collapse in the ^{11}B nmr spectrum; the high-field doublet (δ +23.5) is unchanged. In the ^{1}H nmr, the high-field quartet centered at τ 9.85 (Figure 3b) is the only H–^{11}B resonance present.

The low-field doublet (δ −5.0) in the ^{11}B spectrum and the low-field quartet (τ 5.25)[13] in the ^{1}H spectrum of $C_2B_5H_7$ may be assigned to the lone equatorial B–H group on the basis of area considerations alone. The two remaining doublets in the ^{11}B nmr spectrum and the quartets in the ^{1}H nmr spectrum are of equal area and can be equivocally assigned to positions 1,7 or 5,6.

Analysis of the microwave spectrum conclusively shows that in $B_5C_2H_4D_3$ the three deuterium atoms are attached to the equatorial borons (3,5,6). Hence the remaining doublet in the ^{11}B nmr (δ +23.5) can be assigned to the apical borons at positions 1 and 7. The resonance at δ −2.0 belongs to the equatorial borons.

Similarly in the ^{1}H nmr spectrum, the quartet centered at τ 9.85 can be assigned to the protons on the apical borons. The remaining unassigned quartet at τ 6.00 belongs to the equatorial borons at positions 5 and 6.

Hence the apical boron resonances are located at higher field than the equatorial boron resonances in agreement with the corresponding resonances found in related systems, *e.g.*, B_5H_9, B_5H_{11}, B_6H_{10}, and $C_2B_4H_8$.

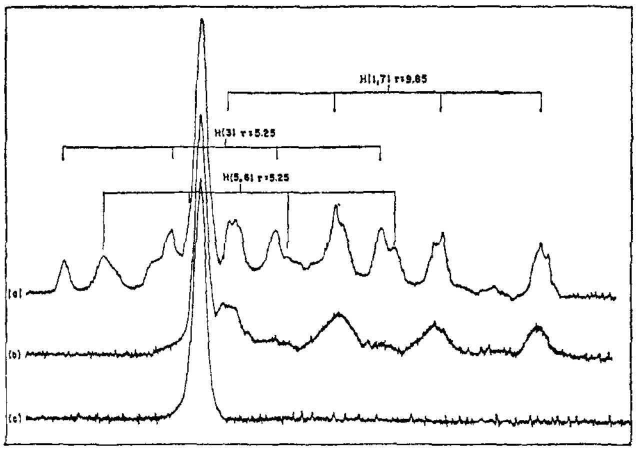

Figure 3. ^{1}H nmr spectra: (a) undeuterated; (b) 3,5,6-deuterated; (c) 1,3,5,6,7-deuterated. All spectra chemical shifts were measured using tetramethylsilane as the reference compound. The spectra were measured at 60 Mc.

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[13] Naturally occurring boron consists of 81% ^{11}B (I = $^{3}/_{2}$; magnetogyric ratio, 1366 cycles/gauss sec) and 19% ^{10}B (I = 3; magnetogyric ratio 457.5 cycles/gauss sec). The quartets assigned to the ^{11}B-attached hydrogens in the ^{1}H spectrum are usually well defined, whereas the smaller septets of the ^{10}B-attached hydrogens are buried under the labyrinth of all other resonances.

Organometallic Exchange Reactions. IV. Lithiomethyltrimethylsilane and *t*-Butyllithium in Hydrocarbon Solvents[1]

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Abstract: The ^{7}Li and ^{1}H spectra of mixtures of *t*-butyllithium and lithiomethyltrimethylsilane [$LiCH_2Si(CH_3)_3$] in cyclopentane and toluene solutions have been obtained. The spectra are consistent with attainment of an equilibrium involving random distribution of the two kinds of alkyl groups among tetrameric species. Attainment of equilibrium is very slow in cyclopentane, with an estimated half-life of 6–8 hr. The rate-determining process appears to be: $[LiC(CH_3)_3]_4 \rightarrow 2[LiC(CH_3)_3]_2$. At temperatures in the range +10 to +20° the spectra undergo a change which is identified with a slowing of intramolecular exchanges within tetramers. Intermolecular exchanges are much faster in toluene than in cyclopentane. Intramolecular exchange is only slightly faster.

