the extract of 25 kg. of *Crinum powellii* provided 8 mg. (0.00002%) of ismine picrate, m.p. 157–159°.

The pure base had a m.p. of 99.5–100.5° and no optical activity; λ_{max} 242 mμ (ε 13,700), 294 (6400); addition of acid caused these peaks to shift to 254 (4600), 292 (4750). The infrared spectrum (potassium bromide) showed peaks at 3430, 3370, 1605, 1575, 1240, 1035, 930, 875, 840, 760, and 750 cm.$^{-1}$

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 70.05; H, 5.88; N, 5.44; N—CH_3, 5.82; active hydrogen, 0.78 for 2. Found: C, 70.28; H, 5.65; N, 5.38; N—CH_3, 5.40; OCH_3, 0.00; active hydrogen, 0.79.

Ismine picrate crystallized from ethanol as prisms, m.p. 158–159°.

Anal. Calcd. for $C_{21}H_{18}N_4O_{10}$: C, 51.85; H, 3.73; N, 11.52. Found: C, 51.95; H, 3.78; N, 11.45.

O,N-Diacetylismine. Ismine (77 mg.), 3 ml. of acetic anhydride, and 120 mg. of sodium acetate were heated together on a steam bath for 45 min. The excess anhydride was destroyed by potassium bicarbonate solution, and the mixture was extracted with benzene, which was washed with dilute hydrochloric acid and water and distilled. The residue was 102 mg. of an oil which was distilled at 110° (0.001 mm.). The infrared spectrum (chloroform) showed peaks at 1735 and 1650 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61. Found: C, 66.57; H, 5.74.

5-Methyl-8,9-methylenedioxy-6-phenanthridone. Ismine (95 mg.) was dissolved in 5 ml. of 6*N* hydrochloric acid and heated on a steam bath for 30 min. The solution was then cooled, made basic with sodium hydroxide, and treated with 1.2 g. of potassium ferricyanide. After stirring overnight the suspension was filtered to yield a precipitate of 46 mg. of the phenanthridone, m.p. 244–245°, unchanged by admixture of known material[11]; the infrared spectra of the two materials were identical.

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LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS
NATIONAL HEART INSTITUTE
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MD.

(11) H. Kondo and S. Uyeo, *Ber.*, **68**, 1756 (1935). We are indebted to Professor Uyeo for supplying an authentic sample of this material.

The Stereochemistry of Additions to Olefins. II. Synthesis of the Isomeric 2-Chloro-4-*t*-butylcyclohexanols[1,2]

NORMAN A. LE BEL AND ROBERT F. CZAJA

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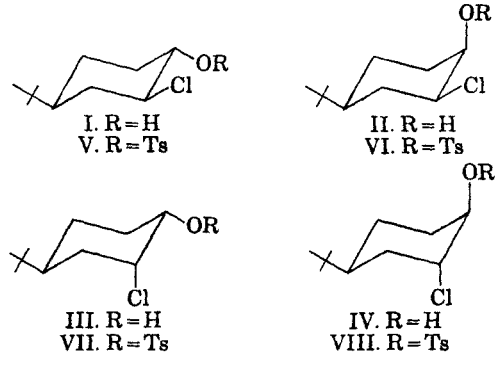
The wealth of information to be gained from stereochemical and kinetic studies of the reactions of vicinally disubstituted *t*-butylcyclohexanes has been aptly expressed by Sicher and his co-workers.[3] Curtin and Harder[4] have used the phenyl group in a similar manner to effect conformational homogeneity. Although the more bulky *t*-butyl group has distinct advantages over phenyl, it may deform the cyclohexane ring to a greater degree. In the course of other studies, we felt it desirable to obtain as intermediates the four isomeric 2-chloro-4-*t*-butylcyclohexanols (I–IV) and their corresponding *p*-toluenesulfonates (V–VIII). This report describes the preparation and structure proof of these compounds.



Sodium borohydride reduction of *cis*-2-chloro-4-*t*-butylcyclohexanone[5] produced a mixture of 2^t-chloro-4^t-*t*-butylcyclohexanol (I)[6] and 2^c-chloro-4^c-*t*-butylcyclohexanol (II). The isomers, which were formed in nearly equal amounts (40% I, 48% II) were separated by chromatography.

