scale factors were obtained before and after each experiment from separate audio side band spectra which were derived from H_1 and located within several hertz of the original satellites. In each case, the before and after scale factors agreed to less than 0.001 Hz/cm.

For all seven temperature experiments described above, the average scale factor never varied by more than 0.02 Hz/cm, and most values were within 0.01 Hz/cm of the average, 0.99 Hz/cm. In the remaining temperature experiments, an audio side band, generated by a frequency of 8.6–9.2 Hz, was produced from one transition of the satellite doublet, and measured with respect to the remaining transition about 1.5 Hz away. At any temperature, a maximum expected error of 0.02 Hz/cm in the above average scale factor (0.99 Hz/cm) would introduce a maximum total scaling error of 0.03 Hz in $J_{CC'}$ but for most cases, the scaling error is thought to be less than 0.01 Hz. Nmr data for **3** are shown in Table III.

Experimental Section

2,3-Dideuterio-1,3-butadiene (2). 2,3-Dideuterio-2,3-butanediol was prepared by reduction of biacetyl with lithium aluminum deuteride according to the procedure of Loewus, Westheimer, and Vennesland.[32] The crude 2,3-dideuterio-2,3-butanediol was distilled through a Vigreux column under vacuum, and the major fraction was collected at 89–92° (21 mm) (reported 95–105° (40 mm)).

2,3-Dideuterio-2,3-butanediol was acetylated in the usual manner[33] using an excess of acetic anhydride and pyridine. The crude product was distilled through a Vigreux column, and the major fraction of 2,3-dideuterio-2,3-diacetoxybutane was collected at 94.0–94.5° (22 mm).

2,3-Dideuterio-2,3-diacetoxybutane (3 g) was added dropwise into a heated Vycor column containing Vycor chips under an atmosphere of N_2 at 585°, using the procedure of Shlechter, Othmer, and Brand.[34] The crude gaseous product was purified by passage through an ice-cooled trap, followed by a bubbler containing 10% aqueous sodium hydroxide solution and a second bubbler containing water. The wet gas was passed through a tube containing a weighed mixture of carbon disulfide and hexamethyldisilane. The nmr tube, which was immersed in a Dry Ice–acetone bath, was evacuated and sealed under vacuum. The mixture was found to be 8.3% (w/w) 2,3-dideuterio-1,3-butadiene (**2**) and 4.6% hexamethyldisilane in carbon disulfide solvent.

1,1,4,4-Tetradeuterio-1,3-butadiene (3). 2,2,5,5-Tetradeuterio-2,5-dihydrothiophene 1,1-dioxide was prepared from sulfolene by alkaline deuterium exchange according to the method of Cope, Berchtold, and Ross.[35] Eight exchanges yielded 99.3% isotopic purity (by nmr integration). Recrystallization from 2:1 THF–pentane gave a mp 63–65° (reported mp 66.8–67.3°).

The above dihydrothiophene 1,1-dioxide (5 g) was pyrolyzed at 130° to generate **3** at a convenient rate. Gaseous **3** was bubbled through two traps, each containing about 100 ml of 10% aqueous sodium hydroxide solution to remove the sulfur dioxide by-product formed in the reaction. The purified **3** was passed through a tube containing Drierite, and into two preconstricted tared nmr tubes containing known weights of hexamethyldisilane. The nmr tubes were immersed in Dry Ice–acetone contained in a dewar flask. In order to minimize boiling of **3** during high temperature experiments, one of these filled nmr tubes was sealed under nitrogen at atmospheric pressure. The second nmr tube, sealed under vacuum, was used for the remaining variable-temperature study. Both samples contained 11% (w/w) hexamethyldisilane in neat **3**.

Acknowledgment. The authors are grateful to the National Science Foundation for Grant No. GP-3815 which provided support for this work.