Evidence has been presented in previous papers of this series for the tetrameric character of simple alkyllithium compounds in ether at temperatures on the order of −50°. Intermolecular exchange between tetramers has been demonstrated,[3] and a quantitative assessment of the exchange rate for methyllithium has been made. On the basis of rather sparse evidence[4,5] it appears that intermolecular exchanges between alkyllithium species in hydrocarbon solvents are much slower than in ether. The purpose of the research reported in this paper has been to learn more about the exchanges in hydrocarbon solution.

We have chosen to study the exchange between *t*-butyllithium (I) and lithiomethyltrimethylsilane (II). Since each is tetrameric in hydrocarbon solvents,[6,7]

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[2] (a) National Science Foundation Summer Fellow, 1964–1965; Dow Chemical Co. Fellowship, 1964–1965; Toni Co. Fellowship, 1965–1966; (b) Alfred P. Sloan Research Fellow.

[3] L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).

[4] M. Weiner and R. West, *ibid.*, **85**, 485 (1963).

[5] T. L. Brown and J. A. Ladd, *J. Organometal. Chem.*, **2**, 373 (1964).

[6] M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

[7] (a) G. E. Hartwell and T. L. Brown, *ibid.*, **3**, 1656 (1964); (b) R. H. Baney and R. J. Krager, *ibid.*, **3**, 1657 (1964).

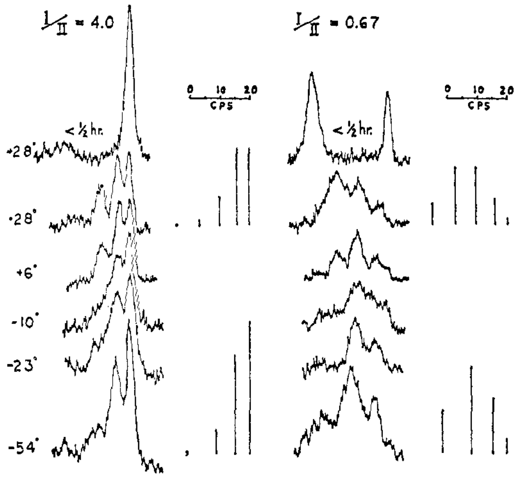

Figure 1. ^{7}Li nmr spectra of cyclopentane solutions containing *t*-butyllithium (I) and lithiomethyltrimethylsilane (II). The top spectrum in each column shows the appearance of the spectrum shortly after preparation. All others refer to equilibrium mixtures. The calculated spectra on the right of each column refer to different assumptions regarding intramolecular and intermolecular exchanges.

one anticipates, by analogy with other known systems,[8] a near-random distribution of the two types of alkyl groups among tetramer bonding sites, yielding five tetrameric species, $I_{4-n}II_n$. The identification of these might be accomplished through observation of the ^{7}Li spectra of mixtures, since the ^{7}Li chemical shifts are different for the two compounds (in cyclopentane, I is at −0.89 ppm; II is at −1.96 ppm from aqueous LiBr external standard).

Experimental Section

Materials. Lithium metal was obtained from the Foote Mineral Co. as a dispersion in hexane, the 1% sodium alloy from Lithium Corporation of America as a dispersion in mineral oil. *t*-Butyllithium was prepared as previously described[9] and purified by vacuum sublimation at 65–70°. Purity of the sample was tested by inspection of the proton resonance spectrum. Lithiomethyltrimethylsilane was prepared as previously described[10] and purified by vacuum sublimation at 100–105°, and its purity was tested by examination of the proton resonance spectrum.[11] The time for completion of preparative reaction can be greatly shortened by using cyclohexane as solvent and refluxing after adding the reactants. Coupling does not seem to be a problem, and a 60–70% yield is possible after about 1.5 hr.

Mallinckrodt reagent grade toluene and Aldrich cyclopentane were chromatographed through silica gel, flushed with argon to deaerate, and stored over sodium wire.

Solutions, usually 0.5 *M*, were prepared in an argon atmosphere glove box, from which traces of oxygen and water were removed by continuous circulation of the atmosphere through columns packed with molecular sieves and MnO.[12] Concentrations of solutions were determined by titration with potassium acid phthalate solution to a phenolphthalein end point. Relative concentrations of *I vs.* II were determined by integration of the methyl proton magnetic resonance signals. The solutions were sealed under vacuum in standard nmr tubes and stored in Dry Ice prior to use.

