off into 50 ml of distilled water, separation of the two phases, extraction with 10 ml of pentane to remove pyvalic acid, and evaporation of the aqueous layer to dryness.

(10) The progress of the elution can be monitored by occasionally spotting a fluorescent TLC plate and examining the plate under short-wave uv light; the pyridine appears as a dark blue spot.

Carbon-13 Nuclear Magnetic Resonance Examination of Some [1-^{2}H]-4-*tert*-Butylcyclohexyl Derivatives

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Recently in this journal, one of us reported[2] the preparation of *cis*- and *trans*-4-*tert*-butylcyclohexane-*1*-d_1, and their characterization by infrared and ^{2}H nuclear magnetic resonance spectroscopy. These compounds, and their 1-oxy precursors, appeared attractive subjects for ^{13}C NMR examination, as considerable insight into the effects of ^{2}H substitution on ^{13}C spectra in a geometrically well-defined cycloalkyl system would result, and complement information available for other ^{2}H-substituted systems.[3-8] In addition, the 4-alkylcyclohexyl system frequently is employed in stereochemical and mechanistic studies, and with the growing use of ^{13}C NMR in this area, it is important to provide parameters for this system.

***trans*-4-*tert*-Butylcyclohexyl mesylate** provides a well-separated spectrum which is relatively straightforward to assign. C_1, bearing the mesyl ($-OSO_2CH_3$) function, resonates at lowest field (82.16 ppm) and C_4, $(CH_3)_3C$, and $(CH_3)_3C$ are assigned on the bases of chemical shifts and intensities. Differentiation between $C_{2,6}$ and $C_{3,5}$ is based on the expected greater shielding of $C_{3,5}$, as these carbons are located γ and anti-periplanar to the oxy function.[9] Examination of the spectrum of the 1-^{2}H isomer of this (trans) mesylate confirms the assignment of C_1 (signal now not visible under our pulse conditions) and of $C_{2,6}$ which has experienced a two-bond upfield (i.e., negative) ^{2}H isotope effect of -0.13 ppm, while the signal assigned to $C_{3,5}$ is unaffected within experimental error. This is consistent with other observations that three-bond ^{2}H isotope effects on chemical shifts are quite small.[3,4] We also anticipated that the $C_{3,5}$ signal should be perceptibly broader than that of $C_{2,6}$, because of the operation of significant vicinal ^{2}H–^{13}C coupling.[5,6] The signal of $C_{3,5}$ appears marginally broader, but a strong effect would not be expected for a dihedral angle of 60° (vide infra).

The spectrum of *trans*-4-*tert*-butylcyclohexyl tosylate is similar in many respects to that of the mesylate, and assigned with the same criteria. Another measure of the two-bond isotope effect (at $C_{2,6}$) is provided (-0.11 ppm).

***trans*- and *cis*-4-*tert*-Butylcyclohexane-*1*-d_1.** The spectrum of *tert*-butylcyclohexane was reported previously by Roberts,[10] but at the frequency employed several signals were not well separated, and assignments could not be definite. The cis isomer (i.e. axial ^{2}H) was examined initially as mass spectral examination showed it to be ~90% ^{2}H enriched, and hence the regular *tert*-butylcyclohexane (~10%) would serve as a useful internal standard for isotope shifts. One and two-bond isotope effects of -0.43 and -0.09 ppm (i.e., at C_1 and $C_{2,6}$, respectively) are measured, while any three-bond isotope effect must be less than 0.05 ppm.

The spectra of the above compounds are reproduced in Figure 1, and using the *tert*-butyl resonance as standard, it is clear that there are significant differences in the one- and two-bond isotope effects. This is not surprising as differences in other spectroscopic properties of equatorial and axial ^{2}H are well established.[11] The difference appears greater for the two-bond isotope effect.

