-bis(hydroxymethyl)cyclohexane (16). A solution of 2.85 g (12.3 mmol) of **15** in 80 ml of THF was added to a stirred suspension of 4.08 g (107 mmol) of lithium aluminum hydride in 100 ml of THF. The mixture was refluxed for 2 hr and the products were isolated as above to give 1.65 g (76%) of **16**. Two recrystallizations from methanol–benzene (1:1) gave 1.19 g (55%) of pure **16**: mp 180–181°; ir (Nujol) 3300–3150, 1485, 1340, 1315, 1280, 1215, 1190, 1100, 1087, 1060, 1040, 995, 975, 940, 900, 855, 820, 730 cm^{-1}; NMR (Table I); MS *m/e* (rel intensity) 177 (5.4), 159 (1.5), 141 (9.8), 140 (6.8), 123 (9.1), 110 (21.1), 87 (25.0), 85 (44.3), 54 (100.0).

Anal. Calcd for $C_8H_{16}O_4$: C, 54.5; H, 9.2. Found: C, 54.4; H, 9.0.

Dimethyl 4α,5β-Dihydroxycyclohexane-1β,2β-dicarboxylate (18). A solution of 12.0 g (59 mmol) of 85% *m*-chloroperoxybenzoic acid and 9.90 g (50 mmol) of dimethyl *cis*-1,2,3,6-tetrahydrophthalate[13] in 300 ml of benzene was stirred at room temperature for 2.5 days. The precipitated *m*-chlorobenzoic acid was removed and the benzene solution was extracted with 5% sodium bicarbonate (4 × 200 ml). The solution was dried, filtered, and evaporated under vacuum to give 9.67 g (90%) of a light yellow oil, that consisted of a 5:1 mixture of trans and cis epoxides of *cis*-1,2,3,6-tetrahydrophthalate.

The monoepoxide (1.0 g) was refluxed in 50 ml of water for 2 hr. Water was removed under vacuum and the residue was extracted with Et_2O (4 × 200 ml). Removal of the solvent left 1.08 g (100%) of **18** as a colorless, viscous oil: ir (film) 3450, 1735, 1440, 1265, 1215, 1165, 1065, 1015, 1000, 945, 920, 890, 850, 820, 785, 690 cm^{-1}; NMR (D_2O) δ 1.70 (m, 2 H), 2.3 (m, 2 H), 2.9 (m, 1 H), 3.2–3.6 (m, 3 H), 3.68 (s, 6 H).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.7; H, 7.0. Found: C, 51.8; H, 6.8.

Dimethyl 4α,5β-Dihydroxycyclohexane-1β,2α-dicarboxylate (17). Dimethyl *cis*-1,2,3,6-tetrahydrophthalate (16 g) was epimerized to a 74:26 mixture of *trans*- and *cis*-1,2,3,6-tetrahydrophthalates by refluxing in 200 ml of CH_3OH containing 1.96 g of potassium hydroxide. The solvent was removed under vacuum. The residue was dissolved in benzene and extracted with water. The solution was dried, filtered, and distilled at 75–80° (9.5 Torr) to give 9.60 g (48.5 mmol) of a mixture of 76% *trans*- and 24% *cis*-1,2,3,6-tetrahydrophthalate. This was stirred with 10.6 g (52 mmol) of 85% *m*-chloroperbenzoic acid in 300 ml of $CHCl_3$ at room temperature for 20 hr. This mixture of monoepoxides (6.50 g) was refluxed in 300 ml of water for 4 hr. Water was removed under vacuum to give 6.67 g (97%) of a 3:1 mixture of **17** and **18**. **17** was isolated by crystallization from benzene. A second recrystallization from benzene gave pure **17**: mp 123–124°; ir (Nujol) 3350, 3275, 1730, 1335, 1280, 1250, 1205, 1185, 1162, 1050, 1035, 940, 915, 887 cm^{-1}; NMR (Table I).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.7; H, 7.0. Found: C, 51.8, H, 6.8.

Acknowledgments. We thank Dr. Glen A. Berchtold of MIT for providing unpublished experimental details of syntheses and spectra of 7,8-dioxabicyclo[2.2.2]oct-2-ene-*trans*-5,6-dicarboxylic acid and 3α,8α-dioxatricyclo-[5.1.0.$0^{2,4}$]octane-5α,6β-dicarboxylic acid (the acids corresponding to **11** and **4**), and Dr. Patrick McCurry of Carnegie-Mellon for helpful discussions.