Nmr Spectra. ^{7}Li spectra were obtained at 23.3 Mc in a field of 14,092 gauss using a Varian Associates Model DP60 spectrometer. Aqueous lithium bromide solution (7 g of commercial grade LiBr/10 ml of solution) was employed as an external standard for room temperature chemical shift measurements. A Varian Associates A-60 spectrometer was used to obtain the proton spectra.

Low temperatures were obtained using standard accessories supplied by Varian Associates. After allowing the system to come to equilibrium at each temperature, a number of spectra were recorded. In all cases the data represent an average of three or more scans through each spectrum.

Results and Discussion

^{7}Li Spectra. The initial observation of importance is that the approach of mixtures of I and II to equilibrium in cyclopentane is remarkably slow (Figure 1). The half-life at room temperature (about 28°) for intermolecular exchange of alkyl groups leading to a statistical distribution, starting from pure I and II, is estimated to be about 6 hr. The rate-determining process is probably a dissociation of one of the tetramers, $Li_4R_4 \rightarrow 2Li_2R_2$. From the manner in which the spectra change with time in the early stages of exchange it is deduced that dissociation of *t*-butyllithium tetramer (I_4) is rate determining. If one begins with II_4 and I_4, and if the dissociation of the former is rapid relative to the latter, then the species II_2I_2 and II_3I will both appear in the spectrum before any significant quantity of $II(I)_3$ is seen. In the present case, the species rich in II appear first as the exchanges proceed.

Arrival at equilibrium is characterized by time invariance of the spectrum and by a correspondence of the observed relative intensities with those calculated assuming a random distribution of alkyl groups. Figure 1 shows the spectra obtained from two representative samples, with different ratios of I and II. The calculation of the distribution of the five species for any fraction of I (f_I) is easily accomplished using eq 1.

$$F_{I_{4-n}II_n} = f_I^{\,4-n} f_{II}^{\,n} \frac{4!}{n!(4-n)!} \qquad (1)$$

The chemical shifts of the two outer peaks correspond to the shifts observed for the pure components, I and II. Thus the other three peaks are due to mixed species. No effort was made to measure the relative areas of the peaks, because of varying degrees of overlap. However, the calculated spectra exhibit a reasonable agreement with the observed heights in various mixtures investigated. Thus, the statistical model, with assumption of a random distribution of alkyl groups, is fairly closely followed.

The fact that the observed spectrum corresponds to the relative intensities expected for the five $I_{4-n}II_n$ requires that there be rapid intramolecular exchange which leads to equivalence of the four lithium atoms in each tetramer. The possibility of a rapid intramolecular exchange in alkyllithium polyhedra was advanced earlier,[13] but the present results constitute the first evidence for it.

Equilibrium cyclopentane solutions were examined at lower temperatures in the hope of discerning a slow exchange limit for the intramolecular processes. In the limit of slow intramolecular exchange, there are eight chemically distinct lithium sites among the five $I_{4-n}II_n$ species. However the chemical shift of the

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[8] J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

[9] C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).

[10] J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963).

[11] The nmr spectrum in cyclopentane gave the following coupling constants (cps): $J_{Si^{29}-CH} = 6.05 \pm 0.05$ for the CH$_3$, $J_{Si^{29}-CH} = 10.8 \pm 0.1$ for the CH$_2$, and $J_{C^{13}-H} = 116.7 \pm 1$ cps for the CH$_3$. Those for the methyl groups are lower than any previously reported; *cf.* H. Schmidbaur, *J. Am. Chem. Soc.*, **85**, 2336 (1963).

[12] T. L. Brown, D. W. Dickerhoof, G. L. Morgan, and D. A. Bafus, *Rev. Sci. Instr.*, **33**, 491 (1962).

