

Study of Molecular Reorientation in Liquid with Raman Spectroscopy (II)

Anisotropic Rotation of C_6F_6 in Neat Liquid

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Anisotropic rotation of C_6F_6 in neat liquid is investigated by the analysis of the ν_1 and ν_{15} (both C-F stretching) bands of Raman spectrum and diffusion constants for the spinning ($D_{||}$) and tumbling (D_{\perp}) motions are obtained by the rotational diffusion theory. The same analysis is also carried out for the ν_2 and ν_{16} (both C-C stretching) bands and both results are compared with the results obtained for benzene in neat liquid. The results show that the reorientation of C_6F_6 is highly anisotropic and the anisotropy is greater for C_6F_6 than benzene. This is due to the fact that the spinning rate is about the same but the tumbling rate is sharply reduced for C_6F_6 .

1. Introduction

Raman spectroscopy is widely used in studying molecular reorientation in liquids.¹⁻³ Previously, we studied the anisotropic rotation of $CDCl_3$ ⁴ in neat liquid with Raman spectroscopy complemented by NQR data. Currently, various techniques such as Raman, IR, NMR, *etc.* are available and valuable informations on molecular reorientation can be obtained by any of these techniques alone^{3,5} or by some combinations of different methods.^{6,7} Use of only one method provides an independent result which could be used in cross-checking the reliability of other techniques. In this regard, it is always desirable to have an independent method of extracting necessary information whenever that is possible.

It is well known⁸ that NMR technique is one of those independent methods. However, only the gross informations such as reorientational correlation times rather than correlation functions themselves can be obtained in this method. Also various parameters included in the relaxation time expression are often unknown or estimated with crude assumptions.⁹

Raman spectroscopy is an attractive alternative for such an independent method. Not only can it provide reorientational correlation functions and corresponding correlation times but also it can produce a number of independent results through the analysis of a variety of spectral bands. To be sure, the analysis of Raman spectral bands does not always give independent results as was shown in our earlier work on $CDCl_3$. But recently, Tanabe⁵ showed a possibility of getting an independent result by analyzing the ν_1 and ν_{15} bands of benzene which are assigned to the same C-H stretching vibrational modes with different symmetries. Using the isolated binary collision model of Fischer and Laubereau,¹⁰ he was able to estimate the vibrational contribution to the anisotropic component of ν_{15} band from the ν_1 band. The same type of analysis is employed in this work for hexafluorobenzene in neat liquid.

Considerable attention has been paid to the reorientation of benzene in the liquid state. Assuming that rotations about symmetry axes are governed by the rotational diffusion process, a question of interest was the degree of anisotropy of the reorientational motion. Two contradictory results were re-

ported. Bartoli and Litovitz³ claimed that the reorientation is nearly isotropic and Gillen and Griffiths⁶ found highly anisotropic motion. Recent investigations^{5,7} show that highly anisotropic reorientation is more likely.

In spite of the similar structure to benzene molecule, the reorientation of hexafluorobenzene has seldom been studied with Raman spectroscopy. Some time ago, Fujiyama and Crawford¹¹ reported a highly anisotropic reorientation of hexafluorobenzene with IR spectroscopy. However, their result was obtained by neglecting the contribution of vibrational relaxation to the IR band widths.

The purpose of this work is to provide an independent method of investigating the anisotropic nature of reorientational motion of hexafluorobenzene in neat liquid with Raman spectroscopy. The ν_1 and ν_{15} (both C-F stretchings) bands are analyzed by the isolated binary collision model and diffusion constants characterizing the spinning ($D_{||}$) and tumbling (D_{\perp}) motions are obtained in terms of the theory¹² of anisotropic rotational diffusion for symmetric top molecules. The same procedure is also applied to the ν_2 and ν_{16} (both C-C stretching) bands and both results are compared with the results obtained for benzene in neat liquid.

2. Experimental

Raman spectra were recorded with Japan Spectroscopic Company model R-300 laser Raman spectrophotometer modified with EG&G Princeton Applied Research model 1120/1105 photon counting system. 514.5 nm line of Spectra Physics model 164-06 Argon ion laser was used as the exciting source with 200 mW output power. All the measurements were performed at room temperature ($20 \pm 2^\circ C$). To obtain the parallel ($I_{||}$) and perpendicular (I_{\perp}) components of a Raman band, polarizer/polarization scrambler assembly was used.