Registry No.—**1**, 26549-64-4; **2**, 57236-59-6; **3**, 57236-60-9; **4**, 57236-61-0; **5**, 57197-04-3; **8**, 38201-52-4; **9**, 57197-05-4; **10**, 57236-62-1; **11**, 57197-06-5; **12**, 57197-07-6; **13**, 57197-08-7; **14**, 57197-09-8; **15**, 57236-63-2; **16**, 57236-64-3; **17**, 57197-10-1; **18**, 57236-65-4; dimethyl 3-hydroxyphthalate, 36669-02-0; *cis*-dimethyl-1,2,3,6-tetrahydrophthalate, 4841-84-3.

References and Notes

(1) For a recent review of epoxidation stereochemistry, see G. Berti, *Top. Stereochem.*, **7**, 93–251 (1973).
(2) For an excellent review on photooxygenation, see R. W. Denny and A. Nickon, *Org. React.*, **20**, 164 (1973), and references cited therein.
(3) H. Z. Sable and J. G. Buchanan in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1972.
(4) T. W. Graig, G. R. Harvey, and G. A. Berchtold, *J. Org. Chem.*, **32**, 3743 (1967).
(5) J. Staroscik and B. Rickborn, *J. Am. Chem. Soc.*, **93**, 3046 (1971).
(6) B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).
(7) K. Gollnick and G. O. Schenck in "1,4 Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, N.Y., 1967, p 255 ff.
(8) Reference 2, pp 162–163.
(9) K. K. Maheshawari, P. De Mayo, and D. Wiegand, *Can. J. Chem.*, **48**, 3265 (1970).
(10) C. H. Forster and G. A. Berchtold, *J. Am. Chem. Soc.*, **94**, 7939 (1972); E. Vogel et al., *Angew. Chem., Int. Ed. Engl.*, **13**, 398 (1974); **11**, 935, 937 (1972); H. Prinzbach et al., *ibid.*, **11**, 940, 942 (1972).
(11) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).
(12) R. Albrecht and C. Tamm, *Helv. Chim. Acta*, **10**, 2216 (1957).
(13) S. A. Cerefice and E. K. Fields, *J. Org. Chem.*, **39**, 971 (1974).
(14) B. A. Chiasson and G. A. Berchtold, *J. Am. Chem. Soc.*, **96**, 2898 (1974).
(15) Endo peroxide **11** of dimethyl 1,2-dihydrophthalate and the diol **15** obtained by catalytic hydrogenation of the endo peroxide were reported by G. O. Schenck, *Angew. Chem.*, **64**, 12 (1952), but were not characterized.
(16) *cis*-4α,5β-Dihydroxyhexahydrophthalic acid, the dicarboxylic acid corresponding to **18**, was prepared by hydrogen peroxide–formic acid hydroxylation of *cis*-1,2,3,6-tetrahydrophthalic acid by J. E. Franz, J. F. Herber, and W. S. Knowles, *J. Org. Chem.*, **30**, 1488 (1965).
(17) H. B. Henbest, *Proc. Chem. Soc., London*, 159, (1963).
(18) P. Chamberlain, M. L. Roberts, and G. H. Whitman, *J. Chem. Soc. B*, 1374 (1970).
(19) J. H. H. Chan and B. Rickborn, *J. Am. Chem. Soc.*, **90**, 6406 (1968).
(20) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).
(21) M. Nakajima, A. Hasegawa, and N. Kurihara, *Chem. Ber.*, **92**, 2708 (1962).
(22) R. W. Gleason and J. T. Snow, *J. Org. Chem.*, **34**, 1963 (1969).
(23) M. Narayanaswamy, V. M. Sathe, and A. S. Rao, *Chem. Ind. (London)*, 921 (1969).
(24) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 817.
(25) B. C. Hartman and B. Rickborn, *J. Org. Chem.*, **37**, 4246 (1972).
(26) H. W. S. Chan, *Chem. Commun.*, 1550 (1970).
(27) E. L. Eliel, A. W. Burgstahler, D. E. Rirard, and L. Haefele, *J. Am. Chem. Soc.*, **77**, 5092 (1955).