

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Synthesis, Assignment of Configuration and Dehydration of *cis*- and *trans*-2-*t*-Butylcyclohexanol¹

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cis-2-*t*-Butylcyclohexanol was isolated from a mixture of *cis*- and *trans*-2-*t*-butylcyclohexanol (85% *cis* isomer) obtained from the catalytic reduction of *o*-*t*-butylphenol. *trans*-2-*t*-Butylcyclohexanol was obtained from a mixture of *cis* and *trans* isomers (85% *trans* isomer) which results from the reduction of 2-*t*-butylcyclohexanone with sodium in alcohol. Reduction of 2-*t*-butylcyclohexanone with lithium aluminum hydride gives a binary mixture of equal amounts of the isomeric alcohols. The configurational assignments are based on (a) the method of synthesis, (b) comparison of infrared spectra, (c) relative rates of esterification and oxidation and (d) products of dehydration. The isomeric alcohols were dehydrated by heating with *p*-toluenesulfonic acid and phosphoric acid. The only volatile dehydration products observed were 3-*t*-butylcyclohexene and/or 1-*t*-butylcyclohexene. Dehydration of the *cis*-alcohol with phosphoric acid gives 1-*t*-butylcyclohexene. The *trans*-alcohol gives a binary mixture of the *t*-butylcyclohexenes consisting of 60% of 1-*t*-butylcyclohexene. Dehydration of the *cis*-alcohol with *p*-toluenesulfonic acid gives a binary mixture of *t*-butylcyclohexenes consisting of 84% of 1-*t*-butylcyclohexene. Under similar conditions the product obtained from the *trans*-alcohol contains 68% of 1-*t*-butylcyclohexene. The isomeric *t*-butylcyclohexenes are interconverted under the conditions of the *p*-toluenesulfonic acid-catalyzed dehydration, but not under the conditions of the phosphoric acid-catalyzed dehydrations.

The isomeric 2-*t*-butylcyclohexanols were of interest in connection with a study of the kinetics and products of solvolysis of the *p*-toluenesulfonate derivatives. This paper describes the synthesis, assignment of configuration and products of dehydration of the isomeric 2-*t*-butylcyclohexanols. The kinetics and products of ethanolysis and acetylation of the *p*-toluenesulfonate derivatives of the isomeric alcohols are described in the following paper.³

The epimeric 2-*t*-butylcyclohexanols were obtained as mixtures by reduction of *o*-*t*-butylphenol and 2-*t*-butylcyclohexanone. Hydrogenation of *o*-*t*-butylphenol in the presence of a nickel catalyst gave a 95% yield of a mixture consisting substantially of 85% of the *cis* (I) and 15% of the *trans* isomer II. The composition of the product, which contained small amounts of a third component, was estimated from the percentage transmission at 10.34 μ (*cis*-alcohol) and 9.47 μ (*trans*-alcohol).

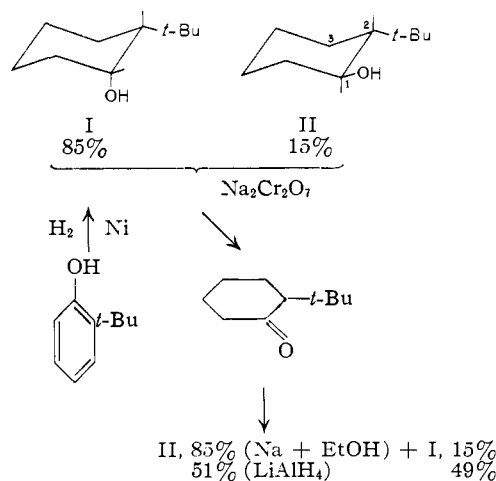
The catalytic reduction of *o*-*t*-butylphenol has been investigated previously by Schmerling⁴; however, configurations were not assigned to the isomeric 2-*t*-butylcyclohexanols and neither isomer was obtained in a pure form. In the present work it was found that the pure *cis* isomer can be obtained readily from the reduction product by recrystallization of the solid *p*-nitrobenzoate to constant melting point.

Reduction of 2-*t*-butylcyclohexanone⁴ with sodium and alcohol gave a mixture of alcohols (85% *trans*, 15% *cis*) from which pure *trans*-2-*t*-butylcyclohexanol (II) was readily obtained by recrystallization. That the compound obtained by this method is indeed the epimer of the one described above was demonstrated by the oxidation of both isomers to 2-*t*-butylcyclohexanone. The reduction of 2-*t*-butylcyclohexanone with lithium aluminum hydride gave a binary mixture of I and II consist-

ing of 51% of the *trans* isomer II. The melting points of the isomeric alcohols and of several derivatives are given in Table I. The melting points of all of the solid compounds included in Table I were depressed by the corresponding geometric isomer. The transformations involved in the preparation of the *t*-butylcyclohexanols are illustrated below.

TABLE I
MELTING POINTS OF THE ISOMERIC 2-*t*-BUTYLCYCLOHEXANOLS AND DERIVATIVES

Isomer	Alcohol	<i>p</i> -Nitrobenzoate, °C.	Naphthylcarbamate, °C.	<i>p</i> -Toluenesulfonate, °C.	Acetate, °C.
<i>cis</i>	56.8–57.7	88.8–89.2	161.4–162	69–70 dec.	34.5–35.4
<i>trans</i>	84.4–85.0	48.1–49.9	129.8–131	66.5–66.8	Oil



An interesting structural feature of the 2-*t*-butylcyclohexyl system is that both stereoisomers are presumably conformationally homogeneous. Scale models indicate that non-bonded steric interactions preclude chair conformations with an axial *t*-butyl group. Winstein and Holness⁵ have estimated that the two chair conformations of *t*-butylcyclohexane differ in stability by 5.4–5.8 kcal./mole. It appears that the difference is at least this large since examination of scale models

(1) This work was supported in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) (a) Socony-Vacuum Oil Co. Fellow, 1953–1954; (b) Carbide and Carbon Fellow, 1955–1956.