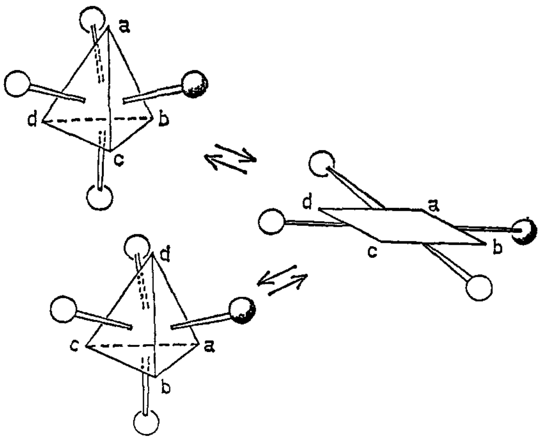
[13] T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

^{7}Li atom may be expected to depend principally on the "local environment," *i.e.*, on the nature of the three groups bonded to the adjacent three faces.[3] On the basis of this "local environment" hypothesis, four distinct ^{7}Li resonances are expected, arising from 3II, 2II,I, II,2I, and 3I environments. Assuming a random distribution of the alkyl groups, this time among only four possibilities, the following equation can be used in a manner similar to eq 1, where f_I is the fraction of I present.

$$F_{I_{3-n}II_n} = f_I^{3-n} f_{II}^{n} \frac{3!}{n!(3-n)!} \qquad (2)$$

The ^{7}Li nmr spectra of cyclopentane solutions undergo a marked change in the temperature interval +10 to −20°, as shown in Figure 1. This change, which occurs as rapidly as the sample can be cooled, is clearly associated with intramolecular processes, since it has already been established that the intermolecular processes are very slow. At temperatures of −25° and lower the spectra match very well with the four-line spectrum predicted for slow intramolecular exchange, with local environment determining chemical shift. Although the spacing between the peaks produced by the four local environments is not constant, it is roughly 6–8 cps. It is easily understood, therefore, that the fourth group, which is on the opposite side of the tetramer from the lithium, and not bonded to it through covalent interactions, should exert a weak effect on the ^{7}Li chemical shift. We have found that even substitution of an alkoxide group for an alkyl group on the tetramer does not appreciably affect the chemical shift of the opposite lithium atom.[3] Some broadening of the resonance lines may, however, occur from these slight effects.

Although each of the tetramers present in solution may undergo intramolecular exchange at a different rate, the rates must be closely similar for all of the species, since the spectra undergo metamorphosis over a fairly narrow temperature interval. In the earlier discussion of intramolecular exchange processes, it was suggested that the intermediate might be a planar square of lithium atoms, with the alkyl groups bonding in three-center bridge bonds along the sides of the square.[13] In the tetramer each alkyl group is bonded equivalently to three lithium atoms, abc; in the postulated transition state to two lithium atoms, perhaps ab. In returning to the tetrahedral configuration it may again be bonded to abc, or on the other hand, to abd, as shown. In a sense, intramolecular exchange is a manifestation of the solvent cage effect, since the transition state can also be thought of as two dimers which are twisting with respect to one another so as to effect the required exchange of alkyl groups among the bonding sites. The ratio of intra- to intermolecular exchange rates, however, is on the order of 10^6. It is quite unlikely that a cage effect alone could account for a difference of this magnitude. The precise configuration of the high-energy form remains a matter of speculation at this time.



In summary, the ^{7}Li data for cyclopentane solutions establish that: (a) Intermolecular exchange between I and II is very slow and is rate determined by dissociation of *t*-butyllithium tetramer. (b) Intermolecular exchanges between *any* tetrameric species are slow on the nmr time scale at room temperature. This conclusion follows from the observation that the ^{7}Li spectra of samples at equilibrium show no evidence of exchange collapse between any of the five distinct species. (c) A marked change in the spectra between +10 and −20° corresponds to a slowing of intramolecular exchange.

A similar study of the ^{7}Li spectra of mixtures of I and II was carried out in toluene solutions. Spectra of two representative samples at various temperatures are shown in Figure 2. From observation of a number of samples it is clear that the toluene spectra below −30° have the same intensity distribution among four distinct ^{7}Li resonances as the low-temperature cyclopentane spectra. (The ^{7}Li chemical shifts for I and II in toluene are −0.40 and −1.36 ppm, respectively, from the aqueous LiBr standard. Thus, the separation of the ^{7}Li resonances is about the same in toluene as in cyclopentane.) The transition from rapid to slow intramolecular exchange occurs in the temperature range −5 to −30°, about 10 to 15° lower than in cyclopentane.

