TABLE I

MONOCHLORODODECANE ISOMER DISTRIBUTION IN CHLORINATED DODECANE[a]

		4,5,6 isomers		2,3 isomers		
Solvent[b]	N_1	% of secondary chlorides	% of total chlorides	% of secondary chlorides	% of total chlorides	1 isomer
Benzene	0.13	58.0	56.1	41.2	39.2	4.8
Benzene	0.31	58.9	55.8	41.1	39.1	5.1
Benzene	0.52	59.0	55.8	41.0	38.9	5.2
Benzene	0.84	60.0	57.1	40.0	37.9	5.0
None	0.56	56.9	51.0	43.1	38.4	10.6
None	0.76	56.3	50.1	43.7	39.1	10.8
None	0.86	55.5	49.2	44.5	40.0	10.8

[a] Chlorination carried out at 70–75°. [b] Four moles/mole of RH.

TABLE II

MONOCHLORIDE DISTRIBUTION IN CHLORINATED HEPTANE

	Monochloride isomer distribution, %[a]			
Chlorination agent	1	2	3	4
Chlorine	15	35 (41)[b]	34 (40.0)	16 (19)
N-Chlorosuccinimide	15.4	38.4 (45.4)	31.9 (37.7)	14.2 (16.9)
t-Butylhypochlorite	9.4	44.7 (49.3)	31.5 (34.8)	14.4 (15.9)
Trichloromethanesulfonyl chloride	2	50 (51)	32 (32.6)	16 (16.4)
Carbon tetrachloride	2.0	49.0 (50.0)	35.0 (35.7)	14.0 (14.3)

[a] Determined by g.l.p.c. using 8% β,β'-iminodipropionitrile on 60–80-mesh Chromosorb R. [b] The numbers in parentheses are based on only the secondary chlorides as calculated by us.

is well recognized in the field of polymer chemistry where helical polymers are extended by a good solvent.[9]

Experimental Section

Chlorination Procedure.—The chlorinations were carried out at 70–75° in a 1-l. flask equipped with a mechanical stirrer, condenser with gas outlet, thermometer, and gas-inlet sparger. After the flask was charged with paraffin, the system was purged with nitrogen. Chlorine was then added from a lecture bottle while the system was illuminated by a GE 150-w. flood lamp placed 2–3 in. from the flask. Chlorine was added at about 0.5 g./min. until the reaction was terminated. Nitrogen was used to purge the mixture and the product was washed three times with water and dried over $MgSO_4$.

Analytical Procedures.—Analyses of the chlorination products were performed by g.l.p.c. using an F and M Model 500 programmed gas chromatograph containing 10% silicone gum nitrile (LP-125) on 70–80-mesh Diatoport S. For separation of the monochlorides into primary and secondary chlorides, a 6 ft. × 0.25 in. column was used with helium gas carrier at 30 p.s.i.g. and 40 cc./min. with temperature programming from 100 to 240° at 15°/min. For separation into the 1, combined 2 and 3, and remaining isomers, a 12 ft × $^1/_8$ in. column was used with helium carrier gas at 30 p.s.i.g. and 50 cc./min. with temperature programming from 75 to 240° at 5.6°/min. The decomposition to olefin was <1.4% and the reproducibilities were ±1 and ±3% for the secondary and primary chlorides, respectively. The response factors for 1-chlorododecane and 2-chlorododecane were determined and the latter response factor was used for all secondary monochlorides.

Materials.—The dodecane used was between 96 and 98% pure by g.l.p.c. with the major impurity being the C_{12} isoparaffin. Benzene was washed with sulfuric acid, sodium hydroxide, water, and then dried. G.l.p.c. analysis showed no impurities.

Acknowledgment.—The authors wish to thank Dr. Glenn A. Russell of Iowa State University for many helpful discussions and Messrs. A. N. Kresge and J. Svoboda of our laboratories for their contribution to this work.

(9) This information can be found in any complete book in polymer chemistry.

Lithium Aluminum Hydride Reduction of 1-Methyl-*cis*- and -*trans*-4-*t*-Butylcyclohexene Oxide

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To facilitate the identification of several 1,2-substituted 4-*t*-butylcyclohexanes, we found it necessary to synthesize the isomeric 1-methyl-4-*t*-butylcyclohexene oxides and to study the products of their reaction with lithium aluminum hydride. The results provide further evidence that steric effects can modify the normal stereoelectronic preference for diaxial ring opening[2] in the hydride reductions of cyclohexene oxides.[3]

Epoxidation of 1-methyl-4-*t*-butylcyclohexene, as expected,[4] afforded a mixture of 1-methyl-*trans*- and -*cis*-4-*t*-butylcyclohexene oxide, 1 and 2, respectively, in the approximate ratio of 45:55. Consequently, pure samples of each epoxide were obtained by the reaction sequences outlined in Schemes I and II. The intermediates were characterized by elemental analysis and infrared, and in some cases, n.m.r. spectroscopy. 2-Methyl-5-*t*-butylcyclohexanone was obtained by dehydration of the mixture of diols from the hydroxyla-

(1) A. P. Sloan Foundation Fellow, 1961–1965.