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Conformational Analysis of 2-Methylbutane[1]

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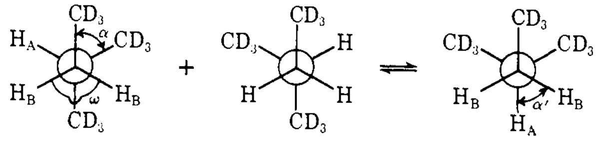
Abstract: The AB_2 deuterium-decoupled pmr spectrum of 2-methylbutane-d_9 (**1**) was determined at ten temperatures in the range −91 to +72°. The observed temperature dependences of the three nmr parameters (ν_A, ν_B, and J_{AB}) were ascribed to changes in conformer population with temperature (eq 1). These parameters were subsequently used in a least-squares analysis to obtain quantitative estimates of ΔH and the intensive nmr parameters of conformers **1a** and **1b**. The value of ΔH for the equilibrium **1a** $\rightleftharpoons$ **1b** is 888 ± 18 cal/mol ($\Delta S = -1.376$ eu). The torsional angle, α, for **1a** was estimated to fall between 60 and 72° from the calculated vicinal coupling constant.

Rotational isomerism in 2-methylbutane has been observed by Raman,[3] infrared,[4] ultrasonic,[5] and thermodynamic[6] methods, and estimates were made of both the enthalpy difference between the two possible conformers and their barrier to interconversion.

Szasz and Sheppard concluded from Raman[3] that the enthalpy difference for the equilibrium **1a** $\rightleftharpoons$ **1b** was



1a C_i **1b** C_s

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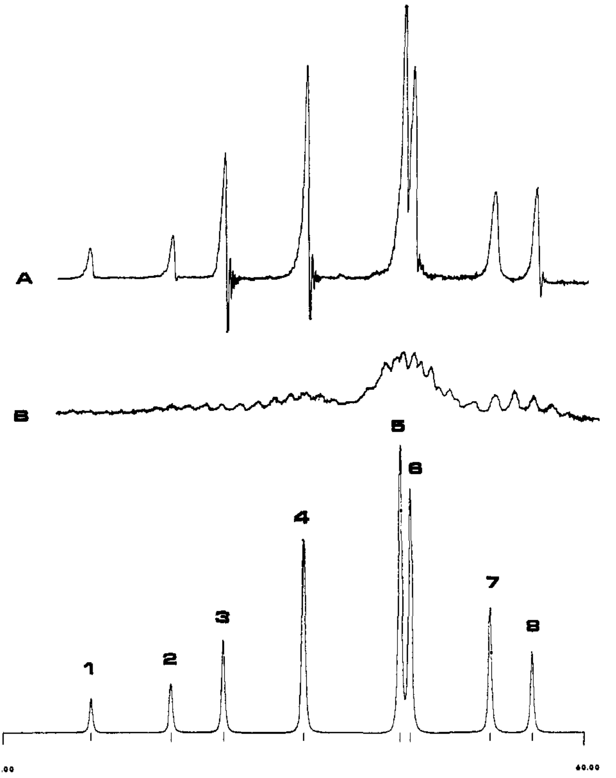

Figure 1. The 60-Mc/sec nmr spectra of **1** at (a) 35.5° with deuterium decoupling, (b) 35.5° without deuterium decoupling, and (c) the calculated theoretical spectrum using the spectral parameters obtained from LAOCOON3 at 35.5°.

either less than 200 cal/mol or greater than 1000 cal/mol. Brown and Sheppard[4] drew no quantitative conclusions from their infrared study. Scott and coworkers[6] concluded from their heat capacity measurements that the C_s conformer, **1b**, is at least several thousand cal/mol less stable than **1a**, the C_i conformer. More recently, Au-Chin,[7] using theoretical considerations, has estimated ΔH for **1a** $\rightleftharpoons$ **1b** as 1.33 kcal/mol.

This work attempts to confirm through variable-temperature nmr that **1a** is the more stable conformer in the equilibrium **1a** $\rightleftharpoons$ **1b** and to determine more precisely the enthalpy difference between **1a** and **1b**. In addition, the derived vicinal coupling constants will be used to estimate the torsional angle, α, for the C_i conformer.