The effect of the slit broadening on the Raman band widths was corrected using the formula.¹³

$$\delta_t = \delta_a [1 - (S/\delta_a)^2] \quad (1)$$

where δ_t and δ_a are the true and apparent (observed) band widths (FWHM's) and S is the spectral slit width. All the mechanical slits in the double monochromator were set at 200μ width. Spectral slit width of the instrument was obtained

by measuring the widths of Neon emission lines at several wavelengths, 18717.550, 18511.446, and 17342.993 cm⁻¹ in the present experiment. Since the spectral slit width is proportional to $\bar{\nu}^2$ ¹⁴, $\ln S$ vs. Raman shift frequency ($\bar{\nu}_R = \bar{\nu}_0 - \bar{\nu}$) plot results in a straight line in the first order approximation. And the spectral slit widths for the several Raman bands of hexafluorobenzene can be easily estimated from the calibration curve.

Isotropic (I_{iso}) and anisotropic (I_{aniso}) components of a Raman band can be evaluated from the well-known relations¹⁵

$$I_{iso} = I_{\parallel} - \frac{4}{3} I_{\perp} \quad (2)$$

$$I_{aniso} = I_{\perp} \quad (3)$$

Instead of evaluating the full profiles of I_{iso} and I_{aniso} and then measuring the FWHM's of each profile, band widths of above components were calculated directly from those of I_{\perp} and I_{\parallel} and the depolarization ratios following the procedure suggested by Tanabe and Hiraishi.¹³

Hexafluorobenzene was purchased from the Aldrich Chemical Co. and used without further purification.

3. Results and Discussion

The Raman spectrum of hexafluorobenzene obtained with the present experimental arrangement is shown in Figure 1. With the benzenelike structure, the normal mode analysis for hexafluorobenzene is easily done, and vibrational assignments for Raman-active fundamentals were carried out by Delbouille¹⁶ and also by Steele and Whiffen.¹⁷ Vibrational assignments together with the depolarization ratios (ρ) for the Raman active fundamentals studied in this work (ν_1 , ν_2 , ν_{15} , and ν_{16}) are listed in Table 1. The parallel and perpendicular components of the above fundamentals are shown in Figures 2-5.

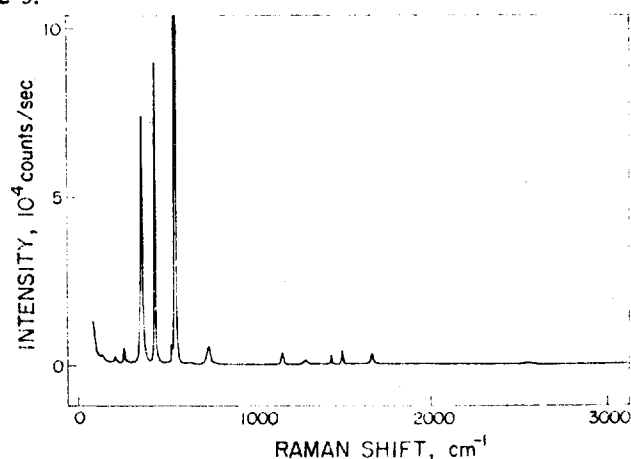


Figure 1. Raman spectrum of hexafluorobenzene.

TABLE 1: Vibrational Assignment of Some Raman Active Fundamentals of C₆F₆

Assignment	Frequency, cm ⁻¹	ρ^a
A _{1g} ν_1 (C-F)	1490	0.091
ν_2 (C-C)	560	0.041
E _{2g} ν_{15} (C-F)	1655	0.75
ν_{16} (C-C)	1157	0.75

^a Calculated with peak heights.

A_{1g} fundamentals (ν_1 and ν_2) are strongly polarized and the widths of the isotropic and anisotropic components were calculated as described in the experimental section. Two nontotally symmetric modes (ν_{15} and ν_{16}) are completely

