Preparation of cis- and trans-4-tert-Butylcyclohexane-1- d_1 and Their Identification by Infrared Spectra and ²H Nuclear Magnetic Resonance¹

Totes

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It is generally accepted that when the bulky tert-butyl group is introduced into a cyclohexane ring, it assumes a favored equatorial position and stabilizes the resulting conformation.² If a reducible function and deuterium are introduced in the 1 position of 4-tert-butylcyclohexane, the resulting compound has considerable potential for studying the stereochemistry and mechanism of reductions involving secondary carbon atoms. In those cases where cis- and trans-4-tert-butylcyclohexane-1- d_1 (5 and 6, respectively) are possible final products, it is necessary that distinguishing features of these compounds be recognized and

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identified. It was necessary, therefore, to synthesize 5 and 6 for subsequent comparison. Table I lists all of the compounds prepared together with the physical data used in their identification.

cis- and trans-4-tert-butylcyclohexane- $1-d_1$ of suitable purity for this study were prepared readily and in good vield from 4-tert-butylcyclohexanone. 4-tert-Butylcyclohexanone was reduced using a LiAlH₄-AlCl₃ mixture according to the method of Eliel-Martin-Nasipuri³ to give trans-4-tert-butylcyclohexanol (1). Compound 1 was allowed to react with p-toluenesulfonyl chloride in dry pyridine at 0° to give an 89% yield of the p-toluenesulfonyl ester (3). Compound 3 when heated at 90° with an excess of $NaBD_4^4$ in hexamethylphosphoramide gave a better than 70% vield of 5. Approximately 10% of 3 was found on workup to have been converted to 1, presumably by NaBD₄ attack on sulfur. If the above procedure is modified by using a LiAlD₄⁵-AlCl₃ mixture for the initial reaction and $NaBH_4$ in the final reduction, the isolated product is 6 in equally good yields. Both 5 and 6 were purified by elutriation with pentane through a column packed with 10%

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HOH	Mp 82.0-82.5° (lit. ^b mp 82.5-83.0°); ir 3615, 3440 cm ⁻¹ (OH); ¹ H nmr & 0.82 (s, 9 H, <i>tert</i> -butyl), 3.12-3.54 (m, 1 H, H-C-O-), 2-4 varies with concn (s, 1 H, OH)
D ОН	Mp 81-82°; ir 3615, 3440 cm ⁻¹ (OH), 2090 cm ⁻¹ (C-D); ¹ H nmr 5 0.82 (s, 9 H, <i>tert</i> -butyl), 2-4 varies with concn (s, 1 H, OH)
HOTS	Mp 88-89° (lit. ^c mp 89.4-90°); ir 1601, 1165, 1180 cm ⁻¹ (tosylate); ¹ H nmr & 0.80 (s, 9 H, <i>tert</i> - butyl), 2.38 (s, 3 H, benzylic), 3.92-4.26 (m, 1 H, H-C-O-), 7.00-7.67 (m, 4 H, aryl)
DOTs	Mp 89-91°; ir 2185 cm ⁻¹ (C-D), 1601, 1165, 1180 cm ⁻¹ (tosylate); ¹ H nmr & 0.80 (s, 9 H, <i>tert</i> - butyl), 2.38 (s, 3 H, benzylic), 7.00-7.67 (m, 4 H, aryl)
ДН	Bp ^d 171-172° (737 mm); n^{25} D ^d 1.4483; ir ^e 2120-2140 cm ⁻¹ (C-D), 804, 818 cm ⁻¹ ; ² H nmr +5.98 ppm relative to CDCl ₃
H	Bp ^f 170-171° (737 mm); n^{25} D ^f 1.4444; ir ^e 2140-2160 cm ⁻¹ (C-D), 1130 cm ⁻¹ ; ² H nmr +5.42 ppm

Table I

Data



Mp 72-73°; ir 2165 cm⁻¹ (C-D), 1345, 1325, 1165 cm⁻¹ (mesylate); ¹H nmr & 0.82 (s, 9 H, tert-OMs buty1), 2.83 (s, 3 H, -S-CH₃)

^a Solids were recrystallized from pentane before melting point determinations. Unless otherwise specified, ir spectra were made on a Beckman IR-10 using 0.1-0.2-g samples/ml of CHCl₃. ¹H nmr were taken on a Varian T-60 using CCl₄ as solvent. ^b Reference 2. ^c S. Winstein and N. J. Holness, J. Amer. Chem. Soc., 77, 5562 (1955). d The mass spectrum of this material indicates that it is a mixture of 90% of 5 and 10% tert-butylcyclohexane. e Spectrum taken on a neat sample in a cavity cell (NaCl) with 0.1-mm path length. / The mass spectrum of this material indicates that it is a mixture of 97% 6 and 3% tert-butylcyclohexane. g D. S. Noyce, B. E. Johnson, and B. Weinstein, J. Org. Chem., 34, 463 (1969).

