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PRELIMINARY COMMUNICATION

4-tert-Butylcyclohexyllithium

Alexandrou[1] has reported unsuccessful attempts to synthesize 4-tert-butylcyclohexyllithium from the *cis*- and *trans*-bromides by a variety of methods. We now report the direct preparation of this potentially valuable reagent and discuss some preliminary results regarding the stereochemistry of substitution at the carbon–metal center.

cis-4-tert-Butylcyclohexyl chloride (7–10% *trans*-isomer), prepared from a mixture of the alcohol isomers (80% *trans*-) by reaction with triphenylphosphine dichloride[2], reacts readily with lithium metal sand (1% sodium content) in refluxing n-pentane. 4-tert-Butylcyclohexyllithium (I) (*ca.* 35% yield) is sparingly soluble in n-pentane, however, and after successive extractions of the solid reaction products in a dry box, the organometallic compound may be recrystallized from n-pentane (white, pyrophoric crystals). Carbonation of a pentane slurry of (I) at −70°, followed by conversion to the methyl esters with diazomethane yields methyl *trans*-4-tert-butylcyclohexylcarboxylate (b.p. 74°, 0.5 mm (ref. 3), $< 4\%$ *cis*-isomer, GLC at 142°, $10' \times \frac{1}{4}''$ polypropylene glycol (15%) on Chromosorb W). Carbonation of the mother liquor of (I) yields the same ratio of acids. The PMR spectrum of (I) in hydrocarbon solvents is that of a typical 4-tert-butylcyclohexyl derivative with a broad α-methinyl

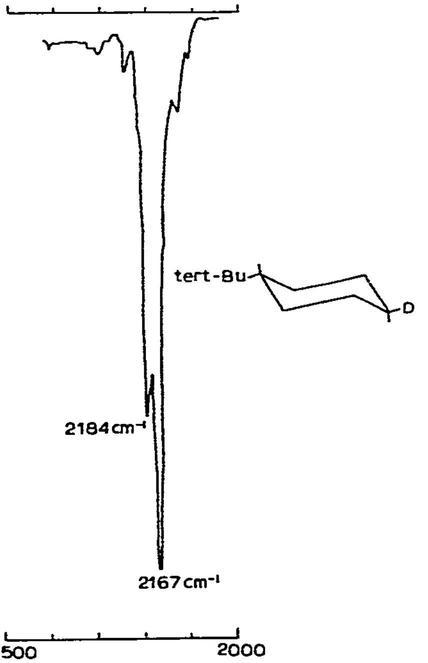

Fig. 1. Absorption spectrum of 4-tert-butylcyclohexane-1-d_1 in the carbon–deuterium stretching region.

multiplet at τ 10.54. The low solubility of (I) in hydrocarbon solvents has prevented any further analysis of the α-methinyl resonance, however*.

Reaction of (I) with deuterium oxide yields 4-tert-butylcyclohexane-1-d_1. A portion of the infrared spectrum of the product is shown in Fig. 1. A doublet is observed which consists of a medium intensity band at 2184 cm^{-1} with a strong absorption at 2167 cm^{-1}. Previous studies[4] have shown that symmetric and asymmetric stretching modes for *equatorial* deuterons appear as a doublet ($\Delta\bar{\nu} \simeq 15$ cm^{-1}) in this range with the high frequency band being the weaker of the two. *Axial* C–D bands appear at lower frequencies (2114–2164 cm^{-1}, $\Delta\bar{\nu} \simeq 25$ cm^{-1}) with the high frequency portion of the doublet being the stronger band. We conclude that the deuterolysis product is primarily the *trans*-form and that the reaction proceeds with predominant retention of configuration.

Bromination of (I) with molecular bromine in pentane yields 4-tert-butylcyclohexyl bromide containing predominantly the *cis*-isomer**. The stereochemistry of the reaction appears to depend to some degree on the reaction temperature; at $-70°$ the *cis/trans* ratio of bromides is 3.75, while at 25° the ratio is 1.70. Thus, reaction with Br_2 proceeds with predominant inversion of configuration, in agreement with earlier results[5], with the effect of temperature remaining unexplained at this time.

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* Diethyl ether and tetrahydrofuran are very rapidly cleaved by (I) at temperatures above $-20°$.

** *Cis/trans* ratios for the bromide were determined on a 0.01″ × 150′ Carbowax K-1540 Golay column, 88°, 2 ml/min. Integrated intensities of the α-methinyl protons at τ 5.37 and 6.07 for the *cis* and *trans* bromides respectively confirmed the analysis.