The structures of I and II were assigned partly on the basis of dehydrochlorination experiments. Treatment of pure I with potassium *t*-butoxide produced *trans*-4-*t*-butylcyclohexene oxide (IX) in good yield. When I was heated with potassium hydroxide in isopropyl alcohol, the diaxial glycol X[7] was the major product. On the other hand, I gave 2^t-ethoxy-5^t-*t*-butylcyclohexanol (XI) when it was refluxed with potassium hydroxide in ethanol. These latter are the predicted products of diaxial opening[8] of the epoxide group of IX with hydroxide and ethoxide, respectively.

The *cis, cis* isomer(II) underwent base-catalyzed elimination to give 4-*t*-butylcyclohexanone, iso-

(1) Paper I. N. A. Le Bel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

(2) Supported by the Office of Ordnance Research, U. S. Army under Contract No. DA-20-018-ORD-20046.

(3) J. Sicher, F. Sipos, and M. Tichey, *Coll. of Czech. Chem. Comm.*, **26**, 847 (1961).

(4) D. Y. Curtin and R. J. Harder, *J. Am. Chem. Soc.*, 82, 2357 (1960).

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

(6) The nomenclature adopted in ref. 4 is utilized.

(7) This diol was identical with that formed by saponification of the hydroxy acetate mixture obtained in the peracetic acid oxidation of 4-*t*-butylcyclohexene. Epoxidation of the olefin with perbenzoic (*cf.* ref. 3) and monoperphthalic acids gave a mixture of the epoxides IX and XII in a ratio of about 1:1, as evidenced by lithium aluminum hydride reduction and infrared analysis of the mixture of *cis*-4-*t*-butyl- and *trans*-3-*t*-butylcyclohexanols. K. S. Sardessai, unpublished results.

(8) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 67 (1956).

lated as its 2,4-dinitrophenylhydrazone in 56% yield. No attempt was made to recover the anticipated by-product resulting from ring contraction.[4]

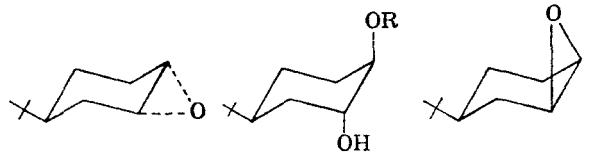
When *trans*-2-chloro-4-*t*-butylcyclohexanone was reduced with sodium borohydride only one chlorohydrin, 2^{e}-chloro-4^{t}-*t*-butylcyclohexanol (III) was obtained. Base treatment led to the formation of 4-*t*-butylcyclohexanone in 88% yield (as the 2,4-dinitrophenylhydrazone). This high yield is due to the facile *trans*-diaxial dehydrochlorination, and lends support to the *cis*-chlorine axial, hydroxyl equatorial nature of III.

Because it was unlikely that the mixture of diaxial chlorohydrins, to be obtained by hydrogen chloride opening of the mixture of 4-*t*-butylcyclohexene oxides, could be separated, a sample of the pure *cis*-epoxide (XII) was desired. This conversion was effected by the standard three-step sequence from the *trans*-epoxide (IX). Acetolysis of IX afforded the glycol monoacetate X (R=Ac) which was converted to the tosylate. Treatment with methoxide gave *cis*-4-*t*-butylcyclohexene oxide (XII). The reaction of XII with anhydrous hydrogen chloride afforded the diaxial chlorohydrin IV in quantitative yield.

TABLE I

Compound	Conformation	Stretching Frequency, Cm.$^{-1}$ O—H	C—OH	C—Cl
I	OH-e, Cl-e	3570	1065	728
II	OH-a, Cl-e	3560	956, 1007	728
III	OH-e, Cl-a	3560	1070	679
IV	OH-a, Cl-a	3605	950, 1007	702
X	OH-a, OH-a	3600	995, 1042	—
XI	OH-a, OC_2H_5-a	3600	995, 1079	—

Further support for the structure assignments to compounds I–IV is apparent in the infrared spectra and the pertinent data are summarized in Table I. The band positions for the C—OH and C—Cl stretching modes are consistent with the respective conformations of the two substituents.[9,10] The