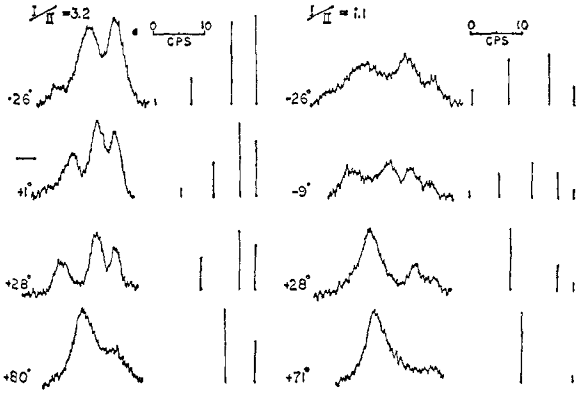


Figure 2. ^{7}Li nmr spectra of toluene solutions containing I and II. The calculated spectra shown to the right of the observed spectra refer to various assumptions regarding intramolecular and intermolecular exchange. Where certain of the mixed species undergo intermolecular exchange, the collapsed line is shown in the calculated spectrum at a weighted chemical shift, and with a total relative intensity given by the sum of the relative abundances of the exchanging species.

At temperatures above −5° the toluene spectra show evidence of rapid intermolecular exchanges. As the temperature is raised, the lines corresponding to individual tetrameric species undergo a progressive collapse, beginning with species richest in II. Thus at 28°, for example, the spectrum consists of

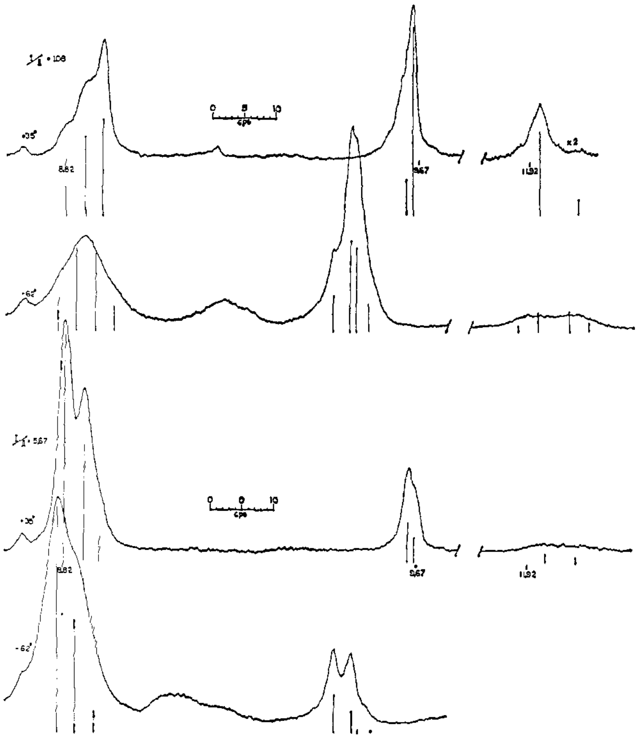


Figure 3. Proton magnetic resonance spectra of mixtures of *t*-butyllithium (I) and lithiomethyltrimethylsilane (II) in toluene.

three lines. The one at lowest field is an exchange-collapsed resonance, corresponding to II_4, II_3I, and II_2I_2. The remaining two lines correspond to $II(I)_3$ and I_4. The line corresponding to the exchanging species has a relative intensity equal to the sum of the relative concentrations of the three exchanging species and a chemical shift value which is a weighted average of the three chemical shifts of the exchanging species. Calculated and observed spectra are shown in Figure 2 for a number of different temperatures. As temperature is increased, exchange collapse occurs progressively, until at the highest temperature observed, 80°, only the *t*-butyllithium tetramer (I_4) is distinguishable from the single major absorption corresponding to all the other (exchanging) tetramers. It is quite evident from these results that the *t*-butyllithium tetramer is considerably less liable to exchange than the tetramer of lithiomethyltrimethylsilane. This result is consistent with the conclusion drawn from the cyclopentane data that dissociation of I_4 is rate determining in that solvent.