Table I. Carbon-13 NMR Parameters[a] for 4-*tert*-Butylcyclohexyl Systems

Registry no.	Compd	Carbon 1	2,6	3,5	4	$(CH_3)_3C$	$(CH_3)_3C$	Others
	X = Y = H	26.61	27.09	27.44	48.01	27.30	32.26	
	(reported[10])	27.2	27.8	28.2	48.9	27.7	32.7	
53042-76-5	X = H; Y = D[b,c]	26.18	27.00	27.44	48.01	27.30	32.26	
		(−0.43)	(−0.09)	~0[e]				
17553-36-5	X = D; Y = H	26.16	26.93	27.32	47.94	27.27	32.24	
	[corrected against $(CH_3)_3C$ as standard][b]	26.19	26.96	27.35	47.97	27.30	32.27	
		(−0.42)	(−0.13)	(−0.09)				
18508-90-2	Y = H; X = OSO_2CH_3	82.16	33.31	26.65	46.74	27.57	32.25	38.81
53111-68-5	Y = D; X = OSO_2CH_3[b]	n.o.	33.18	25.62	46.72	27.57	32.26	38.81
		[d]	(−0.13)	(~0)[e]				
7453-05-6	Y = H; X = $OSO_2C_6H_4CH_3$	81.78	32.58	25.30	46.12	27.24	31.88	21.39; 126.30; 128.44 133.53; 142.86
53042-75-4	Y = D; X = $OSO_2C_6H_4CH_3$[b]	n.o.	32.47	25.33	46.12	27.24	31.91	21.41; 126.33; 128.41 133.59; 142.86
		[d]	(−0.11)	(~0)[e]				

[a] Spectra recorded at 22.625 or 67.89 MHz (Bruker). Chemical shifts for dilute $CDCl_3$ solutions referenced to internal Me_4Si. [b] Values in parentheses are isotope shifts in parts per million. [c] $J_{^{13}C-^2H}$ = 19.2 Hz. [d] Signal not observable under our pulse conditions. [e] Not greater than experimental error.