IX. X. R=H XI. R=C_2H_5 XII.

frequency values for the O-H stretching bands are probably accurate only to about 10 cm.$^{-1}$; nevertheless the frequency shifts (ν *cis* and *trans*-4-*t*-butylcyclohexanol = 3615 cm.$^{-1}$) for compounds I–III are consistent with intramolecular hydrogen bonding. The corresponding values for compounds IV, X, and XI are due to the free O—H, and our measurements are not sufficiently precise to detect small amounts of flexible form that may be present.[3]

The diaxial chlorohydrin (IV) was found to be converted to the epoxide XII ($t_{1/2}$ at 25° = *ca.* 4 min.) at a rate much faster than the diequatorial isomer I undergoes transformation to IX ($t_{1/2}$ at 55° = 39 min.).

Each of the chlorohydrins was converted to the corresponding tosylate (V–VIII) in good yield.

EXPERIMENTAL[11]

Reduction of cis-2-chloro-4-t-butylcyclohexanone. To 50 g. (0.21 mole) of *cis*-2-chloro-4-*t*-butylcyclohexanone[5] dissolved in a benzene-absolute methanol mixture (2:7, 1175 ml.) was added 20 g. of sodium borohydride.[12] After stirring for 5 hr. at 20°, the excess borohydride was decomposed by the addition of 400 ml. of water. The mixture was stirred for an additional 0.5 hr. and was acidified with 10% hydrochloric acid. The products were extracted with benzene, and the extracts were washed with 10% sodium bicarbonate solution and water and were dried. Distillation of the benzene at atmospheric pressure gave 61.5 g. of crude liquid residue. The infrared spectrum of the liquid residue showed no absorption in the carbonyl region. The crude product was distilled at 62–63° (0.40–0.45 mm.) to yield 46.54 g. of a liquid, $n_D^{24.8}$ 1.4746. The freshly distilled mixture was chromatographed on 1 kg. of Merck acid-washed alumina. The column was eluted successively with 2475 ml. of 3% ether-pentane, 5175 ml. of 5% ether-pentane, 2925 ml. of 10% ether-pentane, and finally with 1350 ml. of 100% ether. Fractions of 225 ml. were collected. Fractions 2–30 solidified on standing and yielded white crystals. Fractions 31–37 afforded a colorless liquid which did not solidify. Fractions 38–53 yielded a pale yellow solid.

2^{e}-Chloro-4^{e}-t-butylcyclohexanol (II). The material from fractions 2–30 of the chromatography was combined to give 23.65 g. (46.8%). A portion of this was sublimed and white, cotton-like crystals were obtained, m.p. 48.5–49.5°.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 63.17; H, 9.96; Cl, 18.29.

2^{t}-Chloro-4^{t}-t-butylcyclohexanol (I). Fractions 38–53 were combined to give 20.20 g. (40.0%). A portion of this product was recrystallized several times from *n*-pentane and white crystals were obtained, m.p. 68–69°.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 62.71; H, 9.70; Cl, 18.70.

trans-4-t-Butylcyclohexene oxide (IX). A solution of potassium *t*-butoxide was prepared by dissolving 4.4 g. (0.108 g.-atom) of potassium in 300 ml. of dry *t*-butyl alcohol. To this was added slowly 20.0 g. (0.104 mole) of 2^{t}-chloro-4^{t}-*t*-butylcyclohexanol (I) and the mixture was stirred at 45–50° for 3.5 hr. The reaction mixture was cooled and poured into an ice water mixture. The aqueous layer was extracted with pentane. The extract was washed with dilute hydrochloric acid and sodium bicarbonate solution and was dried over anhydrous magnesium sulfate. Distilla-

(9) R. A. Pickering and C. C. Price, *J. Am. Chem. Soc.*, 80, 4931 (1958). A. Nickon, *J. Am. Chem. Soc.*, 79, 243 (1957). Cf. also ref. 5.

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Edition, Wiley, New York, 1958, p. 331.

(11) All melting and boiling points are uncorrected. Infrared spectra were obtained in carbon disulfide with a Beckman IR-4 recording spectrophotometer equipped with sodium chloride optics. Analyses are by Midwest Microlabs Inc., Indianapolis, Ind.