Results and Discussion

Under conditions of deuterium decoupling, 2-methylbutane-d_9 (**1**) gives rise to eight nmr transitions, corresponding to a spectrum of the type AB_2.[8] Initial values of ν_A, ν_B, and J_{AB} were obtained from eq 1–3,[9] where

$$\nu_A = \nu_1 \qquad (1)$$

$$\nu_B = (\nu_5 + \nu_7)/2 \qquad (2)$$

$$J_{AB} = {}^1/_3[(\nu_8 - \nu_6) + (\nu_4 - \nu_1)] \qquad (3)$$

ν_A and ν_B are the chemical shifts of H_A and H_B (relative to hexamethyldisilane), and J_{AB} is the vicinal proton coupling across the 2,3 C–C bond. These initial values were subsequently inputed into iterative LAOCOON3[10] calculations along with the corresponding experimental frequencies of all eight transitions to obtain best least-squares values of ν_A, ν_B, and J_{AB}. Figure 1 shows undecoupled and deuterium-decoupled spectra of **1** along with a LAOCOON3 computed spectrum.

These LAOCOON3 derived parameters were used independently to determine the best solution values to eq 4[11,13] where P_{aj} and P_{bj} are the jth of l intensive parameters of conformers **1a** and **1b**, and $P_{ij}°$ is the jth of l observed parameters at the ith of k temperatures, T_{ij}. As solution of eq 4 varying all of the unknowns, including ΔH and ΔS, was not achieved, it was found necessary to reduce the number of unknowns by one through assuming $\Delta S = -R \ln 2$ (-1.376 eu), the statistical value corresponding to two enantiomeric C_s conformers.[14]

$$\ln\left(\frac{P_{aj} - P_{ij}°}{P_{ij}° - P_{bj}}\right) = \frac{-\Delta H}{RT_{ij}} + \frac{\Delta S}{R} \qquad (4)$$

A number of requirements which must be satisfied for the quantitative application of eq 4 to conformational analysis have been discussed critically.[13] It is essential that P_{aj} and P_{bj} both be temperature independent so that the observed temperature dependences, $P_{ij}°$, reflect only changes in conformer population. We use as an operational criterion of this condition, the self-consistency of the independent eq 4 solution values of ΔH provided by the respective nmr parameters and the chemical shift difference, δ_{AB}. These solution values of ΔH obtained in the single parameter calculations are presented in Table I (solutions 1–4). They are seen to fall within the probable errors of one another, and therefore meet our operational criterion for the temperature independence of the respective intensive parameters. Therefore, it is felt justified to use as the most reliable solution of eq 4 these values obtained in a single combined parameter calculation of ν_A, ν_B, and J_{AB} (solution 4). This multiple parameter calculation leads to an enthalpy difference $\Delta H = 888 \pm 18$ cal/mol at $\Delta S = -1.376$ eu for the equilibrium **1a** $\rightleftharpoons$ **1b**. Figure 2 shows the theoretical temperature dependences of ν_A, ν_B, and J_{AB} corresponding to solution 5 (Table I) along with the experimental values of these parameters.

The derived vicinal coupling constants for conformers **1a** and **1b** obtained in solution 5 of Table I allow us to estimate the torsional angle, α, for the C_i conformer **1a**, using the theoretical relationship[15] between dihedral angle, ϕ, and vicinal coupling, J

$$J = A(\cos^2 \phi + n \cos \phi) \qquad (5)$$

In these calculations, the projected torsional angle, ω, in both **1a** and **1b** is assumed to be 120°. Since the C_s

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Table I. Solution Parameters[a] of Equation 1 Using Temperature Dependences of J_{AB}, ν_A, ν_B, and δ_{AB} at Fixed Values of ΔS