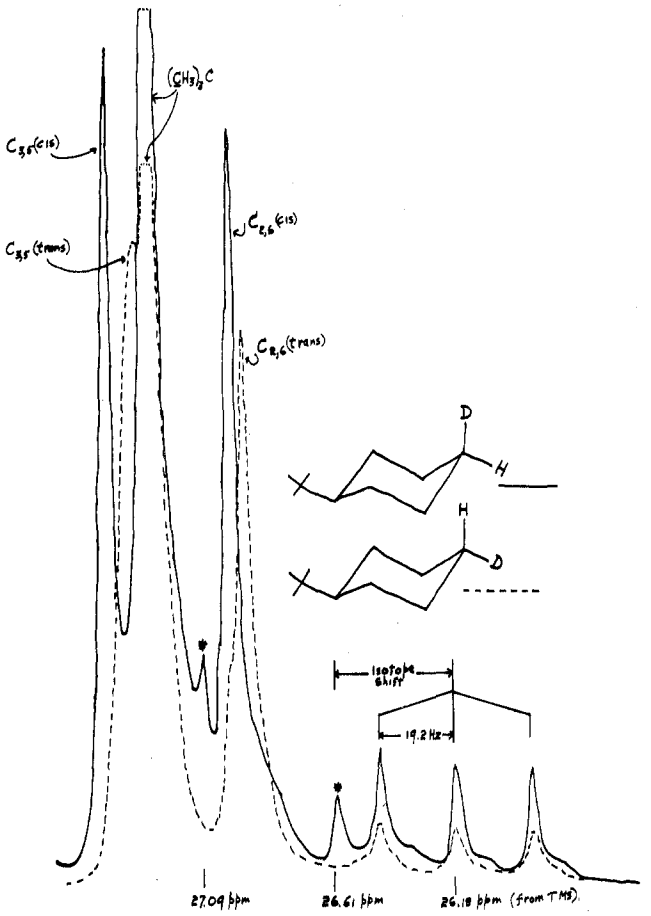

Figure 1. High-field part of the 67.89-MHz ^{13}C spectra (500-Hz expansion) of *trans*-4-*tert*-butylcyclohexane-*1*-d_1 (broken line) and *cis*-4-*tert*-butylcyclohexane-*1*-d_1 (full line). The signals marked with an asterisk correspond to C_1 (at 26.61 ppm) and $C_{2,6}$ (27.09 ppm) in regular (undeuterated) *tert*-butylcyclohexane, admixed (~10%) with the cis isomer. (The degree of deuteration was much higher in the trans case.) The C_1–D triplet ($J_{^{13}C-^2H}$ = 19.2 Hz) is indicated.

Comparison of the shape and position of the $C_{3,5}$ signals in the two isomers (Figure 1) reveals (a) that when ^2H is equatorial (i.e., trans isomer) $C_{3,5}$ is broader and at higher field than when ^2H is axial. The "broadness" was expected as vicinal ^2H coupling to ^{13}C in other systems is substantial for a dihedral angle of 180°,[5,6] which, of course, exists in the trans compound. In addition, it appears that the (γ)-antiperiplanar array of $C_{3,5}$ and ^2H promotes a greater three-bond isotope effect than when a (γ)-syn situation exists, as in the cis isomer.

Previously, Doddrell and Burfitt[8] had examined the effect of ^2H substitution on the ^{13}C spectra of some 1-^2H-1-substituted heptanes, and for the parent hydrocarbon, a one-bond effect (i.e., at C_1) of −0.28 ppm ($J_{^2H-^{13}C}$ = 19.2 Hz) was observed. These results are in line with the present data. More recently, Colli, Gold, and Pearson[7] reported ^2H isotope effects on the ^{13}C NMR spectra of a number of alkyl systems, but generally the compounds were polydeuterated, so that observed effects were combinations of nearest neighbor and more remote interactions. However, their reported (upfield) isotopic shift for perdeuteriocyclohexane of −1.33 ± 0.2 is quite consistent with the values noted here, i.e., (2 × ~0.4) + (4 × ~0.1) ≃ 1.2.

The spectral data are assembled in Table I.

The present results indicate that incorporation of ^2H in a defined way in a cycloalkyl system can be a substantial aid in assignment of carbon signals two and three bonds removed from the site of incorporation.[12] Alternatively, the effect ^2H might have on the spectra could provide insight into the stereochemical location of the ^2H label.

Experimental Section

The compounds examined have been described in detail elsewhere.[2]

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The Effect of Substrate Micellization on the Hydrolysis of *n*-Decyl Phosphate[1]

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Catalysis and inhibition by micelles of added surfactant have been studied extensively,[3-6] but in only a few cases has the effect of substrate micellization been examined.[7-10] However, the rates of hydrolysis of monoalkyl sulfates are markedly affected by substrate micellization which speeds the acid-catalyzed hydrolysis but retards reaction with hydroxide ion.[7] Monoanions of monoalkyl phosphates decompose spontaneously in a reaction which almost certainly involves elimination of metaphosphate ion and proton transfer to the RO– moiety:[11-13]

$$RO{-}PO_3H^- \longrightarrow ROH + PO_3^- \xrightarrow[\text{fast}]{H_2O} Pi$$

At lower pH nucleophilic attack upon the alkyl and phosphoryl groups becomes important. For example, in the acid-catalyzed hydrolysis of a monoalkyl phosphate water can attack the protonated substrate on either the alkyl or phosphoryl group,[12,13] and halide ion can attack the alkyl group.[14]

$$ROPO_3H_2 \overset{H^+}{\rightleftharpoons} ROPO_3H_3^+ \xrightarrow{H_2O} ROH + H_3PO_4 + H^+$$
$$\searrow^{X^-}$$
$$RX + H_3PO_4 + H^+$$
$$(X = Cl, Br)$$