(3) H. L. Goering and R. L. Reeves, *THIS JOURNAL*, **78**, 4931 (1956).

(4) L. Schmerling, *ibid.*, **69**, 1121 (1947).

(5) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

indicates that the chair form with an axial *t*-butyl group is more strained than boat conformations. These in turn are at least 5–6 kcal./mole (the difference in strain energy between the boat and chair form of a cyclohexane ring⁶) less stable than the chair form with an equatorial *t*-butyl substituent. Thus it appears that each of the isomeric 2-*t*-butylcyclohexanols (and the corresponding derivatives listed in Table I) is conformationally homogeneous with the *t*-butyl group in an equatorial position as represented in the above illustrations.

The indicated configurational assignments are based on several independent observations all of which are consistent. The preponderant formation of the *trans*-alcohol I from the reduction of 2-*t*-butylcyclohexanone with sodium in alcohol is consistent with previous observations that *trans*-alcohols (the epimer with an equatorial hydroxyl group) generally predominate when 2-alkylcyclohexanones are reduced by this method.^{6,7} Similarly, the preponderant formation of the *cis*-alcohol II from the hydrogenation of *o*-*t*-butylphenol parallels previous observations⁸ that *o*-alkyl or arylphenols are converted primarily to the *cis*-2-substituted cyclohexanols under conditions similar to those used in the present work.

The infrared spectra of the isomeric 2-*t*-butylcyclohexanols are also consistent with the configurational assignments. It has been pointed out recently⁹ that a cyclohexanol with an equatorial hydroxyl can be distinguished from the epimer with an axial hydroxyl by the relative intensities of absorption at 2.9 μ (hydrogen-bonded hydroxyl) and 2.75 μ (unassociated hydroxyl). The ratio of the optical densities at 2.9 and 2.75 μ is considerably higher for carbon disulfide solutions (0.4 *M*) of *trans*-2-*t*-butylcyclohexanol than for similar solutions of the *cis*-alcohol.

trans-2-*t*-Butylcyclohexanol, which has an equatorial hydroxyl group, is esterified more rapidly and oxidized more slowly than the *cis* isomer as would be expected.^{6,10} An indication of the relative rates of esterification was obtained from the length of time required for the formation of a noticeable precipitate of pyridine hydrochloride in the reaction of the alcohols with *p*-toluenesulfonyl chloride in dry pyridine at 0°. Each isomer was esterified a number of times under identical conditions; with the *trans*-alcohol a detectable precipitate was observed after about two hours whereas with the *cis* isomer about two days were required. An indication of the relative rates of oxidation of the isomeric alcohols by potassium dichromate was obtained by interrupting the reactions and determining the compositions of the isolated binary mixtures of 2-*t*-butylcyclohexanone and unreacted alcohol. Under conditions where the *trans* isomer was oxidized to the extent of 33%, the *cis* isomer was oxidized to the extent of 58%.

(6) W. Klyne, in W. Klyne, "Progress in Stereochemistry," Academic Press, Inc., New York, N. Y., 1954, Chap. II.

(7) G. Vavon, *Bull. soc. chim.*, [4] **49**, 937 (1931).

(8) C. C. Price and J. Karabinos, *THIS JOURNAL*, **62**, 1159 (1940), and references therein.

(9) E. G. Peppiatt and R. J. Wicker, *J. Chem. Soc.*, 3122 (1955).

(10) D. H. R. Barton, *ibid.*, 1027 (1953).

Dehydration of *cis*- and *trans*-2-*t*-Butylcyclohexanol.—The isomeric alcohols were dehydrated by heating with *p*-toluenesulfonic acid (200°) or by heating with 85% phosphoric acid (130–150°). The reactions were carried out so that the formation of gaseous products could be detected and the volatile products were identified by their infrared spectra. In all cases the spectrum of the isolated product corresponded to that of 1-*t*-butylcyclohexene or a mixture of 1- and 3-*t*-butylcyclohexene and there was no evidence for the formation of other distillable products. The compositions and yields of the *t*-butylcyclohexene isolated from the dehydrations are summarized in Table II. As indicated in this table, the *p*-toluenesulfonic acid-catalyzed dehydrations gave lower yields of olefin (and greater amounts of undistillable tars) than the phosphoric acid-catalyzed dehydrations.

TABLE II
PRODUCTS OF DEHYDRATION OF *cis*- AND *trans*-2-*t*-BUTYLCYCLOHEXANOL

Isomer	Method ^a	Yield, ^b %	% composition ^c 1- <i>t</i> -butyl- cyclohexene
<i>cis</i>	CH ₃ C ₆ H ₄ SO ₃ H	48	84
<i>trans</i>	CH ₃ C ₆ H ₄ SO ₃ H	38	68
<i>cis</i>	H ₃ PO ₄	85	100
<i>trans</i>	H ₃ PO ₄	83	60

^a *p*-Toluenesulfonic acid-catalyzed reactions were carried out at 200°; phosphoric acid-catalyzed reactions were carried out at 135–150°. ^b Yield of *t*-butylcyclohexene. ^c Composition of binary mixture of 1- and 3-*t*-butylcyclohexene; accuracy estimated to be $\pm 2\%$.