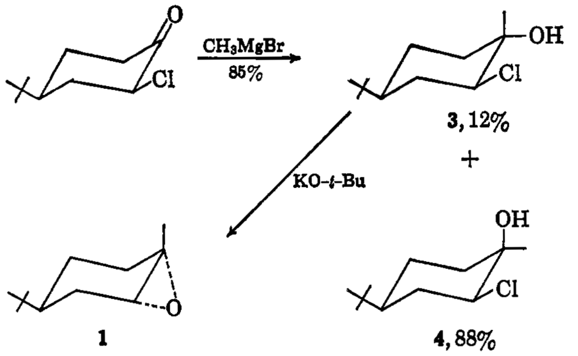
(2) A. Furst and P. A. Plattner, Abstracts, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, p. 409.

(3) A summary, discussion, and pertinent leading references are given by E. L. Eliel, "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y.. 1956, pp. 130–134; *cf.* also F. H. Newth, *Quart. Rev.* (London), **13**, 41 (1959).

(4) *Cf.* the epoxidation of 4-*t*-butylcyclohexene: (a) J. Sicher, F. Sipos, and M. Tichy, *Collection Czech. Chem. Commun.*, **26**, 847 (1961); (b) N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, **26**, 4768 (1961); (c) B. Rickborn and J. Quartucci, *ibid.*, **29**, 2476 (1964).

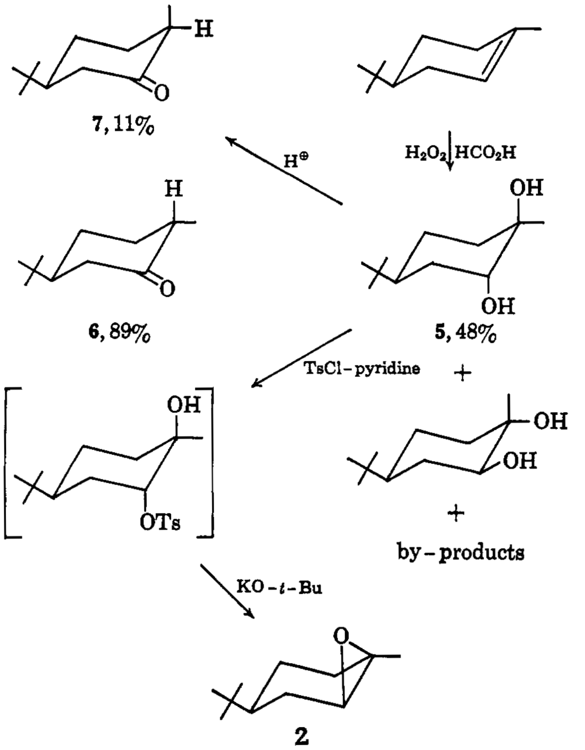
SCHEME I

PREPARATION OF 1-METHYL-*trans*-4-*t*-BUTYLCYCLOHEXENE OXIDE



SCHEME II

PREPARATION OF 1-METHYL-*cis*-4-*t*-BUTYLCYCLOHEXENE OXIDE

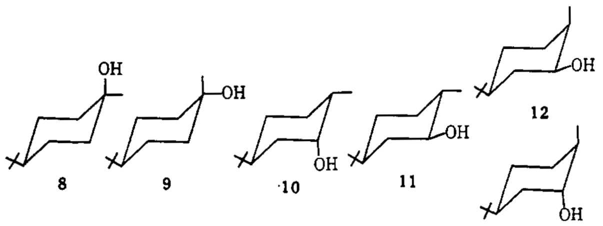


tion of 1-methyl-4-*t*-butylcyclohexene as a mixture of *trans* and *cis* isomers (89:11). Equilibration with sodium methoxide showed little change in the relative proportions (90% **6**, 10% **7**), and the major isomer was thus assigned the structure **6** (*trans*, equatorial methyl).

Reductions of the epoxides **1** and **2**, a mixture of the epoxides obtained from peracid oxidation of 1-methyl-4-*t*-butylcyclohexene, and the equilibrium mixture of ketones **6** and **7** were carried out by reflux in ether with excess lithium aluminum hydride. The product distributions were obtained by g.c. analysis, and identification was made by a comparison of g.c. retention times and infrared spectra. The data is summarized in Table I. Authentic samples of 1-methyl-*cis*- (**8**) and -*trans*-4-*t*-butylcyclohexanol (**9**) were available from addition of methyl magnesium bromide to 4-*t*-butylcyclohexanone. Reduction of the ketone mixture (90% **6**, 10% **7**) produced a mixture of the four 2-methyl-5-*t*-butylcyclohexanols. Partial separation by alumina chromatography was effected. The axial methyl isomers **12** were obtained as a low-melting solid and comprised 10% of the mixture as expected (from *cis*-ketone **7**). Infrared data indicated that the *cis,cis* isomer (equatorial OH, axial methyl) was the major constituent. Isomers **10** and **11** were obtained by the preparation of 3,5-dinitrobenzoate derivatives from appropriate fractions followed by saponification. Their structures followed from infrared and n.m.r. measurements, relative rate of oxidation (to *trans* ketone **6**), and relative retention time on alumina.