Notes



Figure 1. ²H nmr spectra of (A) trans-4-tert-butylcyclohexane-1 d_1 (B) cis-4-tert-butylcyclohexane-1- d_1 , and (C) Li-NH₃-EtOH reduction product of the methanesulfonate ester of trans-4-tertbutylcyclohexanol-1- d_1 . The resonance peak at 33,772,228 Hz results from CDCl₃ used as an internal reference.

AgNO₃-SiO₂. The pentane was removed subsequently by careful distillation.

Products 5 and 6 were examined on a CEC-21-110B mass spectrometer to determine their composition and isotopic purity. The mass spectra indicate that 5 is a mixture of 90% monodeuterated tert-butylcyclohexane and 10% tertbutylcyclohexane and that 6 is a mixture of 97% monodeuterated tert-butylcyclohexane and 3% tert-butylcyclohexane.

Both 5 and 6 were examined by ir methods. A characteristic feature of 6 is a doublet of medium intensity between 2140 and 2160 cm^{-1} due to symmetric and asymmetric stretching of the equatorial C-D bond. The doublet component of lower wave number is the more intense of the two. These results are in agreement with the spectrum obtained by Glaze and Selman⁶ from a product obtained by the deuterolysis of 4-tert-butylcyclohexyllithium and assumed by them to be 6. This doublet also agrees with the expected absorption of equatorial C-D bonds in cyclohexane as predicted by Corey, et al.⁷ Other identifying features of the spectrum for 6 are weak absorption at 1130 cm^{-1} and no absorption between 800 and 820 $\rm cm^{-1}$.

The ir spectrum for 5 shows a doublet of moderate intensity between 2120 and 2140 cm^{-1} with the component of higher wave number being the more intense. Two moderately strong absorptions occur at 804 and 818 cm⁻¹, respectively. No characteristic absorptions were noted for 5 between 1100 and 1140 cm⁻¹.

To ensure that the ir absorptions selected for identifying 5 and 6 did not arise from tert-butylcyclohexane, its spectrum was taken for comparison. This spectrum confirms that the absorptions assigned to 5 and 6 do result in each case from the deuterated product. In summary, 5 and 6, singly or in combination, are indicated and are differentiated readily by the presence or absence of ir absorptions in the 800-820- and 1100-1140-cm⁻¹ regions.

The ²H nmr spectra of both 5 and 6 were examined. Although limited examples of the use of ²H nmr have appeared in the literature,⁸⁻¹⁴ its potential has not been exploited probably because of the limited availability of equipment needed to resolve and enhance the relatively insensitive deuterium signal. It was found that ²H nmr can readily distinguish both qualitatively and quantitatively between 5 and 6. Using a Varian HR-220 and utilizing free Fourier transform techniques,¹⁵ 5 and 6 gave broad singlets sufficiently separated for easy identification and integration. Relative to CDCl₃ as an internal reference, the chemical shifts of 5 and 6 were found to be +5.98 and +5.42ppm,¹⁶ respectively.

To substantiate that ir and ²H nmr spectra could be used to follow the course of a chemical reduction, the methanesulfonate ester of trans-4-tert-butylcyclohexanol- $1-d_1$ (8) was prepared by allowing 2 to react with methanesulfonyl chloride in pyridine at 0°. Recrystallized 8 was reduced with a Li-NH3-EtOH mixture according to the modified Birch reduction procedure of Wilds and Nelson.¹⁷ Ir analysis of the isolated reduction product clearly indicated the presence of both 5 and 6. ²H nmr analysis of the product substantiated the presence of two products, and integration of the peak areas indicated that approximately 80% of the product underwent inversion while 20% retained its original configuration. The previous statement does not imply that the reduction necessarily occurs by a typical SN2 mechanism. There is some evidence that such reductions may involve intermediate carbanions and that the ratio of products reflects the ratio of pyramidal carbanions and/or their protonation rather than the stereochemistry of the process.^{18,19}

In Figure 1, the ²H nmr spectra of both 5 and 6 as well as the Birch reduction product are reproduced for inspection and comparison.

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Registry No.---1, 21862-63-5; 2, 30461-17-7; 3, 7453-05-6; 4, 53042-75-4; 5, 53042-76-5; 6, 17553-36-5; 7, 18508-90-2; 8, 53111-68-5; tert-butylcyclohexane, 3178-22-1; 4-tert-butylcyclohexanone, 98-53-3.

References and Notes

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