The compositions of the binary mixtures of 1- and 3-*t*-butylcyclohexene were determined from relative intensities of bands at 9.67 μ (1-isomer) and 10.2 μ (3-isomer). By this analytical method the composition of synthetic mixtures could be determined to within $\pm 2\%$.

For comparison purposes pure 1-*t*-butylcyclohexene was prepared by dehydration of 1-*t*-butylcyclohexanol,¹¹ and pure 3-*t*-butylcyclohexene was prepared by the reaction of *t*-butylmagnesium bromide with 3-bromocyclohexene. That the homogeneous products obtained by these reactions were *t*-butylcyclohexenes was demonstrated by the reduction of each to *t*-butylcyclohexane.

When 1-*t*-butylcyclohexene was heated with *p*-toluenesulfonic acid to 200° the recovered olefin was found to be partially isomerized to 3-*t*-butylcyclohexene and a considerable amount of undistillable tar was formed. Although these conditions differ from those of the dehydration experiments—during dehydration most of the olefin distilled from the reaction mixture as formed—the results of this control experiment suggests that the *t*-butylcyclohexenes are partially isomerized under the conditions of the *p*-toluenesulfonic acid-catalyzed dehydrations.

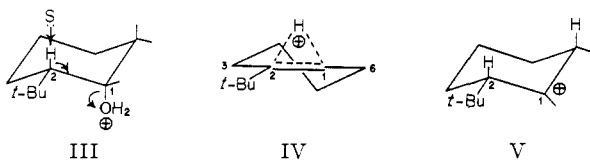
Both 1- and 3-*t*-butylcyclohexene were isomerized to only a slight extent when heated with phosphoric acid. This shows that the 1-*t*-butylcyclohexene isolated from the dehydration of the *cis*-alcohol was the only olefin formed. Even though the olefins are not interconverted under the

(11) L. Bateman and R. P. Koch, *ibid.*, 600 (1944).

conditions of the dehydration of *trans*-alcohol with phosphoric acid it does not necessarily follow that the composition of the isolated product corresponds to the composition of the kinetically controlled product. It is possible that the conversion of olefin to non-volatile tars, which were formed in all of the dehydrations, results in fractionation of the mixture of olefins. Thus the composition of the isolated product cannot be taken as a measure of the relative rates of elimination in the two directions.

The fact that the compositions of the dehydration products differ for the isomeric alcohols shows that dehydration of both isomers does not proceed entirely *via* the 2-*t*-butylcyclohexyl carbonium ion (a common intermediate for both isomers). The present results parallel previous observations that different products result from the dehydration of the isomeric 2-phenylcyclohexanols with phosphoric acid.^{8,12} It has been pointed out^{6,10} that in general different products result from the dehydration of epimeric cyclohexanols.

As shown in Table II, with phosphoric acid the *cis*-alcohol is converted to 1-*t*-butylcyclohexene, one of the two possible *trans* elimination products. Two mechanisms have been suggested to account for the apparently preferred *trans* elimination in reactions of this type and the present observation appears to be consistent with either of these. These are: (a) an E₂-type process in which a solvent molecule (S) acts as the base as illustrated by III^{5,13} and (b) an E₁-type elimination in which a bridged cation IV represents the only intermediate.^{5,14} It is clear that the dehydration of the *cis*-alcohol does not involve a classical 2-*t*-butylcyclohexyl carbonium ion V since there is evidence that this ion is not converted exclusively to 1-*t*-butylcyclohexene. This is indicated by the mixture of *t*-butylcyclohexenes resulting from the dehydration of the *trans*-alcohol which likely involves V as an intermediate and by the acid-catalyzed (CH₃C₆H₅SO₃H) interconversion of the *t*-butylcyclohexenes which presumably involves V as an intermediate.



The clean conversion of the *cis* alcohol to 1-*t*-butylcyclohexene is somewhat surprising. For the E₂-type process (III) the opposite orientation might be predicted since the reactive species is presumably an 'onium compound and the Hoffman rule might be expected to apply. Indeed, regard-

(12) C. C. Price, J. A. McCoy and E. Eliel, Abstract of Papers Presented before the Division of Organic Chemistry of the American Chemical Society, Minneapolis, Minn., Sept., 1955, p. 55-O; C. J. Collins and H. J. Schaeffer, *ibid.*, p. 56-O; H. J. Schaeffer and C. J. Collins, *THIS JOURNAL*, **78**, 124 (1956).

(13) P. D. Bartlett in Gilman, "Organic Chemistry, An Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 52; D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951).

(14) S. Winstein and B. K. Morse, *THIS JOURNAL*, **74**, 1134 (1952).

less of whether polar¹⁵ or steric¹⁶ factors are considered to determine the orientation in E₂-eliminations of 'onium compounds, the conjugate acid of the *cis*-alcohol might be expected to give a preponderant amount of 3-*t*-butylcyclohexene by an E₂-type process. Perhaps the observed Saytzeff orientation is indicative that an E₂-type process is not involved. For the process involving the bridged ion IV, preponderant formation of 1-*t*-butylcyclohexene would be expected since C₂ is more favorably substituted¹⁷ than C₆ for the formation of a bridged ion simultaneous with the C₁-oxygen bond cleavage. Saytzeff orientation is generally attributed to parallelism between rates and heats of reaction, *i.e.*, the more stable product is formed the fastest.¹⁵ Brown and co-workers^{16,18} recently have shown that steric strains, as well as hyperconjugation,¹⁵ need be considered in assessing the relative stabilities of the two possible elimination products (and the corresponding transition states). It seems likely that steric factors may be responsible to a large extent for the orientation observed in the present case. That is, the non-bonded steric interactions in 3-*t*-butylcyclohexene (with the *t*-butyl group in a pseudo-equatorial¹⁹ position) may be larger than in 1-*t*-butylcyclohexene in which the ring carbon containing the *t*-butyl group is planar.