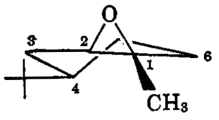
TABLE I

REDUCTIONS WITH LITHIUM ALUMINUM HYDRIDE

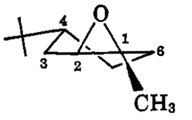


Compd.	Product distribution, % 8	9	10	11	12
2	99.5	..	..	..	...
1	...	32	60	8	0.02
1 + 2	54	19	24	3	...
6 (90%) + 7 (10%)	...	..	17	73	10

Stereospecific reduction of the *cis* epoxide **2** obviously proceeds through the most stable conformation **13**. Attack at C-2 is favored both by diaxial ring opening and by sterically accessible attack at the secondary carbon atom, the latter effect reinforcing the former. The preference for the product of diaxial opening is more pronounced than with the 4-*t*-butylcyclohexene oxides.[5]



13



14

The two effects would be in opposition with the *trans* epoxide **1**. Reaction *via* the more stable, half-chair conformation **14** by attack at C-1 (diaxial opening) is still preferred despite the opposing steric effect. The major product, *cis*-2-methyl-*trans*-5-*t*-butylcyclohexanol (**10**), must arise by direct reduction. The results obtained from reduction of the mixture of ketones **6** and **7** suggest that a maximum of 10% of product (2% of **10** and 8% of **11**) could have arisen by conversion of epoxide **1** to *ketone* **6** and subsequent reduction. Only 32% of reduction occurs at C-2 to produce equatorial tertiary alcohol **9**. We see no distinct advantage for a pathway to this compound by way of diaxial opening of the less stable boat conformation. Reaction through **14** to give **9** initially in the twist conformation is feasible.[5] As for the mechanism of conversion of **1** to **6**, a process involving oxidation of the oxyanion of the initially formed **10** (*cf.* ref. 5) seems attractive. Support is given by the recognition that the ratio of axial to equatorial secondary alcohols, **10**:**11** = 60:8, is close to the ratio 89:11 reported for the reduction of *trans*-4-*t*-butylcyclohexene oxide in the absence of aluminum chloride.[5]

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[5] B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).

Experimental Section

1-Methyl-*cis*- and -*trans*-4-*t*-butylcyclohexanol.—A mixture of the alcohols **8** and **9** was prepared in 99% yield by the addition of methylmagnesium bromide to 4-*t*-butylcyclohexanone.[7] G.c. analysis was carried out on a column packed with 20% Polyglycol E-4000 on 35–80-mesh Chromosorb P. The column was preconditioned with several large injections of tri-*n*-butylamine. At 150° and 8 p.s.i.g., 1-methyl-*cis*-4-*t*-butylcyclohexanol (**8**) had a retention time of 20 min.; that of the *trans* isomer (**9**) was 26 min. Analysis of the mixture showed 57% **8** and 43% **9**.

Separation was effected by chromatography on alumina using ether–pentane mixtures as eluent. The axial alcohol **8** was recrystallized twice from hexane, m.p. 71–72° (lit. m.p. 70.5–71°,[8a,b] 66–67°,[8c] 71°[8d]). The n.m.r. spectrum showed the following significant resonances: *t*-Bu, −0.89; C-CH_3, −1.17; and OH, −1.92 p.p.m. 1-Methyl-*trans*-4-*t*-butylcyclohexanol (**9**) was recrystallized from hexane, m.p. 99–100.5° (lit. m.p. 97.5–98°,[8a,b] 89–90°,[8c] 97.8°[8d]). The infrared spectrum was similar to that reported[8d] except for the absence of a band at 930 cm.$^{-1}$. The n.m.r. spectrum showed *t*-Bu, −0.83; C-CH_3, −1.10; and OH, −2.95 p.p.m. The **3,5-dinitrobenzoate** of **9** had m.p. 146–147° (lit.[8c] m.p. 156.5–157°).

1-Methyl-4-*t*-butylcyclohexene.—Dehydration of a mixture of 1-methyl-*cis*- and -*trans*-4-*t*-butylcyclohexanol with *p*-toluenesulfonic acid in benzene gave 1-methyl-4-*t*-butylcyclohexene (90%), b.p. 60–62° (6 mm.), $n^{25}D$ 1.4578 (lit.[8c] b.p. 74–75° at 11 mm., $n^{16}D$ 1.4626). G.c. indicated that the olefin was pure.[9]

Epoxidation of 1-Methyl-4-*t*-butylcyclohexene. A. Perbenzoic Acid.—To 188 ml. (0.103 mole) of dry perbenzoic acid solution in chloroform at 5° was added 15.20 g. (0.10 mole) of 1-methyl-4-*t*-butylcyclohexene in 1-ml. portions over a 15-min. period. The temperature of the reaction mixture was controlled at 5–7° during the addition; the mixture was allowed to stand for an additional 90 min. at ice-bath temperature. After washing with 10% sodium hydroxide solution and water, the mixture was dried and the chloroform was removed by distillation. Distillation of the residue gave 15.1 g. (90%) of a mixture of epoxides **1** and **2**, b.p. 71.5° (5.5 mm.), $n^{25}D$ 1.4520.