(12) D. H. R. Barton, D. A. Lewis, and J. F. McGhie, *J. Chem. Soc.*, 2907 (1957).

tion afforded 12.56 g. (77%) of *trans*-4-*t*-butylcyclohexene oxide (IX), b.p. 51° (0.5 mm.), n_D^{25} 1.4601 (lit.[3] b.p. 96–97° at 10 mm., n_D^{20} 1.4623).

2ᵗ-Hydroxy-4ᶜ-t-butylcyclohexanol (X). The *trans,trans*-chlorohydrin (I) (5 g., 0.027 mole) was treated with 100 ml. of 5% potassium hydroxide in dry isopropyl alcohol at 55° under a nitrogen atmosphere for 2 hr.[4] The product was isolated as described above and 4.0 g. of a yellow oil was obtained. This oil solidified upon standing and was recrystallized from *n*-pentane, m.p. 141–142°. The mother liquor (2.0 g.) was distilled and 0.21 g. of the *trans*-oxide (IX) was isolated, n_D^{25} 1.4602. Approximately 1 g. more of the solid was obtained, yielding a total of 2.7 g. (51%) of 2ᵗ-hydroxy-4ᶜ-*t*-butylcyclohexanol (X). A mixed melting point with the diol obtained from the peracetic acid epoxidation of 4-*t*-butylcyclohexene showed no depression.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.78; H, 11.67. Found: C, 69.69; H, 11.74.

2ᵗ-Ethoxy-5ᵗ-t-butylcyclohexanol (XI). The *trans,trans*-chlorohydrin (I) (1 g., 0.006 mole) was heated at reflux temperature for 24 hr. with 125 ml. of a 5% solution of potassium hydroxide in absolute ethanol. After the reaction mixture was worked up, 1.03 g. (98%) of a white crystalline solid was obtained. An analytical sample was recrystallized from pentane and melted at 95–97°.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.22; H, 12.08.

Reduction of trans-2-chloro-4-t-butylcyclohexanone. Ten grams (0.04 mole) of *trans*-2-chloro-4-*t*-butylcyclohexanone[5] was reduced with sodium borohydride by the procedure employed for the *cis*-chloro ketone. After distillation of the product, 9.5 g. of liquid which solidified immediately was obtained. Upon recrystallization from *n*-pentane 8.8 g. (87%) of crystalline 2ᶜ-chloro-4ᵗ-*t*-butylcyclohexanol (III), m.p. 76–77°, was recovered.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 62.71; H, 9.90; Cl, 18.48.

4-t-Butylcyclohexanone. A. Dehydrochlorination of II. The *cis,cis*-chlorohydrin (II) (1 g., 0.006 mole) was heated under reflux for 2 hr. with 125 ml. of a 5% solution of potassium hydroxide in methanol. The oil obtained on work-up was treated directly with an excess of 2,4-dinitrophenylhydrazine reagent. The precipitated hydrazone was purified by chromatography on alumina and elution with benzene. Pure 4-*t*-butylcyclohexanone 2,4-dinitrophenylhydrazone (1 g., 56%) was obtained and was recrystallized from 95% ethanol, m.p. 148.5–151.5°. A mixed melting point determination with an authentic sample (m.p. 151–152°) showed a m.p. of 149–152°.

B. Dehydrochlorination of III. By a procedure similar to that employed for the *cis,cis*-isomer (II) the *cis,trans*-chlorohydrin(III) (2.0 g. 0.01 mole) was converted to the 2,4-dinitrophenylhydrazone of 4-*t*-butylcyclohexanone, 3.1 g. (88%). After recrystallization from 95% ethanol, the derivative melted at 151–152° and showed no depression on admixture with an authentic sample.