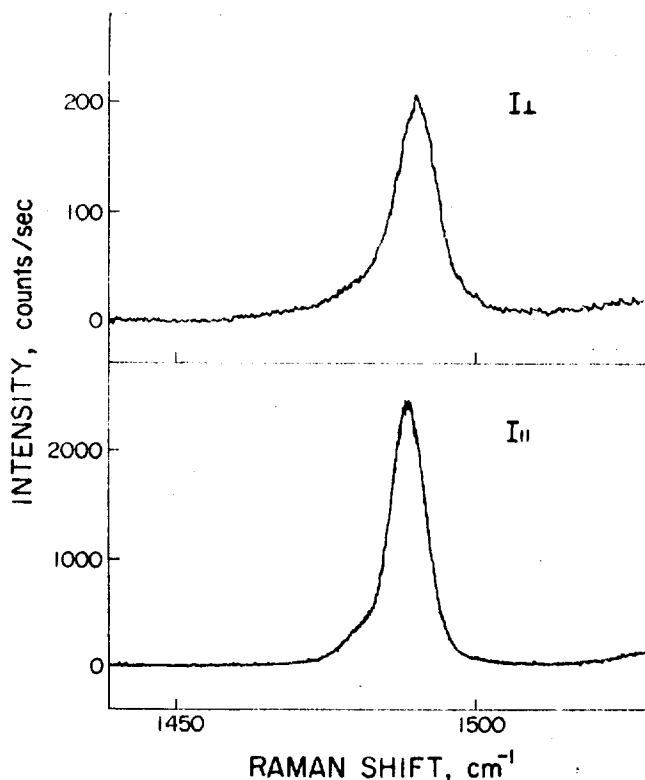


Figure 2. Parallel (I_{\parallel}) and perpendicular (I_{\perp}) components of ν_1 band. Time constants used were 1 sec. for I_{\parallel} and 10 sec. for I_{\perp} .

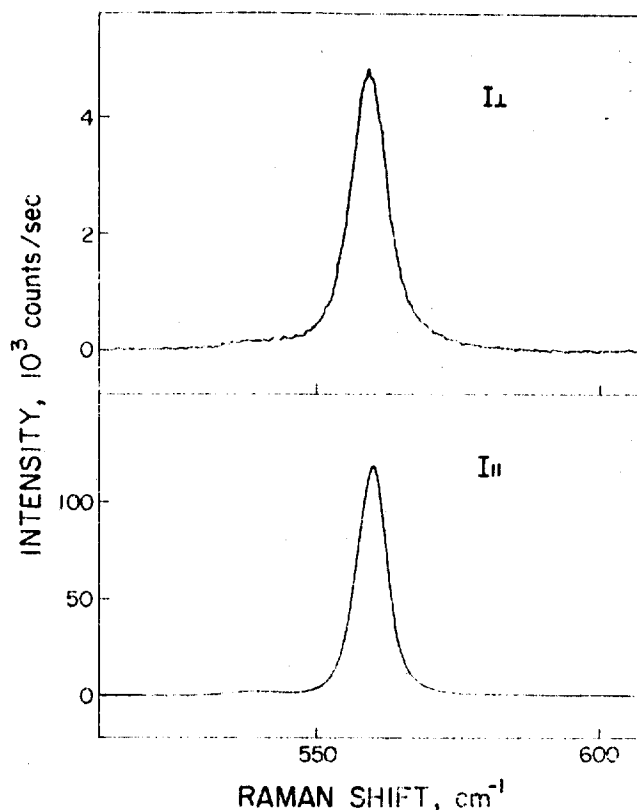


Figure 3. Parallel (I_{\parallel}) and perpendicular (I_{\perp}) components of ν_2 band. 1 sec. time constant was used.

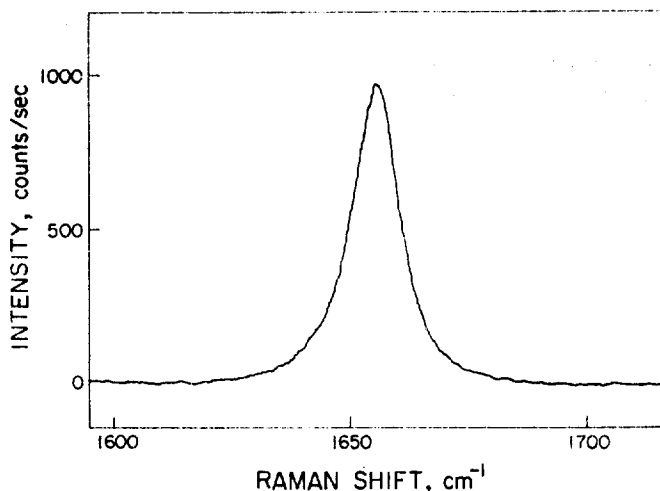


Figure 4. Perpendicular component of ν_{15} band. 10 sec. time constant was used.