B. *m*-Chloroperbenzoic Acid.—A solution of 3.533 g. (0.0174 mole) of *m*-chloroperbenzoic acid (FMC Corp., minimum purity 85%) in 60 ml. of anhydrous ether was cooled by an ice bath while 2.560 g. (0.0168 mole) of olefin in 10 ml. of ether was added. The mixture was allowed to warm to room temperature and to stand for 2 hr. Work-up was carried out in the manner described above. There was obtained 2.30 g. (82%) of epoxide mixture (**1** and **2**), b.p. 72–73° (5 mm.), $n^{25}D$ 1.4520. The infrared spectrum was identical with that of the perbenzoic acid product.

Hydroxylation of 1-Methyl-4-*t*-butylcyclohexene.—To a solution of 10.3 ml. (0.10 mole) of 30% hydrogen peroxide in 48 ml. of 90.6% formic acid was added 12.2 g. (0.08 mole) of 1-methyl-4-*t*-butylcyclohexene. The temperature was maintained at 40–45° both during the 30-min. addition period and for 1 hr. thereafter. At the end of this time the mixture had become homogeneous. After standing 12 hr. at room temperature, the formic acid was removed by distillation (6 mm.). The residue was warmed with a solution of 6.42 g. of sodium hydroxide in 12 ml. of water. The mixture was then extracted with six 25-ml. portions of warm ethyl acetate. Removal of the ethyl acetate from the extract at reduced pressure gave a semisolid residue.

In this experiment the crude residue was chromatographed using 455 g. of Merck acid-washed alumina; however a small-scale experiment indicated that a preferable procedure consisted of recrystallizing the residue from hexane prior to chromatography. The recrystallization appeared to remove carbonyl compounds without major loss of diols. In the chromatography, 200-ml. fractions were taken and the eluent consisted of increasing percentages of ether in pentane: fractions 1–7, 20%; 8–11, 30%; 12–14, 40%; 15–17, 50%; 18–22; 60%; 23–29, 70%; and 40–48, pure ether. At fraction 49, the eluent was changed to methanol–ether mixtures: Fractions 49–51, 1.25%; 52–54; 2.5%; 55–57, 5%; 58–61, 10%; and 62–65, pure methanol. From fractions 2–7 there was obtained a liquid product (1.030 g.) which was subjected to short-path distillation (0.4 mm., 55° oil bath) to effect separation from a less volatile viscous liquid which constituted about 20% of the material. The distillate gave a positive test with 2,4-dinitrophenylhydrazine reagent and showed absorption at 5.84, 6.00, and 6.17 μ in the infrared spectrum. G.c. (Polyglycol E-4000) showed it to be a mixture of three major and numerous minor components.

The major product of the reaction was the diaxial glycol **5**, which was found in fractions 15–41 (8.124 g.). Fractions 15–18 and fractions 33–41 were recrystallized from ether–hexane before combining with fractions 19–32 to give 7.225 g. of material, m.p. 117–118.5°. A further recrystallization was carried out to provide material for elemental analysis: m.p. 118.5–119.5°, $\nu_{\max}^{\mathrm{KBr}}$ 1012 and 1036 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.91. Found: C, 71.40; H, 11.79.

The other major product was found in fractions 59–61 (2.0509 g., m.p. 110–116°). Fractional recrystallization from ether–hexane gave 1.4738 g. of fine needles, m.p. 115.5–116.5°. A further recrystallization gave material for elemental analysis, m.p. 116–117°.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.91. Found: C, 71.17; H, 11.96.

This isomer was assigned the structure *trans*-1-methyl-*cis*-4-*t*-butylcyclohexane diol (diequatorial diol) on the basis of its infrared ($\nu_{\max}^{\mathrm{KBr}}$ 952 and 1071 cm.$^{-1}$) absorption.

1-Methyl-*cis*-4-*t*-butylcyclohexene Oxide (2).—The monotosylate of the diaxial diol (**5**) was prepared as follows. A solution of 3.716 g. (20.0 mmoles) of **5** in 8 ml. of pyridine was stirred and cooled in an ice bath, and 7 ml. of water was added. The solution was warmed to room temperature and poured into 250 ml. of water. The tosylate was extracted with three 30-ml. portions of ether; the extract was washed with 5% hydrochloric acid (100 ml.), 5% sodium bicarbonate solution (50 ml.), and with two 25-ml. portions of water and was dried. Evaporation of the ether yielded the crude monotosylate as a yellow viscous liquid (3.371 g.).