2ᵗ-Acetoxy-5ᵗ-t-butylcyclohexanol (X. R = Ac). *trans*-4-*t*-Butylcyclohexene oxide (6.2 g., 0.04 mole) was treated with 50 ml. of glacial acetic acid and 2 drops of concd. sulfuric acid at 60° for 2 hr. The acidic reaction mixture was cooled, poured into 300 g. of crushed ice, and carefully neutralized with sodium carbonate. The product was extracted with ether, and the extracts were dried and concentrated. The crude residue, 8.9 g., show infrared absorption at 3510, 1740, and 1248 cm.$^{-1}$

2ᵗ-Acetoxy-5ᵗ-t-butylcyclohexyl tosylate. The crude hydroxy acetate (8.9 g.) was converted to the tosylate by way of the usual low temperature reaction with tosyl chloride and pyridine.[13] After workup, there was obtained 13 g. of a yellow oil. Trituration with pentane resulted in crystallization. The crystals were collected and washed several times with pentane to give 7.3 g. of acetoxy tosylate, m.p. 90–94°, infrared, 1740 and 1239 cm.$^{-1}$, no OH.

cis-4-t-Butylcyclohexene oxide (XII). 2ᵗ-Acetoxy-5ᵗ-*t*-butylcyclohexyl tosylate 6.75 g. (0.018 mole) was heated under reflux for 3 hr. with 50 ml. of a 2.5% solution of potassium hydroxide in absolute methanol.[14] After dilution of the reaction mixture with cold dilute hydrochloric acid, the product was extracted with pentane. The extract was washed, dried and concentrated and the concentrate was cooled. Approximately 0.30 g. of a solid, m.p. 150.5–151.5° was obtained. No attempt was made to identify this compound. The pentane filtrate was further concentrated and 2.25 g. of a yellow oil remained. Distillation afforded 2.03 g. (33%)[15] of *cis*-epoxide (XII), b.p. 58–59° (2.5 mm.), $n_D^{22.9}$ 1.4589 (lit.[3] b.p. 85° at 11 mm., n_D^{22} 1.4608).

2ᵗ-Chloro-4ᶜ-t-butylcyclohexanol (IV). A solution of 1.5 g. (0.009 mole) of the *cis*-epoxide (XII) in 225 ml. of anhydrous chloroform was saturated with dry hydrogen chloride. The mixture was allowed to stand for 24 hr. Cold water was added and the chloroform layer was separated and washed with sodium bicarbonate solution. The organic layer was dried and concentrated to give 1.9 g. of a crude yellow oil which solidified. Recrystallization from pentane afforded 1.75 g. (94%) of IV, m.p. 75–76°.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04; Cl, 18.60. Found: C, 62.86; H, 10.03; Cl, 18.60.

Chlorohydrin tosylates. Employing the usual procedure, 15 g. (0.08 mole) of the chlorohydrin II was converted to its tosylate (29.8 g.). Recrystallization from 95% ethanol produced 20.2 g. (74%) of 2ᶜ-chloro-4ᶜ-*t*-butylcyclohexyl tosylate (VI), m.p. 94.5–95.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 59.46; H, 7.37; Cl, 10.52.

2ᵗ-Chloro-4ᵗ-t-butylcyclohexyl tosylate (IV) was recrystallized from 95% ethanol, m.p. 88.5–89.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 59.31; H, 7.35; Cl, 10.24.

2ᶜ-Chloro-4ᵗ-t-butylcyclohexyl tosylate (VII) was recrystallized from 95% ethanol, m.p. 109–110°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; S, 9.29. Found: C, 58.94; H, 7.56; S, 9.58.

2ᵗ-Chloro-4ᶜ-t-butylcyclohexyl tosylate (VIII) was recrystallized from 95% ethanol, m.p. 116.5–117.5°.

Anal. Calcd. for $C_{17}H_{25}SO_3Cl$: C, 59.19; H, 7.31; Cl, 10.28. Found: C, 58.99; H, 7.42; Cl, 10.39.

Department of Chemistry
Wayne State University
Detroit 2, Mich.

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(15) Yield based on *trans*-4-*t*-butylcyclohexene oxide.

Preparation of Alkyl Chlorophosphines

Wm. A. Henderson, Jr., Sheldon A. Buckler, Nancy E. Day, and Martin Grayson

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Because of our need for certain alkyl chlorophosphines, we have evaluated the reported methods for converting primary and secondary alkyl phosphines to these valuable intermediates. The substituted phosphines are readily available from free radical[1] and base-catalyzed[2] reactions of phosphine with olefins.

(1) A. R. Stiles, F. F. Rust, and W. E. Vaughn, *J. Am. Chem. Soc.*, **74**, 3282 (1952).