In the *trans*-alcohol the fixed geometry precludes a concerted *trans* elimination and it seems likely that in this case dehydration involves the initial formation of V followed by the loss of an axial hydrogen²⁰ to give olefin.

It is interesting to note that ring contraction (migration of C₃ from C₂ to C₁) is not involved in the dehydration of the equatorial *trans*-alcohol. Ring contraction is generally involved in dehydrations of equatorial alcohols if C₂ is suitably substituted¹⁷ for this type of Wagner-Meerwein rearrangement. For example, ring contraction occurs if C₂ is substituted with (a) two alkyl groups,^{6,10} (b) an alkyl and a hydroxyl group,⁶ (c) a hydroxyl group,⁶ or a phenyl group.¹² Evidently a single alkyl substituent at C₂ is not sufficient for ring contraction. This is also indicated by the observation that ring contraction is not involved in the dehydration of *trans*-2-methylcyclohexanol.²¹

It is also of interest that cleavage of the C₂-*t*-butyl bond does not occur. Whitmore and co-workers²² have observed that in a number of cases

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. VIII.

(16) H. C. Brown and I. Moritani, *THIS JOURNAL*, **78**, 2203 (1956), and previous papers in this series.

(17) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1112 (1952).

(18) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

(19) D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954).

(20) It seems likely that the proton eliminated from a carbonium ion will be one which is perpendicular to the plane of the σ -bonds of the planar positive carbon atom, *i.e.*, the C-H bond is in the same plane as the vacant *p*-orbital of the positive carbon. According to this interpretation only adjacent axial hydrogen atoms will be eliminated from cyclohexyl cations and if the conformation is fixed as in the present system, E₁ eliminations with an equatorial leaving group will result in *cis* elimination.

(21) C. C. Price, *THIS JOURNAL*, **61**, 1847 (1939).

(22) F. C. Whitmore, *Chem. Eng. News*, **26**, 671 (1948); F. C. Whitmore and E. E. Stahly, *THIS JOURNAL*, **67**, 2158 (1945); **55**, 4153 (1933); see also W. A. Mosher, *ibid.*, **69**, 2139 (1947).

C₂-C₃ bond cleavage results from carbonium ion reactions if C₃ is a quaternary carbon atom. In the present system this type of elimination would result in the formation of cyclohexene and a *t*-butylcarbonium ion which would presumably be converted to isobutene. Neither of these cleavage products was observed and a control experiment demonstrated that cyclohexene, if formed, would survive the conditions of the dehydration and product isolation. Apparently cleavage cannot compete with dehydration (without rearrangement) because in the present system the *t*-butyl group, unlike the C₂ and C₆ axial hydrogen atoms, is not in a favorable position²⁰ for elimination.

Experimental²³

cis-2-*t*-Butylcyclohexanol.—2-*t*-Butylphenol²⁴ (375 g.) was hydrogenated at 200° and 4900 p.s.i. using a nickel-on-kieselguhr catalyst²⁵ according to the method of Schmerling.⁴ After removal of the catalyst (filtration) and solvent (distillation), 368 g. (95% yield) of hydrogenation product, b.p. 82–112° (20 mm.), was obtained. Infrared analysis shows that this product consists of 84% of the *cis* and 16% of *trans* isomer together with minor amounts of other materials. Bands at 10.34 μ (*cis* isomer) and 9.47 μ (*trans* isomer) were used for this analysis. At room temperature this material was a solid contaminated with a viscous oil which was partly removed by filtration.

The crude (solid) *cis*-2-*t*-butylcyclohexanol, 320 g., was converted to *cis*-2-*t*-butylcyclohexyl *p*-nitrobenzoate, m.p. 88.8–89.2° (absolute ethanol), in 82% yield using a previously described²⁶ general procedure.

Anal. Calcd. for C₁₇H₂₃NO₄: C, 66.86; H, 7.59. Found: C, 67.18; H, 7.63.

The *p*-nitrobenzoate was saponified, using 1.3 *N* sodium hydroxide in 90% ethanol. The product was steam distilled from the alkaline medium and extracted with ether from the distillate. After removal of ether and ethanol from the dried extracts and distillation of the residue, *cis*-2-*t*-butylcyclohexanol, b.p. 99–103° (23 mm.), m.p. 56.8–57.7°, was obtained in 93% yield.

Anal. Calcd. for C₁₀H₂₀O: C, 76.86; H, 12.90. Found: C, 76.62; H, 12.82.

cis-2-*t*-Butylcyclohexyl α-naphthylcarbamate²⁷ melted at 161.4–162.0° (ethanol).

Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36. Found: C, 77.52; H, 8.18.

cis-2-*t*-Butylcyclohexyl *p*-toluenesulfonate was prepared by a modification of the general method of Tipson.²⁸ In a typical preparation 2.00 g. (12.8 mmoles) of *cis*-2-*t*-butylcyclohexanol was added to a chilled (0°) solution of 2.44 g. (12.8 mmoles) of *p*-toluenesulfonyl chloride in 7 ml. of dry pyridine and the reaction mixture was stored in a refrigerator at 0° for 28 days. The solution was poured into ice-cold 6 *N* hydrochloric acid and the *p*-toluenesulfonate was separated from the aqueous acid by ether extraction. The solid *p*-toluenesulfonate obtained by evaporation of the ether was recrystallized twice from petroleum ether at low temperatures and 1.65 g. of material which melted at 61.2° (dec.) was obtained. Repeated recrystallizations from petroleum ether raised the melting point to the constant value of 69–70° (dec.). The yields of 18 preparations varied from 23–86%.

Anal. Calcd. for C₁₇H₂₃O₃S: C, 65.77; H, 8.44; solvolysis equiv., 172.26. Found: C, 65.84; H, 8.66; solvolysis equiv., 173.2.²⁹

(23) All melting points are corrected. Boiling points are uncorrected.

(24) H. Hart, *THIS JOURNAL*, **71**, 1966 (1949).

(25) We are indebted to the Universal Oil Products Co. for supplying us with this catalyst.

(26) H. L. Goering and J. P. Blanchard, *THIS JOURNAL*, **76**, 5405 (1954).

(27) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 196.

(28) R. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(29) Determined from the "infinity titer" of solvolysis experiments.

cis-2-*t*-Butylcyclohexyl acetate, m.p. 34.5–35.4° (aqueous ethanol), was prepared from pure *cis*-2-*t*-butylcyclohexanol and acetic anhydride.³⁰

Anal. Calcd. for C₁₂H₂₀O₂: C, 72.68; H, 11.18. Found: C, 72.49; H, 11.01.

trans-2-*t*-Butylcyclohexanol.—2-*t*-Butylcyclohexanone was prepared by oxidizing 2-*t*-butylcyclohexanol (obtained from the reduction of 2-*t*-butylphenol) with sodium dichromate in sulfuric acid.³¹ The ketone, b.p. 75–79° (12 mm.), *n*_D²⁵ 1.4570 (lit.⁴ b.p. 62.5° (4 mm.), *n*_D²⁵ 1.4579) was obtained in 91% yield. Lower yields (65%) were obtained from the previously described⁴ chromium trioxide oxidation of 2-*t*-butylcyclohexanol.

2-*t*-Butylcyclohexanone 2,4-dinitrophenylhydrazone was prepared from the ketone in the usual manner and melted at 162–162.5° (ethanol).

Anal. Calcd. for C₁₈H₂₂N₄O₄: C, 57.47; H, 6.63. Found: C, 57.59; H, 6.64.

trans-2-*t*-Butylcyclohexanol was obtained from *t*-butylcyclohexanone as follows: To a stirred solution of 10.0 g. (0.0648 mole) of *t*-butylcyclohexanone in 88 ml. of absolute ethanol was added 4.52 g. (0.196 mole) of sodium at such a rate as to maintain gentle refluxing. When all of the sodium had reacted the reaction mixture was diluted with 110 ml. of water and the resulting solution was extracted with ether. The ether and ethanol were removed from the dried extracts. The crude product, m.p. 65–76°, weighed 9.7 g. (96%), and consisted of about 81% *trans*-alcohol, 14% *cis*-alcohol and ca. 5% unreacted ketone (estimated from absorption at 5.88 μ). After 5 recrystallizations from petroleum ether 4.4 g. of pure *trans*-2-*t*-butylcyclohexanol, m.p. 84.4–85.0°, was obtained. This material depressed the m.p. of the *cis* isomer, m.p. 57°.

Anal. Calcd. for C₁₀H₂₀O: C, 76.86; H, 12.90. Found: C, 76.69; H, 12.98.

Lithium aluminum hydride reduction of 2-*t*-butylcyclohexanone gave a 98% yield of white solid, m.p. 45–65°, which contained 51 ± 2% *trans*-alcohol and 49 ± 2% *cis*-alcohol.

trans-2-*t*-Butylcyclohexyl *p*-nitrobenzoate, m.p. 48.1–49.9° (ethanol), was prepared in yields of 32–59%, by the method used for the preparation of the *cis* isomer.

Anal. Calcd. for C₁₇H₂₃NO₄: C, 66.86; H, 7.59. Found: C, 67.22; H, 7.30.

trans-2-*t*-Butylcyclohexyl α-naphthylcarbamate had m.p. 129.8–131.0° (ethanol).

Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36. Found: C, 77.47; H, 8.29.

trans-2-*t*-Butylcyclohexyl acetate, b.p. 99.7° (15 mm.), *n*_D²⁵ 1.4530, was prepared by the method used for the preparation of the *cis* isomer.

Anal. Calcd. for C₁₂H₂₀O₂: C, 72.68; H, 11.18. Found: C, 72.68; H, 11.23.

trans-2-*t*-Butylcyclohexyl *p*-toluenesulfonate, m.p. 66.5–66.8° (petroleum ether), was obtained in yields of 80–100% by the procedure described above for the preparation of the *cis* isomer.

Anal. Calcd. for C₁₇H₂₃O₃S: C, 65.77; H, 8.44. Found: C, 66.06; H, 8.49.

trans-2-*t*-Butylcyclohexanol reacts faster than the *cis* isomer with *p*-toluenesulfonyl chloride in dry pyridine. A precipitate of pyridine hydrochloride is formed in about 2 hr. at 0° with the *trans*-alcohol and in about 2 days with the *cis*-alcohol. Consequently, shorter reaction times (7 to 8 days) were used for the preparation of the *trans*-tosylate than for the preparation of the *cis*-tosylate (9–28 days).