Solution	$-\Delta S$[b] (fixed)	ΔH[c]	$(J_{AB})_a$	$(J_{AB})_b$	$(\nu_A)_a$	$(\nu_A)_b$	$(\nu_B)_a$	$(\nu_B)_b$	$(\delta_{AB})_a$	$(\delta_{AB})_b$	RMS
1	0.876	795 ± 224[d]	7.11 ± 0.10[d]	4.33 ± 0.31[d]							0.015
	1.376	763 ± 228	7.11 ± 0.11	3.77 ± 0.38							0.015
	1.876	737 ± 230	7.12 ± 0.11	3.04 ± 0.46							0.015
2	0.876	939 ± 24			78.44 ± 0.07[d]	106.02 ± 0.47[d]					0.016
	1.376	907 ± 24			78.40 ± 0.07	111.77 ± 0.57					0.015
	1.876	881 ± 24			78.35 ± 0.07	119.13 ± 0.70					0.015
3	0.876	886 ± 26					65.88 ± 0.06[d]	85.29 ± 0.32[d]			0.012
	1.376	854 ± 26					65.84 ± 0.07	89.29 ± 0.39			0.012
	1.876	827 ± 26					65.81 ± 0.07	94.42 ± 0.48			0.012
4	0.876	1078 ± 61							12.54 ± 0.04[d]	20.92 ± 0.44[d]	0.011
	1.376	1050 ± 62							12.53 ± 0.04	22.72 ± 0.55	0.011
	1.876	1026 ± 63							12.52 ± 0.04	25.02 ± 0.69	0.011
5	0.876	920 ± 18	7.06 ± 0.01	4.13 ± 0.11	78.38 ± 0.05	105.67 ± 0.33	65.95 ± 0.04	85.71 ± 0.25			0.015
	1.376	888 ± 18	7.06 ± 0.01	3.52 ± 0.13	78.34 ± 0.06	111.34 ± 0.41	65.92 ± 0.04	89.82 ± 0.31			0.015
	1.876	862 ± 18	7.07 ± 0.01	2.74 ± 0.16	78.30 ± 0.06	118.59 ± 0.51	65.89 ± 0.04	95.07 ± 0.38			0.015

[a] All nmr parameters are given in Hz. Subscripts a and b denote nmr parameters calculated for conformers **1a** and **1b**, respectively. [b] In cal/(mol deg). [c] In cal/mol. [d] The indicated ± limits are probable errors from the solution of eq 4.

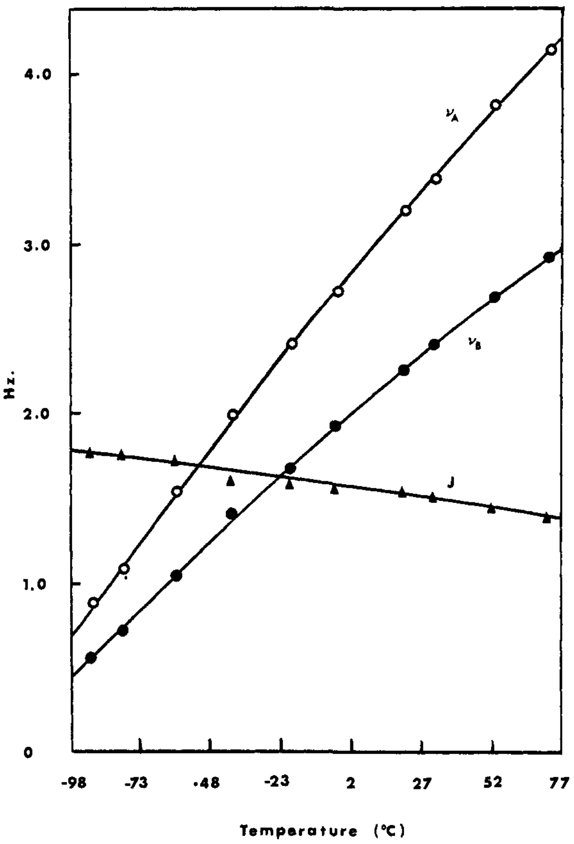

Figure 2. The experimental temperature dependences of ν_A (○), ν_B (●), and J_{AB} (▲), along with their theoretical dependences (solid lines). The theoretical dependences (solid lines) were derived from the combined parameter solution of eq 5 (solution 5 of Table I).

conformer (**1b**) is symmetric, the derived coupling J_b[16] is given by eq 6. For the C_1 conformer (**1a**), the

$$J_b = 3.52 \text{ Hz} = A(\cos^2 60° + n \cos 60°) \qquad (6)$$

corresponding coupling J_a is given by eq 7,[17] where α is

$$J_a = 7.06 \text{ Hz} = \frac{J_g + J_t}{2} = \frac{A(\cos^2 \alpha + n \cos \alpha) + A(\cos^2 (\omega + \alpha) + n \cos (\omega + \alpha))}{2} \qquad (7)$$

the torsional angle between the two gauche related methyl groups. Application of eq 5 to the experimental vicinal couplings for the series ethane, propane, and isobutane allows an estimate to be made of the value for A for a series of hydrocarbons obtained by increasing methyl substitution of an ethane skeleton. For ethane, propane, and isobutane, the experimental vicinal coupling, J_{vicinal}, is given by eq 8, where ϕ_g =

$$J_{\text{vicinal}} = \frac{2J_g + J_t}{3} = \frac{2A(\cos^2 \phi_g + n \cos \phi_g) + A(\cos^2 \phi_t + n \cos \phi_t)}{3} \qquad (8)$$

60° and ϕ_t = 180°. Simplification of eq 8 leads to eq

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(16) J_a and J_b refer here to the vicinal interproton couplings across the 2,3 C–C bond for conformers **1a** and **1b**, respectively.