There is evidence in the 80° spectrum of the beginnings of exchange between the two remaining lines. A single spectrum taken at 91° appeared to show more extensive collapse, albeit obscured by extensive decomposition. It is possible to estimate roughly from these data that intermolecular exchange involving dissociation of I_4 is on the order of 10^3 to 10^4 times faster in toluene than in cyclopentane. This large difference in rate is ascribable to the π-donor character of the aromatic solvent. Since the intact *t*-butyllithium tetramer itself should be immune from direct attack for steric reasons, it is likely that the solvent intervenes in the course of intramolecular exchange to stabilize the dimeric form and thus facilitate intermolecular exchange. Solvent might play a more important role in affecting the rate of intramolecular exchange in polyhedra containing alkyl groups with a lower steric requirement.

Proton Spectra. It has been noted that in mixtures of ethyllithium and *t*-butyllithium[4] the proton spectra in benzene exhibit more than one resonance for the *t*-butyl group protons. We have examined the proton spectra of mixtures of I and II in toluene. Figure 3 shows the spectra for two different ratios. The chemical shifts shown have been corrected to TMS using the ^{13}C–H satellite from the solvent methyl group as internal standard (at far left in Figure 3). The peak at τ 8.82 is due to the methyl protons of the *t*-butyl group. The peak at τ 9.67 corresponds to the methyl protons of the trimethylsilylmethyl group, and the upfield (τ 11.92) peak to the methylene protons of this same species. The mixtures give a series of three lines in the *t*-butyl resonance region, whose relative intensities can be explained using the assumptions discussed above for the ^7Li spectrum. At 28° the ^7Li spectrum exhibits three lines, with II_4, II_3I, and II_2I_2 rapidly exchanging, while $II(I)_3$ and I_4 are slowly exchanging. Each of these species gives rise to a separate, single resonance in the proton spectrum of the *t*-butyl groups (recall that intramolecular exchange is rapid at +28°). The relative intensities must be weighted, however, according to the number of *t*-butyl groups on each species, so the intensity distribution is different from that seen in the ^7Li spectrum.

In the slow exchange limit, below −30°, a local environment model serves to explain the *t*-butyl resonance spectra. The chemical shift for the protons of a particular *t*-butyl group is determined by the nature of the three alkyl groups which are its neighbors on the tetramer. The distribution among the four possibilities is given by eq 2. Thus the intensity distribution in the ^7Li and *t*-butyl proton multiplets should be the same at −30° and below. This has been found to be the case.

The methyl protons of the $-CH_2Si(CH_3)_3$ group exhibit only a doublet at 28°. This is in accordance with expectations, since all but one species containing this group are involved in rapid intermolecular exchange at 28°. The methylene resonances follow the same distribution as for the methyl groups on the silicon. They show a reversed order, since their chemical shifts are related to the inductive effects of the other three alkyl groups on the tetramer, whereas the shifts of the methyl protons in each case are probably due largely to aromatic solvent effects. Figure 3 shows two representative samples, with the calculated spectra near the corresponding set of lines. The figure also shows comparisons with calculated spectra at low temperature, assuming a "local environment" hypothesis. It seems clear that the change in form of the spectrum with lowering of temperature is in accord with the expectations based on the model described above.

The chemical shift of the methyl resonances of the $-CH_2Si(CH_3)_3$ group are quite temperature dependent, as shown in Figure 3. The chemical shift of the methyl proton line in toluene solutions of II was found to vary linearly with $1/T$ in the range +40 to −55°. The effect is probably related to the influence of the aromatic solvent ring currents. Rotation about the bond between the CH_2 carbon and the tetramer possibly leads to a temperature variation of the detailed interaction between the methyl groups and the solvent. The effect is not seen in the methyl resonance of *t*-butyllithium in toluene, nor is there a significant temperature variation of the chemical shift of the methyl resonance of the $CH_2Si(CH_3)_3$ group in cyclopentane solvent.

Line Widths in $LiCH_2Si(CH_3)_3$. The ^7Li and ^1H absorptions in II all exhibit a marked line-width variation with temperature in both cyclopentane and toluene solutions. The variations in half-intensity widths with temperature are shown in Figure 4.