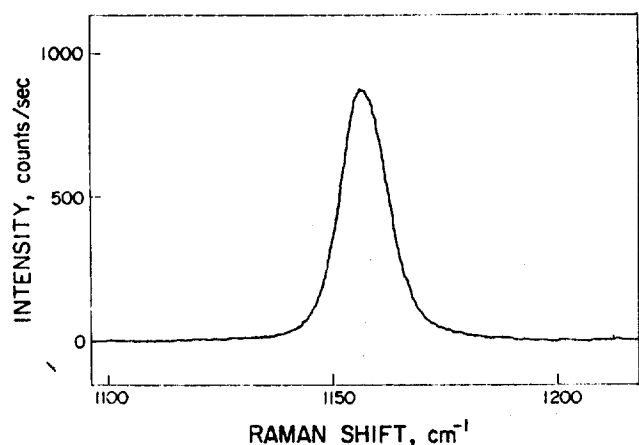


Figure 5. Perpendicular component of ν_{16} band. 10 sec. time constant was used.

TABLE 2: Band Widths of the Isotropic and Anisotropic Components of ν_1 , ν_2 , ν_{15} , and ν_{16}

Vibrational mode	δ_{iso} , cm^{-1}	δ_{aniso} , cm^{-1}
ν_1	5.73 ± 0.22	7.14 ± 0.12
ν_2	5.01 ± 0.30	6.21 ± 0.16
ν_{15}	—	12.18 ± 0.44
ν_{16}	—	11.58 ± 0.19

depolarized ($\rho=3/4$), and the widths of only the anisotropic components were measured. Band width data for the above fundamentals are listed in Table 2. The values represent the averages of at least 12 different measurements.

Isotropic component (I_{iso}) of a Raman band is broadened by the vibrational relaxation only, and is expressed as a Fourier transform of the vibrational correlation function [eq. (4)]. On the other hand, anisotropic component (I_{aniso}) contains contributions from both the vibrational and reorientational relaxation processes. Assuming that the vibrational and reorientational motions are completely decoupled, I_{aniso} is expressed as a Fourier transform of the product of the vibrational and reorientational correlation functions [eq. (5)].

$$I_{iso}(\omega) = \int_{-\infty}^{\infty} \Phi_{vib}(t) \exp(i\omega t) dt \quad (4)$$

$$I_{aniso}(\omega) = \int_{-\infty}^{\infty} \Phi_{vib}(t) \Phi_{reor}(t) \exp(i\omega t) dt \quad (5)$$

Both the vibrational and reorientational correlation functions are assumed to be exponential, *i.e.*,

$$\Phi_{vib}(t) = \exp(-t/\tau_{vib}) \quad (6)$$

and

$$\Phi_{reor}(t) = \exp(-t/\tau_{reor}). \quad (7)$$

Then, the vibrational and reorientational correlation times τ_{vib} and τ_{reor} are given by¹⁸

$$\tau_{vib} = (\pi c \delta_{iso})^{-1} \quad (8)$$

$$\tau_{reor} = [\pi c (\delta_{aniso} - \delta_{iso})]^{-1}. \quad (9)$$

where δ_{iso} and δ_{aniso} are the widths (FWHM's) of the isotropic and anisotropic components, respectively.

For symmetric top molecules, the reorientational correlation time τ_{reor} is given by^{12(b)}

$$\tau_{reor} = [n(n+1)D_{\perp} + m^2(D_{\parallel} - D_{\perp})]^{-1} \quad (10)$$

Here D_{\perp} and D_{\parallel} are the diffusion constants characterizing the tumbling and spinning motions of the figure axis, *i.e.*, C_6 -axis in the case of hexafluorobenzene. The constants n and m are determined by the symmetry of the Raman band ($n=2, m=0$ for A_{1g} modes, and $n=2, m=\pm 2$ for E_{2g} modes).

Band widths of two A_{1g} fundamentals ν_1 and ν_2 provide two separate data for D_{\perp} , $0.22(\pm 0.05) \times 10^{11} \text{ sec}^{-1}$ from ν_1 mode and $0.19(\pm 0.07) \times 10^{11} \text{ sec}^{-1}$ from ν_2 . The agreement between D_{\perp} values from two different fundamentals is excellent within experimental errors.

Reliable determination of D_{\parallel} from Raman spectrum is extremely difficult. In principle, proper treatment of a nontotally symmetric Raman band ($m \neq 0$ in eq. (10)) is expected to provide the needed information. However, depolarization ratio of a nontotally symmetric band equals 3/4, and isotropic component vanishes completely (eq. (2)). Total disappearance of the isotropic component makes it impossible to subtract the contribution of the vibrational relaxation from the anisotropic band width.