The crude monotosylate was stirred with 34 ml. of 0.32 *N* potassium *t*-butoxide in *t*-butyl alcohol. After heating the mixture at 40–50° for 2 hr., it was poured into 200 ml. of water, and the product was extracted with pentane. The extract was washed with five 100-ml. portions of water and dried, and the pentane was evaporated. Short-path distillation of the residue (60–80° pot temperature, 5 mm.) gave 1.471 g. of product, $n^{25}D$ 1.4530. Redistillation gave 0.983 g. (29% based on diol) of epoxide **2**, b.p. 72.5–73.5° (4.9 mm.), $n^{25}D$ 1.4519.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.97. Found: C, 78.52; H, 12.18.

1-Methyl-*trans*-2-chloro-*trans*-4-*t*-butylcyclohexanol (3).—A solution of 28.3 g. (0.15 mole) of *cis*-2-chloro-4-*t*-butylcyclohexanone[10] in 150 ml. of ether was cooled in an ice bath and 128 ml. (0.165 mole) of 1.29 *N* methylmagnesium bromide in ether was added. The product was immediately hydrolyzed by pouring onto a mixture of 150 g. of ice and 10 ml. of concentrated sulfuric acid. After washing with 5% sodium bicarbonate solution and with water, the product was distilled to yield 26.2 g. (85%) of a mixture of the two chlorohydrins, **3** and **4**, b.p. 66–75° (0.4 mm.).

The chlorohydrins were separated by chromatography on 907 g. of Merck acid-washed alumina using 30 l. of pentane–ether eluent in which the concentration of ether was varied from 0 to 50%. The axial isomer **4** was eluted before the equatorial isomer **3**. There was obtained 21.79 g. of **4** and 3.00 g. of **3**, a ratio of 7.26:1.

1-Methyl-*cis*-2-chloro-*cis*-4-*t*-butylcyclohexanol (4) was a liquid, b.p. 58–62° (0.1 mm.), $n^{25}D$ 1.4760, m.p. 18.5–20°.

Anal. Calcd. for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34; Cl, 17.32. Found: C, 64.74; H, 10.53; Cl, 17.56.

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(6) Melting points are corrected and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 or Perkin-Elmer Corp. Infracord recording spectrophotometers. N.m.r. spectra were measured with a Varian DP-60 spectrometer as 20% solutions in carbon tetrachloride with tetramethylsilane as the internal standard. Chemical shift values were obtained by the audio side-band method and are reported in parts per million from tetramethylsilane. Analyses were by Midwest Microlabs, Inc., Indianapolis, Ind.

(7) Generously supplied by the Dow Chemical Co.

(8) (a) C. H. DePuy and R. W. King, *J. Am. Chem. Soc.*, **83**, 2734 (1961); (b) H. Fevre and D. Gravel, *Can. J. Chem.*, **39**, 1548 (1961); (c) B. Cross and G. H. Whitham, *J. Chem. Soc.*, 3892 (1960); (d) W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962).

(9) DePuy and King[8a] report that about 0.8% of exocyclic olefin is present at equilibrium.

(10) N. L. Allinger, J. Allinger, L. Freiberg, R. F. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

1-Methyl-*trans*-2-chloro-*trans*-4-*t*-butylcyclohexanol (3) melted at 76–77°.

Anal. Calcd. for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34; Cl, 17.32. Found: C, 65.12; H, 10.42; Cl, 17.21.

The infrared spectra of **3** and **4** (carbon disulfide) were found to be quite similar. There was little difference in the O–H stretching region; however, a band at 9.7 μ in the spectrum of **4** (axial OH) was absent in the spectrum of **3**. The same phenomenon had been noted in the spectra of the 1-methyl-*cis*- and -*trans*-4-*t*-butylcyclohexanol, respectively.

1-Methyl-*trans*-4-*t*-butylcyclohexene Oxide (1).—To a solution of 1.90 g. (9.25 mmoles) of **3** in 5 ml. of *t*-butyl alcohol was added 18.8 ml. of 0.517 *N* potassium *t*-butoxide in *t*-butyl alcohol. The mixture was heated at 40–45° for 2 hr. and then was poured into 100 ml. of water. The product was extracted five times with 30-ml. portions of pentane, and the extract was washed five times with 10-ml. portions of water. After drying, distillation afforded 1.274 g. (82%) of epoxide **2**, b.p. 72–73° (5 mm.), n^{25}_{D} 1.4520.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.97. Found: C, 78.49; H, 12.14.

2-Methyl-5-*t*-butylcyclohexanone (6 and 7).—The crude mixture from hydroxylation of 10.6 g. of 1-methyl-4-*t*-butylcyclohexene by the above procedure was recrystallized twice from ether–hexane to give 6.8 g. (52%) of diol mixture, m.p. 103–107°. An infrared spectrum showed this material to be free of carbonyl components.