Oxidation of *cis*- and *trans*-2-*t*-Butylcyclohexanol to 2-*t*-Butylcyclohexanone.—A solution of 1.1 g. (0.011 mole) of chromium trioxide in 1 ml. of water and 5.5 ml. of acetic acid was added to a solution of 1 g. (0.0064 mole) of *cis*-2-*t*-butylcyclohexanol in 3 ml. of acetic acid. The mixture was allowed to stand at room temperature for 2.5 hours after which it was steam distilled. The distillate was extracted with ether and after washing (sodium bicarbonate solution) and drying (saturated brine) the combined ether extracts,

(30) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 138.

(31) E. Beckmann, *Ann.*, **250**, 325 (1889).

the solvent was removed by evaporation. The residual ketone was converted to 2-*t*-butylcyclohexanone 2,4-dinitrophenylhydrazone, m.p. 161.9–162.3° (ethanol).

When this procedure was repeated using *trans*-2-*t*-butylcyclohexanol, 2-*t*-butylcyclohexanone 2,4-dinitrophenylhydrazone, m.p. 161.9–162.5° (ethanol), was obtained which did not depress the m.p. of the derivative derived from *cis*-2-*t*-butylcyclohexanol.

The relative rates of oxidation of the epimeric 2-*t*-butylcyclohexanols were determined by analyzing partially oxidized mixtures. Two grams (0.0128 mole) of each epimer was treated with 10.0 ml. of a solution of 5.3 g. of potassium dichromate in 38.5 ml. of water and 2.5 ml. of 98% sulfuric acid. The resulting solutions were thermostated at 50° for 25 min. after which the solutions were diluted with water and extracted three times with ether. The ether extracts were washed with water and dried over magnesium sulfate. After removal of the solvent the compositions of the two mixtures were determined by infrared analysis. Bands at 8.88 μ (ketone) and 10.34 μ (*cis*-alcohol) were used to analyze the mixture resulting from *cis*-2-*t*-butylcyclohexanol, and bands at 8.88 and 9.47 μ (*trans*-alcohol) were used to determine the composition of the mixture resulting from *trans*-2-*t*-butylcyclohexanol. Under the specified conditions *cis*-2-*t*-butylcyclohexanol is 54% oxidized and the *trans*-alcohol is oxidized to the extent of 33%.

1-*t*-Butylcyclohexene.—Nine grams (0.0577 mole) of 1-*t*-butylcyclohexanol,¹¹ m.p. 48.8–51° (lit.¹¹ m.p. 49–50°) was dehydrated by heating to 200° with several crystals of iodine.¹¹ The mixture of water and hydrocarbon which distilled from the reaction mixture was extracted with petroleum ether, b.p. 60–68°, and after drying over magnesium sulfate the petroleum ether solution was passed through an alumina-packed column to remove the iodine which distilled with the hydrocarbon. The petroleum ether solution was fractionated with an efficient wire spiral column and 1.03 g. (13%) of material with a constant boiling point of 166.5° (735 mm.) was collected in four fractions, after a forerun, b.p. 152–166.5°. The physical properties of these fractions, n_D^{25} 1.4596, d_4^{25} 0.8276 (lit.¹¹ b.p. 51° (14 mm.), n_D^{15} 1.4636) including infrared spectra were indistinguishable indicating the material to be homogeneous. This material was shown to be 1-*t*-butylcyclohexene by chemical analysis and by catalytic reduction (platinum oxide) to *t*-butylcyclohexane which was identified by its infrared spectrum.³³

3-*t*-Butylcyclohexene.—An ether solution containing 1 mole of *t*-butylmagnesium chloride³⁴ was added dropwise to a solution of 56.3 g. (0.35 mole) of 3-bromocyclohexene³⁵ in 50 ml. of ether. After the addition was complete the reaction mixture was stirred for 2 hours, and the excess Grignard reagent was decomposed by the slow addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted four times with ether. The combined organic layers were dried (calcium chloride) and distilled to remove the ether. The residue was fractionated and 10.1 g. (21%) of material, b.p. 170.5° (746 mm.), was collected in 6 fractions after a forerun, b.p. 64–170°. The physical properties of these fractions, n_D^{25} 1.4568, d_4^{25} 0.8203, MR 45.9 (calcd. 45.7), including infrared spectra were indistinguishable indicating the material to be homogeneous.³²

Anal. Calcd. for C₁₀H₁₈: C, 86.89; H, 13.11. Found: C, 87.15; H, 12.89.

This material was reduced to *t*-butylcyclohexane (identified by its infrared spectrum³³) by the same method used to reduce 1-*t*-butylcyclohexene to *t*-butylcyclohexane.

Both 1- and 3-*t*-butylcyclohexene are sensitive to air oxidation at room temperature. For this reason samples were stored at 0° and peroxides were removed prior to use by

(32) The physical properties (refractive index and infrared spectrum) of both 1- and 3-*t*-butylcyclohexene change when samples are exposed to air. Evidently the olefins are quite sensitive to air oxidation. This behavior is similar to that reported for 1-methylcyclohexene (ref. 21).

(33) Infrared Spectral Data, National Bureau of Standards A.P.I. Project 44, Serial No. 559.

(34) S. V. Puntambekar and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, 2nd ed., p. 524.