(17) J_g and J_t refer to the gauche and trans vicinal interproton couplings across the 2,3 C–C bond for conformer **1a**.

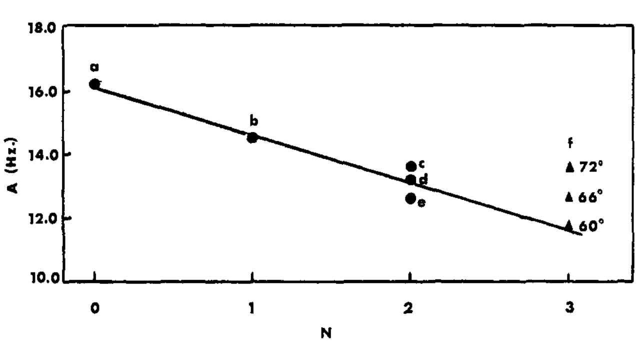


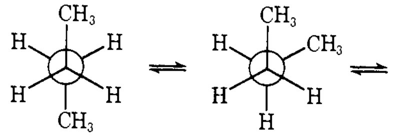
Figure 3. The dependence of A (eq 10) as a function of the number of methyl groups substituted on ethane for ethane (a), propane (b), isobutane (c), cyclohexane (d), and butane (e). The triangles (f) indicate values of A for 2-methylbutane corresponding to α = 60, 66, and 72°.

9. In Figure 3, A is plotted as a function of the number

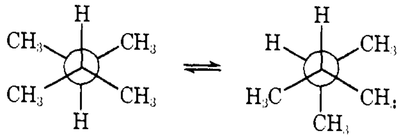
$$A = 3J_{\text{vicinal}}/1.50 = 2J_{\text{vicinal}} \qquad (9)$$

of methyl substitutions, N, for the series ethane,[18] propane,[19] isobutane,[20] butane,[21] and cyclohexane.[22] The qualitative decrease in A with increasing substitution probably limits A to a value no greater than 13.6 Hz, the largest such coefficient obtained for a disubstituted ethane. This value of A is found to correspond to n = 0.02 and $\phi \approx 72°$ upon simultaneous solution of eq 6 and 7. The lower limiting value for ϕ is 60° (n = 0.10, A = 11.7 Hz), corresponding to no increase in the normal sp^3–sp^3 torsional angle. The gauche conformer of n-butane (A = 12.56, n = 0.11), a similar system with one gauche methyl–methyl interaction, has been found to be skewed 66°.[21,23] The gauche butane value for the torsional angle, which is probably the best empirical estimate for α, falls between the lower and upper limits (60–72°) obtained above.

It is of interest to compare the enthalpy change **1a** ⇌ **1b** (ΔH = +888 ± 18 cal/mol) with that found for the comparable butane equilibrium **2a** ⇌ **2b** (ΔH = +681 ± 35 cal/mol).[21] In both equilibria, conformer **a** is the energetically more favorable form due to an additional methyl–methyl interaction present in **b**. For gauche butane (**2b**), this steric interaction is partially relieved by an increase in the torsional angle. The C_s conformer of 2-methylbutane, **1b**, contains two symmetrical methyl–methyl interactions, and cannot undergo torsional deformation. If the additional enthalpy change for **1a** ⇌ **1b** over **2a** ⇌ **2b** of 207 cal/mol is due to unrelieved methyl–methyl interactions, then each such interaction is equivalent to an increase in enthalpy of approximately 104 cal/mol. This analysis would predict an enthalpy difference of approximately 785 cal/mol (681 + 104) for the equilibrium **3a** ⇌ **3b** of 2,3-dimethylbutane. This estimate is in qualitative agreement with the value of 0.95 kcal/mol,[24] obtained by ultrasonic absorption, in which the expected tolerance is approximately ±400 cal/mol.[25]