The solid was dissolved in 10 ml. of benzene containing 0.04 g. of *p*-toluenesulfonic acid monohydrate. On distillation, 0.5 ml. of water was collected in a Dean–Stark trap. After cooling, the mixture was taken up in pentane, and the solution was washed with 5% sodium bicarbonate solution and was dried. Distillation gave five fractions containing 2.55 g. of product and 2.32 g. of a viscous residue (b.p. >100° at 0.55 mm.).

The first two fractions were shown by g.c. (Polyglycol E-4000) to consist chiefly of components with short retention times and which were presumed to be dienes. The latter three fractions showed a major peak which was assumed to be ketone; however, some of the materials with short retention times were still present. Pure ketone was obtained by combining the last three fractions (2.636 g.) and distilling them through a spinning-band column to give 0.47 g., b.p. 42–46° (0.3 mm.). The residue was then distilled through a short-path apparatus to provide an additional 1.65 g. of a fraction, b.p. 52–53° (0.45 mm.), n^{25}_{D} 1.4557. The product showed only a single peak on the Polyglycol g.c. column. An infrared spectrum showed a strong carbonyl band at 1704 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.97. Found: C. 77.99, 78.20; H, 12.10, 11.99.

A 2,4-dinitrophenylhydrazone was prepared which formed orange plates from ethanol, m.p. 171.5–172.5° (lit.[11] m.p. 169–170°).

G.c. analysis of the ketone on TCEP at 149° showed two components in the approximate ratio 89% **6** and 11% **7**.

Equilibration of 2-Methyl-5-*t*-butylcyclohexanone (6 and 7).—A solution of 0.35 g. of the ketone prepared above in 25 ml. of methanol containing 0.25 g. of sodium was heated at reflux for 6 hr. The hot solution was poured onto ice and excess ether was added. The ethereal solution was washed with water and dried. The bulk of the ether was removed by distillation, and the residue was analyzed by g.c. (TCEP). There was detected two components in the ratio 9:1, corresponding exactly to the two components (89:11) obtained above. The isomer present in greatest amounts (retention time 28.8 min.) was assigned the *trans* structure **6** (equatorial methyl), and the other isomer (retention time 31.6 min.) was considered to be **7**. The equilibrium composition for this ketone was not significantly different from that reported for 2-methyl-4-*t*-butylcyclohexanone (91% *cis*, 9% *trans*).[12]

Reduction of 2-Methyl-5-*t*-butylcyclohexanone.—A solution of 0.99 g. (5.91 mmoles) of the ketone (90% **6**, 10% **7**) in 10 ml. of ether was added to a refluxing solution of 0.80 g. (21.1 mmoles) of lithium aluminum hydride in 60 ml. of ether. After an additional 1-hr. reflux, the mixture was hydrolyzed by the successive addition of 0.80 ml. of water, 2.4 ml. of 15% potassium hydroxide solution, and 0.80 ml. of water. After filtration, the solid was washed with ether. Evaporation of the ether (25°, 5 mm.) gave 0.99 g. (99%) of colorless oil. The entire product was used for elution chromatography.

The product from a similar reduction was subjected to g.c. analysis (Polyglycol E-4000 at 148°). Three components were detected: A, 17%, 28.1 min.; B, 73%, 34.6 min.; and C, 10%, 43.1 min. (see Table I).

The reduction product (0.991 g.) was subjected to elution chromatography using 47 g. of Merck acid-washed alumina and the fractions (15 ml.) described in Table II were collected. Further elution, even with neat methanol gave only 0.018 g. of liquid product. G.c. analyses are also given.

TABLE II

Fractions	Eluent	G.c. analysis %A	%B	%C	Wt., g.
1–16	0–6% ether–pentane	..	..	..	...
17–22	10% ether–pentane	95	5	..	0.097
23–29	10% ether–pentane	18	82	..	0.255
30–37	15% ether–pentane	1	95	4	0.255
38–43	15% ether–pentane	2	84	14	0.134
44–50	25% ether–pentane	1	72	26	0.124
51–53	50% ether–pentane	..	..	..	0.013
54–57	50% ether–pentane	..	..	..	0.022

The solid from fractions 54–57 melted at 78–79° and produced a single g.c. peak corresponding to that of peak C in the crude reduction product. The infrared spectrum in the C–O region indicated the presence of an equatorial hydroxyl group; a strong broad band was present at 9.4 μ.

There was also an unknown component present in fractions 38–50 (0.5 and 0.8%) which had a retention time of 12.3 min.

In order to obtain the alcohols giving rise to peaks A and B in a pure state, appropriate fractions were converted to the 3,5-dinitrobenzoates which were recrystallized and saponified.

***trans*-2-Methyl-*cis*-5-*t*-butylcyclohexanol** (11).—The 3,5-dinitrobenzoate of component B (fractions 30–37) was recrystallized twice from hexane to give 0.29 g. (54%), m.p. 119–119.5°.

Anal. Calcd. for $C_{18}H_{24}N_2O_6$: C, 59.33; H, 6.64; N, 7.69. Found: C, 59.51, 59.36; H, 6.95, 6.90; N, 7.82.