(35) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **561**, 80 (1942).

passing a petroleum ether solution of the cycloalkene through an alumina-packed column. The infrared spectrum and refractive index of the material remaining after removal of the petroleum ether were indistinguishable from those of the pure cycloalkene.

Dehydration of *cis*- and *trans*-2-*t*-Butylcyclohexanol. (a) With *p*-Toluenesulfonic Acid.—Dehydrations were carried out in a reaction flask attached to a Vigreux column equipped with a variable take-off still-head. Ice-water was circulated through the condenser and the receiver was cooled in an ice-bath. The side arm of the receiver was connected to a gas trap immersed in a Dry Ice-acetone-bath. In a typical run 13.0 g. (0.86 mole) of *cis*-2-*t*-butylcyclohexanol and 2.0 g. of *p*-toluenesulfonic acid were heated in the reaction flask to 200°. Heating was continued until distillation ceased (about 2 hr.). The material condensed in the gas trap was measured by connecting the trap to a gas buret and amounted to <1% (calculated as isobutylene but not identified).

The distillate and residue were combined, washed with aqueous sodium carbonate, dried over magnesium sulfate, and fractionated with an efficient wire spiral column. After a small forerun (0.41 g.), b.p. 105–165°, n_D^{25} 1.4528, the remaining volatile material, 5.85 g. (49%), distilled at 165–167° and had physical properties including infrared spectra corresponding to a binary mixture of 1-*t*-butylcyclohexene and 3-*t*-butylcyclohexene.

The composition of this binary mixture was found to be 84% 1-*t*-butylcyclohexene and 16% 3-*t*-butylcyclohexene by infrared analysis (see below). The absence of a third component was indicated by the fact that the spectrum of the mixture was a composite of the spectra of the pure components. There was no evidence for the formation of cyclohexene, b.p. 83°, n_D^{25} 1.4451. The residue from the fractionation (3.05 g.) was not investigated.

The product obtained from the dehydration of *trans*-2-*t*-butylcyclohexanol in 38% yield was a binary mixture consisting of 68% 1-*t*-butylcyclohexene and 32% 3-*t*-butylcyclohexene (infrared analysis). No gaseous products were formed and as in the case of the *cis* isomer there was no evidence for the formation of cyclohexene.

In order to determine whether cyclohexene, if formed, could survive and be isolated by the above procedure it was refluxed over *p*-toluenesulfonic acid for 2 hours. The resulting dark mixture was distilled and 60% of the cyclohexene was recovered.

To determine if the *t*-butylcyclohexenes are interconverted under the conditions of the dehydration, 1-*t*-butylcyclohexene was refluxed over *p*-toluenesulfonic acid for 1.5 hr. Most of the cycloalkene was converted to a non-volatile tar and the material which distilled was a binary mixture consisting of 17% 3-*t*-butylcyclohexene and 83% 1-*t*-butylcyclohexene.

(b) With Phosphoric Acid.—*cis*-2-*t*-Butylcyclohexanol (16.4 g., 0.11 mole) and 23 g. of 85% phosphoric acid were heated in the above described apparatus at 130–150° for 5 hr. No material distilled and no gases were evolved. After cooling, water was added and the mixture was extracted with petroleum ether (60–68°). After washing with aqueous sodium carbonate the dried organic layer was passed through an alumina column to remove polar and colored impurities. Control experiments showed that this process did not result in the fractionation (or isomerization) of a binary mixture of 1- and 3-*t*-butylcyclohexene. The petroleum ether solution was fractionated, and after a 1.47-g. forerun (consisting of petroleum ether and 1-*t*-butylcyclohexene) the remaining volatile material, 3.0 g. (20%), distilled at 168–168.5° and was shown by infrared analysis to be 1-*t*-butylcyclohexene containing <1% 3-*t*-butylcyclohexene. This material was collected in 4 fractions having physical properties including infrared spectra that were indistinguishable from each other and from that of pure 1-*t*-butylcyclohexene.

trans-2-*t*-Butylcyclohexanol was dehydrated by this procedure and a binary mixture of *t*-butylcyclohexenes was obtained in 83% yield. This mixture consisted of 60% 1-*t*-butylcyclohexene and 40% 3-*t*-butylcyclohexene.

In order to determine if the products are stable under the conditions of the dehydration 1.17 g. of 1-*t*-butylcyclohexene was heated with 1.0 g. of 85% phosphoric acid at 130–150° for 7.5 hr. The product was isolated as described above and the composition of the recovered binary mixture was

found to be 95% 1-*t*-butylcyclohexene and 5% 3-*t*-butylcyclohexene.

When a sample of 3-*t*-butylcyclohexene was heated with phosphoric acid at 130–160° for 2 hr. the composition of the recovered binary mixture was 6% 1-*t*-butylcyclohexene and 94% 3-*t*-butylcyclohexene. These experiments demonstrate that the *t*-butylcyclohexenes are isomerized to only a slight extent under the conditions of the dehydration.

Infrared Analysis. A. *cis*- and *trans*-2-*t*-Butylcyclohexanols.—The relative transmittances at 9.47 μ (*trans*) and

10.34 μ (*cis*) were measured for synthetic mixtures of *cis*- and *trans*-alcohols (0.4 *M* solutions in CS₂, using 0.1-mm. cells). The compositions of unknown mixtures were read from a plot of the transmittance ratio against percentage composition.