2a **2b**



3a **3b**

Nmr Spectral Determinations. High resolution deuterium-decoupled nmr spectra were taken on a modified Varian A-60 nmr spectrometer, as described previously.[12] Spectra were obtained from a neat sample of 2-methylbutane-d_9 containing ~10% (v/v) hexamethyldisilane, and sealed under vacuum. Spectra were determined at ten temperatures from −91 to +72°, and 12–22 spectra were recorded at each temperature. Frequencies for each transition were calculated from the center at half-height of each peak from audio side band calibration. Scale factor corrections ranged from 0.984 to 0.991 Hz/cm. Average values and the corresponding standard deviations were calculated for each transition and any frequency values whose deviations were greater than twice the standard deviation for that transition were automatically discarded. This process was repeated automatically until experimental values were no longer discarded.

Initial values for ν_A, ν_B, and J_{AB} which were obtained from eq 1–3 were used as input for least-squares LAOCOON3 calculations. For each temperature, any transition whose average experimental frequency differed from the corresponding calculated value by more than twice the LAOCOON3 calculated standard deviation was discarded, and allowed to vary in a second iterative calculation. Table II shows the final results for ten temperatures.

Table II. Temperature Dependences of the Pmr Parameters for **1**

Temp[a]	ν_A[b]	ν_B[b]	J_{AB}[c]	δ_{AB}[c]
71.7	82.321 (0.004)[d]	68.796 (0.004)[d]	6.623 (0.004)[d]	13.525
51.3	82.056 (0.007)	68.605 (0.007)	6.662 (0.007)	13.451
30.8	81.717 (0.010)	68.381 (0.009)	6.716 (0.009)	13.336
19.7	81.563 (0.007)	68.258 (0.006)	6.739 (0.006)	13.305
−4.3	81.180 (0.015)	67.994 (0.013)	6.760 (0.013)	13.186
−20.5	80.933 (0.004)	67.792 (0.004)	6.779 (0.004)	13.141
−41.6	80.593 (0.019)	67.575 (0.019)	6.792 (0.017)	13.018
−61.7	80.227 (0.005)	67.283 (0.005)	6.855 (0.005)	12.944
−80.6	79.866 (0.010)	67.029 (0.010)	6.912 (0.009)	12.837
−91.2	79.703 (0.015)	66.900 (0.015)	6.923 (0.013)	12.803

[a] In °C; accurate to ±1°. [b] Downfield from HMDS in Hz. [c] In Hz. [d] Values in parentheses are standard deviations.

Experimental Section

2-Methylbutane-d_9 was prepared in three steps according to Scheme I.

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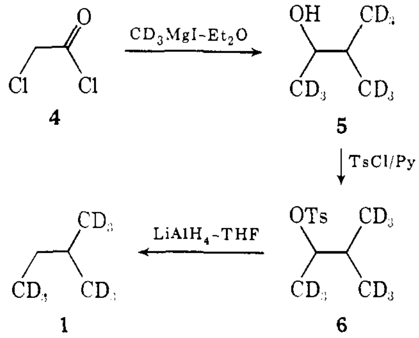
Scheme I



2-Methyl-3-butanol-d_9 (5). 2-Methyl-3-butanol-d_9 (5) was prepared using a procedure similar to that reported by Huston, Jackson, and Spero[26] for the undeuterated compound. The apparatus, which consisted of a 500-ml three-necked flask fitted with a Hofmann condenser, dropping funnel, nitrogen intake, and drying tubes, was dried in an oven for several hours, and flushed with dry nitrogen after assembly. Reagent grade magnesium turnings, 5.20 g (0.214 mol), and a small quantity of methyl-d_3 iodide (Stohler, 99.5% D) were added. The mixture was stirred vigorously and the remaining methyl-d_3 iodide (30 g total or 0.211 mol), dissolved in 100 ml of anhydrous ether, was added dropwise over a 1.5-hr period. Following the addition, the mixture was stirred for an additional 0.5 hr. Chloroacetyl chloride, 5.96 g (0.0527 mol), was dissolved in 100 ml of anhydrous ether, and added dropwise to the Grignard over a 1-hr interval so as to maintain a mild reflux. The ether was removed by distillation and the residue heated for 2 days at 95–100°.