Hydrolysis with aqueous ethanolic potassium hydroxide afforded, after work-up, 0.12 g. of alcohol **11**, b.p. 65–70° (bath temperature) (0.5 mm.). G.c. indicated the alcohol was homogeneous, and the infrared spectrum showed a band at 1053 cm.$^{-1}$ corresponding to equatorial OH.

***cis*-2-Methyl-*trans*-5-*t*-butylcyclohexanol** (10).—The 3,5-dinitrobenzoate of component A (fractions 17–22) was recrystallized twice from hexane to give 0.06 g. (29%), m.p. 121–122° (m.m.p. with the 3,5-dinitrobenzoate of **11**, 102–104°).

Anal. Calcd. for $C_{18}H_{24}N_2O_6$: C, 59.33; H, 6.64; N, 7.69. Found: C, 59.32; H, 6.76; N, 7.68.

Saponification of the ester (0.035 g.) gave the alcohol **10** (0.017 g.); however, g.c. analysis showed both an A peak (**10**) (97.5%) and a B peak (**11**) (2.5%). The presence of a strong band at 10.1 μ in the infrared spectrum of the alcohol **10** indicated that it contained an axial hydroxyl group. The alcohol giving rise to peak A was therefore assigned structure **10**.

Lithium Aluminum Hydride Reduction of 1-Methyl-*cis*-4-*t*-butylcyclohexene Oxide (2).—To a refluxing solution of 0.75 g. (20 mmoles) of lithium aluminum hydride in 50 ml. of ether was added a solution of 0.834 g. (4.96 mmoles) of **2** in 15 ml. of ether. The mixture was refluxed for 24 hr. Hydrolysis by the successive addition of 0.76 ml. of water, 2.28 ml. of 15% potassium hydroxide solution, and 1.0 ml. of water afforded a mixture from which the solids could be readily filtered. The solids were washed with ether and the washings were combined with the filtrate. Ether was distilled from the solution by heating on the steam bath until about 4 ml. of residue remained. The residue was analyzed by g.c. (Polyglycol E-4000 at 150°). Two components were found to be present. One had a retention time corresponding to that of 1-methyl-4-*t*-butylcyclohexene and was present only in the amount of <0.5%. The other component (>99.5%) had a retention time corresponding to that of 1-methyl-*cis*-4-*t*-butylcyclohexanol (**8**). Evaporation of the last of the ether from the reduction product gave a white solid, 0.744 g. (89%), m.p. 72–73°. Authentic **8** melted at 72–73°, and a mixture of the reduction product and authentic **8** was found to melt at 72–73°. The infrared spectra were identical.

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[11] B. Cross and G. H. Whitham, *J. Chem. Soc.*, 1650 (1961).

[12] N. L. Allinger and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, 994 (1961).

Lithium Aluminum Hydride Reduction of 1-Methyl-*trans*-4-*t*-butylcyclohexene Oxide (1).—Complete reduction of epoxide 1 was obtained using the same conditions employed for epoxide 2. Analysis of the product by g.c. (Polyglycol E-4000) showed three peaks 9 (32%), 10 (60%), and 11 (8%) which were eluted in that order. The retention time of peak 9 corresponded to that of an authentic sample, and the infrared spectra were identical. The retention times of 10 and 11 were the same as those of these components produced in the reduction of ketone 6. No detectable amounts of 8 and 12 were observed.

Oxidation of the Reduction Product of Epoxide 1.—To a solution of 101 mg. (0.59 mmole) of the crude reduction product from epoxide 1 in 0.4 ml. of ether was added with stirring 0.21 ml. of a solution prepared from 5 g. of sodium dichromate dihydrate, 3.75 ml. of sulfuric acid, and 21.25 ml. of water.[13] The mixture was cooled at 20° during the addition and was maintained at 25° for 1 hr. After work-up, there was obtained 0.095 g. of a yellow oil which partially solidified on standing. G.c. analysis (Polyglycol E-4000 at 149°) showed the following: two unknown components in trace amounts with retention times of 13.1 and 17.1 min.; 61% of ketone 6 (no trace of 7 was detected on g.c. analysis with TCEP) with retention time of 22.3 min.; 30% of 9 (26.8 min.); 5.3% of alcohol 10 (29.4 min.); and 2.6% of alcohol 11 (34.6 min.). It may be calculated that alcohol 10 is oxidized approximately 2.2 times as fast as 11 under these conditions, lending further support to the assignment.