Tanabe⁵ proposed an approximate method of estimating the vibrational relaxation time for nontotally symmetric Raman band in his study of anisotropic reorientation in liquid benzene. Assuming that the vibrational dephasing is the dominant vibrational relaxation process, the isolated binary collision model of Fischer and Laubereau¹⁰ was used to evaluate the vibrational relaxation widths of the Raman bands of interest. When two Raman bands, ν_i and ν_j , are of the similar vibrational type, the vibrational relaxation widths arising from dephasing may be related by

$$\delta_{vib}(\nu_i) = \left(\frac{\nu_j}{\nu_i} \right)^2 \delta_{vib}(\nu_j). \quad (11)$$

The ν_1 and ν_{15} bands of hexafluorobenzene studied in this work are of the same vibrational type (C-F stretchings). Also, ν_2 and ν_{16} are assigned to the same vibrational modes (C-C stretchings).

The resonant energy transfer¹⁹ process, which is another major contributor to vibrational band broadening, is not expected to be significant for Raman bands of hexafluoroben-

TABLE 3: Diffusion Constants for Anisotropic Rotation of Hexafluorobenzene and Benzene

	$D_{\perp}, 10^{11} \text{ sec}^{-1}$	$D_{\parallel}, 10^{11} \text{ sec}^{-1}$	
C ₆ F ₆	0.22 ± 0.05	1.67 ± 0.17	Raman (ν_1, ν_{15}), this work
	0.19 ± 0.07	2.36 ± 0.10	Raman (ν_2, ν_{16}), this work
	0.25 ± 0.16	—	Raman (ν_2), ref. 3 ^a
	0.157	—	Rayleigh, ref. 20 ^b
	1.8	5.4	IR, ref. 11
C ₆ H ₆	0.63 ± 0.1	0.52 ± 0.16	Raman (ν_2, ν_{13}), ref. 3
	0.54	3.36	Raman (ν_2) + NMR, ref. 6
	0.89	1.80	Raman (ν_1, ν_{15}), ref. 5
	0.64	2.34	Rayleigh + NMR, ref. 7

^a Evaluated from the band width data therein. ^b Evaluated from the single particle reorientation time therein.

zene. The resonant energy transfer between oscillators on adjacent molecules occurs mostly through interactions between transition dipoles or between permanent dipoles, both of which vanish for Raman bands of centrosymmetric hexafluorobenzene.

Therefore, the vibrational relaxation widths of ν_{15} and ν_{16} modes may be estimated from the isotropic band widths of ν_1 and ν_2 , respectively, using eq. (11). With the values thus calculated, the vibrational relaxation widths can be subtracted from the anisotropic band widths in eq. (9).

Diffusion constants for the anisotropic rotation of hexafluorobenzene thus evaluated are listed in Table 3 together with some previously reported values. Diffusion constants for the same motion of benzene in neat liquid are also listed in the table.

Diffusion constant for the tumbling motion (D_{\perp}) of hexafluorobenzene agrees very well with the one evaluated from the previous Raman spectroscopic work by Bartoli and Litovitz³ ($D_{\perp} = 0.25 (\pm 0.16) \times 10^{11} \text{ sec}^{-1}$). The value evaluated from the single particle reorientation time data obtained from depolarized Rayleigh scattering experiments by Bauer, Brauman and Pecora²⁰ also exhibits good agreement with our data. However, IR spectroscopic result reported by Fujiyama and Crawford¹¹ is much larger than the present one. This discrepancy is understandable since the vibrational relaxation widths could not be adequately determined by IR technique and thus were neglected in their work. Also, it is interesting to note that tumbling in C₆F₆ is more difficult than that in C₆H₆, probably due to the presence of heavy fluorine atoms and conspicuous inertial effect thereby.

The values of diffusion constant (D_{\parallel}) for spinning motion of hexafluorobenzene determined from two different sets of Raman bands display slight difference. This difference may originate from different degrees of vibration-rotation coupling in different modes. Alternatively, it may be implied that the present method of estimating the vibrational relaxation widths needs some refinement. A better understanding of the dominant vibrational relaxation mechanisms for each Raman band would be very helpful.

D_{\parallel} determined by IR technique is again larger than the present data probably due to the same reason as discussed for D_{\perp} . Spinning motion of hexafluorobenzene looks as easy as for benzene, which is very surprising when the difficulty

of tumbling motion of hexafluorobenzene is recalled. Also, the reorientational motion in neat liquid hexafluorobenzene is highly anisotropic, certainly more so than in liquid benzene.