The tarry residue was hydrolyzed by addition of ice, 100 ml of ether, and concentrated hydrochloric acid until the mixture was just acidic. The aqueous phase was extracted ten times with about 300 ml of ether, and the ether was dried over anhydrous potassium carbonate and sodium sulfate, and filtered. The filtrate was distilled slowly through a vacuum-jacketed Vigreux column. Several fractions were collected and analyzed by glc. The final two fractions (2.80 g, 55% theory), bp 94–112° (lit. bp 112° (734 mm)), were suitable for the next reaction. The undecoupled nmr spectrum of 5 exhibits three broad signals at δ 1.6 (C–H β to OH), 2.1 (C–H α to OH), and 3.5 (OH), with the expected integration ratio 1:1:1.

Methyl-3-butanol-d_9 Tosylate (6). To a stirred solution of 2.35 g (0.0242 mol) of 5 in 20 ml of dry reagent grade pyridine which was cooled in an ice bath was added dropwise a solution of 9.25 g (0.0484 mol) of *p*-toluenesulfonyl chloride in 20 ml of pyridine. Pyridinium chloride crystallized out after about 15 min. The reaction mixture was sealed in a flask and left for 2 days at 7°. After this time, the mixture was poured over ice and concentrated hydrochloric acid added until the resultant mixture was distinctly acid. The product was extracted three times with ether, and the combined ether extracts were washed with 5% hydrochloric acid and water and then dried over a mixture of anhydrous potassium carbonate and sodium sulfate. After filtration, the ether was removed on a rotary evaporator, and the residue was dissolved in pentane. The pentane was distilled and the process was repeated until no water droplets were observed in the distillate. The dry tosylate (6) was recrystallized three times from pentane, yield 5.36 g (88.5%), mp 20–21°. The undecoupled nmr spectrum of 6 exhibits an AB quartet centered at δ 7.6 (aromatic), a broad doublet at 4.5 (H α to –OTs), a singlet at 2.4 (aromatic methyl), and a multiplet at 1.8 (H β to –OTs), with the expected integration ratio 4:1:3:1.

2-Methylbutane-d_9 (1). Reagent grade tetrahydrofuran (30 ml) was distilled from lithium aluminum hydride into a dry three-necked 100-ml flask. The flask was fitted with a condenser and a pressure-equalizing dropping funnel with an intake for dry nitrogen. Lithium aluminum hydride, 2.0 g (0.052 mol), was added slowly through a powder funnel. The stirred mixture was heated in an oil bath at 65–70°, and 3.0 g (0.012 mol) of three times recrystallized 5 dissolved in 20 ml of dried tetrahydrofuran was added dropwise. The vaporized hydrocarbon, 1, was conducted through a micro purification train connected to the generating apparatus, consisting of bromine water (to remove 2-methyl-2-butene which was previously detected by glpc), sodium thiosulfate solution, and two ethylene glycol bubblers (to remove tetrahydrofuran solvent), and a tube of Drierite. Purified 1 was conducted finally through a finely drawn polyethylene tube into a constricted nmr tube immersed in a Dry Ice–2-propanol bath. A previous undeuterated sample, prepared and purified in the same way, was found by glpc to be pure.

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Stereochemical Control of Reductions. III. An Approach to Group Haptophilicities[1]

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Abstract: The tetrahydrofluorene system 1, angularly substituted with a series of functional groups R, has been catalytically hydrogenated over a palladium catalyst. For each functional group the percentage of cis isomer in the product is taken as a measure of that group's tendency, termed haptophilicity, to be bound to the catalyst surface during olefin reduction and thereby to enforce addition of hydrogen from its own side of the molecule. The nature of haptophilic activity and its correlation with various measures of group electronic characteristics and size are discussed.

Since the work of Linstead on the reduction of phenanthrenes,[3] many of the stereochemical aspects of heterogeneous catalytic hydrogenation have been made comprehensible in terms of the approach, fit, and binding of the reducible molecule to the surface of the catalyst.[4] These concepts have been applied with particular success to molecules whose geometry or substituents present severe steric hindrance to this

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