B. 1- and 3-*t*-Butylcyclohexene.—Compositions of unknown mixtures of the olefins were determined by comparison of the absorption intensities at 9.67 μ (1-isomer) and 10.02 μ (3-isomer) with those of synthetic mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

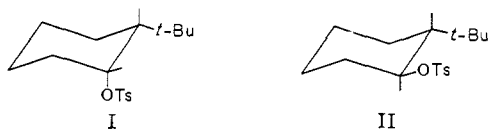
The Solvolysis of *cis*- and *trans*-2-*t*-Butylcyclohexyl *p*-Toluenesulfonate^{1,2}

By HARLAN L. GOERING AND RICHARD L. REEVES³

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The kinetics and products of solvolysis of *cis*- and *trans*-2-*t*-butylcyclohexyl *p*-toluenesulfonate in acetic acid and in ethanol have been investigated. The *cis* (*axial*) isomer is ethanolyzed 5 times faster (30°) and acetolyzed 2 times faster (50°) than the *trans* (*equatorial*) isomer. Both isomers are solvolyzed considerably faster than cyclohexyl *p*-toluenesulfonate; e.g., the *trans* isomer is ethanolyzed 300 times faster (30°) and acetolyzed 240 times faster (50°) than cyclohexyl *p*-toluenesulfonate. The high reactivity of the isomeric 2-*t*-butylcyclohexyl *p*-toluenesulfonates as compared to cyclohexyl and the isomeric 3- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates is attributed to steric acceleration. Only elimination products were isolated from the ethanolysis experiments. The *cis* (*axial*) isomer is converted to 1-*t*-butylcyclohexene and the *trans* (*equatorial*) isomer gives 53% 1- and 47% 3-*t*-butylcyclohexene. Acetolysis of both isomers gives 87–90% olefin together with 2-*t*-butylcyclohexyl acetate. The olefin from the *cis* isomer is 1-*t*-butylcyclohexene; that from the *trans* isomer is 82–86% 1-*t*-butyl- and 14–18% 3-*t*-butylcyclohexene. The acetates were isolated in yields too low for accurately determining the configurational compositions. No evidence was obtained for rearranged solvolysis products.

As pointed out in the previous paper⁴ the isomeric 2-*t*-butylcyclohexanols, like the 3- and 4-*t*-butylcyclohexanols,⁵ are presumably conformationally homogeneous with the *t*-butyl group in an equatorial position. Thus in the isomeric 2-*t*-butylcyclohexyl *p*-toluenesulfonates the tosyl group is *axial* in the *cis* isomer I and *equatorial* in the *trans* isomer II as illustrated below. In order to obtain information concerning the effect of the position of the leaving group, i.e., *axial* or *equatorial*, on the rates and products of solvolysis we have investigated the products and relative rates of ethanolysis and acetolysis of *cis* I and *trans* 2-*t*-butylcyclohexyl *p*-toluenesulfonate II. This information is also of interest for comparison with the recently reported⁵ rates and products of solvolysis of the diastereoisomeric 3- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates.



Results of Kinetic Experiments.—The results of the pertinent kinetic experiments are summarized in Table I. The first-order rate constants (calculated by use of the integrated equation for a first-order reaction) were steady over the ranges that the reactions were followed (to 95% completion in some cases) for both acetolysis and ethanolysis.

(1) This work was supported in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Abstracted from the doctoral dissertation of Richard L. Reeves, University of Wisconsin, 1954.

(3) Socony-Vacuum Oil Co. Fellow, 1953–1954.

(4) H. L. Goering, R. L. Reeves and H. H. Espy, THIS JOURNAL, **78**, 4926 (1956).

(5) S. Winstein and N. J. Holness, *ibid.*, **77**, 5362 (1955).

Most of the first-order constants (*k*) given in Table I are average values and mean deviations of two or more independent kinetic experiments. In each kinetic experiment six or more values of the

TABLE I
RATES OF ACETOLYSIS AND ETHANOLYSIS OF *cis*- AND *trans*-2-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE

Tosylate	Temp., °C.	[ROTs] 10 ² <i>m</i>	[Lyate ion] ^a 10 ² <i>M</i>	<i>n</i> ^b	10 ⁵ <i>k</i> ^c sec. ⁻¹
Acetolysis					
<i>cis</i>	20.11	3–4		2	0.92 ± 0.04
<i>cis</i>	30.12	2–4		4	3.66 ± 0.06
<i>cis</i>	50.03	4.78		1	44.2 ± 1.0
<i>cis</i>	30.12	3–5	19.92	2	4.68 ± 0.10
<i>trans</i>	20.11	3–5		4	0.350 ± 0.012
<i>trans</i>	30.12	4.91		1	1.48 ± 0.04
<i>trans</i>	50.03	3–5		2	21.0 ± 0.2
<i>trans</i>	30.12	3–5	19.92	2	1.78 ± 0.00
Ethanolysis					
<i>cis</i>	29.99	5.73		1	2.84 ± 0.02
<i>cis</i>	29.99	2–3	29.86	2	3.89 ± .01
<i>trans</i>	29.99	4		3	0.57 ± .01
<i>trans</i>	29.99	3–5	29.86	2	0.83 ± .02

^a Lyate ion supplied as the sodium salt. ^b Number of independent kinetic experiments. ^c Where more than one independent kinetic experiment was carried out the reported constants are average values for the separate experiments and the mean deviation; where only one kinetic experiment was carried out the reported constant is the average of 7–11 values determined during the reaction, and the mean deviation.

rate constant were determined from appropriately spaced titrations during the reactions. As shown in Table I acetolyses of the isomeric tosylates in the presence of sodium acetate (initial concentration 0.2 *M*) are first-order and the rate is increased only slightly over that observed in the ab-