4. Summary

The anisotropic reorientation of C₆F₆ in neat liquid was studied by Raman spectroscopy. Diffusion constants for tumbling (D_{\perp}) and spinning (D_{\parallel}) motions around the figure axis were obtained by analyzing ν_1 and ν_{15} band pair (C-F stretching), and also ν_2 and ν_{16} pair (C-C stretching). The reorientational motion of C₆F₆ in neat liquid was found to be highly anisotropic, even more so than that of C₆H₆ in neat liquid.

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Effect of Trialkylborane on the Stereochemistry of Ketone Reduction with Lithium Borohydride

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The effects of trialkylborane on the stereochemistry of ketone reduction with lithium borohydride were studied for the four representative ketones, namely 4-*t*-butylcyclohexanone, 2-methylcyclohexanone, norcamphor, and camphor. The presence of trialkylborane increased the yields of the less stable alcohols. For example, in the presence of tri-*s*-butylborane, 42 % yield of *cis*-4-*t*-butylcyclohexanol was observed whereas only 8 % yield with lithium borohydride alone in the reduction of 4-*t*-butylcyclohexanone. The *in situ* formation of lithium trialkylborohydride, by the hydride transfer from lithium trialkoxyborohydride to trialkylborane, was demonstrated as a possible mechanism for the catalytic effect of trialkylborane.

Introduction

The stereochemistry of the ketone reduction by metal hydride reagents has been extensively studied.¹⁻⁵ In the case of the rigid bicyclic ketones such as norcamphor and camphor, the attack of hydride from the reagents occurs predominantly at the less hindered side of the carbonyl group to provide the less stable isomer of the two possible alcohols as a major product. On the other hand, in the case of the less rigid monocyclic ketones such as 2-methylcyclohexanone and 4-*t*-butylcyclohexanone, the major reduction products are the more stable equatorial alcohol isomer.

There are many attempts and achievements to increase stereoselectivity toward the less stable alcohol isomer by modifying metal hydrides. Among them, some of the recently synthesized trialkylborohydrides possessing great steric requirements have shown excellent selectivities in the reduction of both cyclohexanones and bicyclic ketones.⁶⁻⁹ Thus lithium tri-*s*-butylborohydride, a hindered trialkylborohydride, reduced 4-*t*-butylcyclohexanone and norcamphor to yield 93 % of *cis*-4-*t*-butylcyclohexanol and 99.6 % of *endo*-norborneol, the less stable isomers.

Recently, we have carried out a systematic study for the reaction of lithium borohydride with representative organic compounds.¹⁰ In this study, lithium borohydride showed remarkable contrasts to borane in reducing characteristics, presumably due to its basic character compared to the acidic character of borane. And we have found that trialkylborane exhibits significant catalytic effects¹¹ on the reactions of alcohol, epoxide, and ester with lithium borohydride.

Therefore, it appeared desirable to explore the effect of trialkylborane on the stereochemistry of the ketone reductions with lithium borohydride. Accordingly, we selected a group of model ketones, 4-*t*-butylcyclohexanone, 2-methylcyclohexanone, norcamphor, and camphor, and subjected them to the reduction by lithium borohydride in the presence of trialkylboranes, under the standard condition (0°, THF).

Results and Discussion

In general, all reactions were carried out with a mixture of the compound (0.25 *M*), and various concentrations of the hydride reagents and trialkylboranes in THF at 0°.

After the appropriate time of reaction, the reaction mixture was hydrolyzed with water and oxidized with alkaline hydrogen peroxide. And then THF layer was separated by addition of anhydrous potassium carbonate, dried over anhydrous magnesium sulfate, and subjected to glpc analysis.

Effect of Trialkylborane on the Stereochemistry of Ketone Reduction with Lithium Borohydride. In order to examine the effect of trialkylborane on the stereochemistry of ketone reduction with lithium borohydride, representative ketones, namely 4-*t*-butylcyclohexanone, 2-methylcyclohexanone, norcamphor, and camphor, were reacted at 0° in THF with lithium borohydride itself and with lithium borohydride in the presence of equimolar amount of triethylborane or tri-*s*-butylborane. The total yields of alcohols and the normalized percentage of the less stable alcohols are summarized in Table 1.

As shown in Table 1, for the reaction of monocyclic ketones, as the size of alkyl substituents on boron increased, the per-