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(13) *Cf.* H. C. Brown and C. P. Gary, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

The Aromatization of a Substituted Cyclohexanol by the Action of Sulfuric Acid[1]

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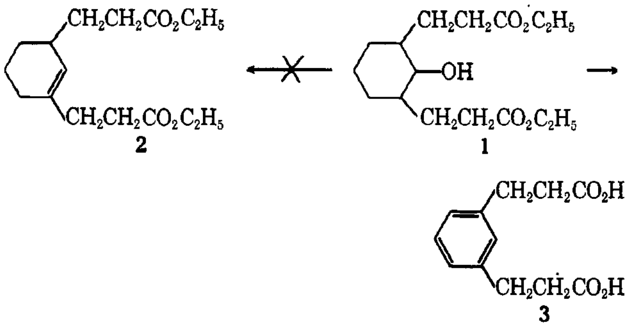
During the course of other investigations it was desired to dehydrate diethyl 2-hydroxy-1,3-cyclohexanedi-β-propionate, mixed isomers 1, to the corresponding olefin 2, the latter compound being a potentially attractive reactant for the preparation of *cis*-1,3-cyclohexanedipropionic acid.[3]

When 1 was treated with the common dehydrating agents such as phosphorus oxychloride–pyridine, phosphoric acid, *p*-toluenesulfonic acid, or phosphorus pentoxide, complex mixtures were obtained from which could be isolated reactant 1 and a δ-lactone fraction (b.p. 170–171° at 0.5 mm.) but none of the desired olefin 2.[4]

In an attempt to avoid ester hydrolysis and to promote dehydration, a 50% sulfuric acid–acetic acid mixture was employed. Heating 1 in such a mixture ultimately resulted in isolating a maximum yield of 30% of a diacid, m.p. 149–150°. Similarly, the δ-lactone fraction also gave the same diacid but in lower yield. This acid was identified as benzene-1,3-dipropionic acid (3), a compound previously reported in the early literature by Kipping.[5] Comparison of the melting points of the acid 3 and its dimethyl ester, m.p. 52–53°, with those reported,[5] as well as elemental analyses and infrared, ultraviolet, and n.m.r. spectra confirm the structure of 3. In addition, during the reaction period, copious amounts of sulfur dioxide were evolved, indicating the reduction of the sulfuric acid.[6]



There are several examples in the literature where sulfuric acid acts as an aromatizing–oxidizing agent. None were found, however, which proceeded *via* dehydration and subsequent aromatization. For example, Doering and Beringer[8] reported the aromatization of cyclohexenone and cyclohexanone derivatives to phenols by the action of sulfuric acid; the reaction was shown to proceed *via* intermediate sulfonic acid derivatives. Similarly, Noyce[9] reported the formation of *p*-methylacetophenone by the action of concentrated sulfuric acid on camphenilone. In these cases, however, the oxygen function is not lost during aromatization.

More analogous to the system reported here is the formation of 1,3-cyclohexadiene by reaction of cyclohexanol with potassium hydrogen sulfate.[10] When 1, however, was treated similarly, elimination did not occur.[6]

No doubt this interesting reaction involves dehydration followed by sulfonation and subsequent elimination of the elements of sulfurous acid, leading ultimately to aromatization. Whether the reaction proceeds *via* the intermediate formation of a δ-lactone or α,β-unsaturated ester, as suggested by formation of some unsaturated ester, or *via* direct sulfonation of an olefin such as 2 cannot be determined at this time.

A brief examination of the reaction of other cyclohexanol systems[11] under a variety of sulfuric acid concentrations and reaction times gave varying amounts of tarry materials, but no distillable aromatic products or products extractable into ether. Whether aromatic materials are present in the tarry residues was not readily determined. In this respect, it is of interest that 3 could be isolated in reasonable yield, while the other alcohols employed failed to give any isolable simple aromatic compounds.

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(2) To whom inquiries should be sent: Central Research Department, Monsanto Company, St. Louis, Mo. 63166.

(3) (a) T. L. Westman, R. Paredes, and W. S. Brey, *J. Org. Chem.*, **28**, 3512 (1963); (b) T. L. Westman and A. E. Kober, *ibid.*, **29**, 2448 (1964).

(4) With phosphorus pentoxide, the crude reaction product had infrared and ultraviolet spectra which indicated the presence of α,β-unsaturated ester. No pure components could be isolated, however.

(5) F. S. Kipping, *J. Chem. Soc.*, 53 (1888).

(6) Similarly, treating the diester 1 with thionyl chloride–pyridine gave the acid 3 in very low yield along with the formation of elemental sulfur during distillation of the product. Heating the diester 1 with potassium hydrogen sulfate[7] gave a product from which only reactant or lactone could be isolated (*vide infra*).

(7) L. Ruzicka and H. Goedhart, *Helv. Chim. Acta*, **14**, 1165 (1931).

(8) W. v. E. Doering and F. M. Beringer, *J. Am. Chem. Soc.*, **71**, 2221 (1949).

(9) D. S. Noyce, *ibid.*, **72**, 924 (1950).

(10) H. Hock and F. Depke, *Chem. Ber.*, **84**, 349 (1951).

(11) The compounds investigated included 2,6-dimethylcyclohexanol (*cis* and *trans* isomers), 2,6-di-*t*-butylcyclohexanol, 2-ethyl- and -methylcyclohexanol, ethyl cyclohexanol-2-acetate, and ethyl cyclohexanol-2-propionate (all mixed isomers).