The temperature dependence of the CH_2 line width is similar to that observed for the CH_2 lines of ethyllithium.[5] It is of interest to consider the line width in terms of exchange processes occurring in solutions of II. From the ^7Li spectra it is evident that intermolecular exchange is still relatively slow for II at +28° in cyclopentane. It might, however, be rapid enough at 40° to decouple the ^7Li-CH_2 scalar interaction. It is significant, therefore, that at 40° the CH_2 line has the same width in both cyclopentane and toluene, since intermolecular exchanges of II_4 are known to be rapid in toluene at temperatures above about −5° (see Figure 2). At temperatures below 40° the CH_2 line widths in the two solvents differ increasingly because of the slowing of intermolecular exchange in cyclopentane. By 28°, intermolecular exchange is slow in cyclopentane; in the range +10 to −20°, intramolecular exchange is slowed. The effect on the Li-CH_2 scalar coupling of a changing rate of intramolecular exchange cannot be responsible, however, for the marked increase in CH_2 line width. In the limit of fast intramolecular exchange, scalar coupling of CH_2 protons with ^7Li leads to a A_2X_4 system, with a small coupling constant J ($I_X = {}^3/_2$). In the limit of *slow* intramolecular exchange, the scalar coupling is of the form A_2X_3, with coupling constant ${}^4/_3J$. The apparent line widths, resulting from the unresolved multiplets, are not expected to differ significantly. The observed broadening must therefore be accounted for in terms of a slowing of rotation about the bond joining the $-CH_2Si(CH_3)_3$ groups to the tetramer, producing magnetically nonequivalent environments. Similar conclusions apply to the toluene data; in this instance, however, inter- and intramolecular exchanges are more rapid, so that the entire CH_2 line-width curve is shifted 10 to 15° to lower temperatures.

Comparable effects are noted in the ^7Li line widths, as shown in Figure 4. The ^7Li line width of *t*-butyllithium is narrow to low temperatures in toluene.[5] It thus appears that line broadening must be associated with scalar coupling and rotational effects, rather than with changes in solvent viscosity. In general, the results reported here are corroborative of those obtained earlier for ethyllithium.[5] It does appear, however, that intermolecular exchange of II_4 in toluene is slightly more rapid than was estimated for ethyllithium in that solvent.

Mechanistic Considerations. The present results bear upon the question of the mechanism (or mechanisms) by which organolithium compounds react in hydrocarbon solvent.

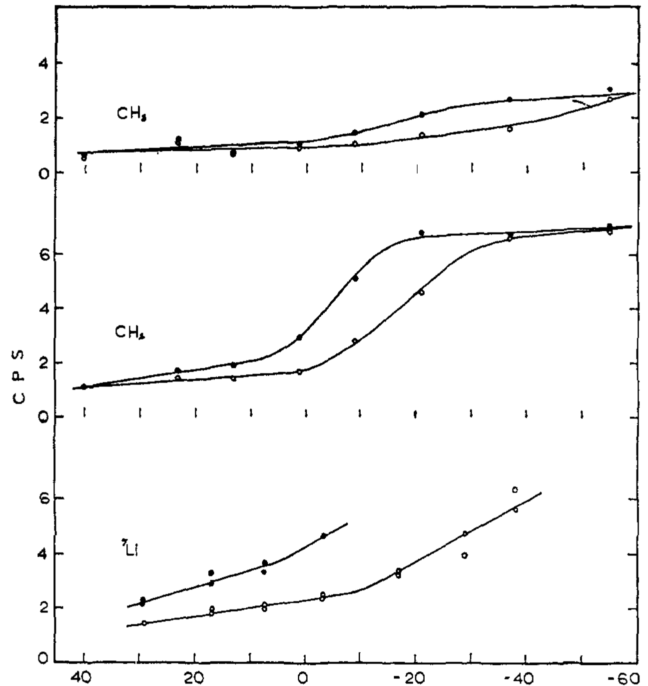


Figure 4. ^7Li and ^1H line widths at half-height for toluene (open circles) and cyclopentane (closed circles) solutions of $LiCH_2Si(CH_3)_3$.

The slowness of intermolecular exchanges in cyclopentane as compared with toluene is comparable to the similar but smaller effect of solvent on the rates of addition to dienes or styrene.[14,15] More striking, however, is the closeness of the rates of initiation of diene polymerization by the isomeric butyllithiums in cyclohexane.[16] The rate of initiation by *t*-butyllithium far exceeds the rate of tetramer dissociation, as measured in the present study. It seems quite likely that at the high concentration of monomer employed, interaction between olefinic monomer and alkyllithium tetramer might significantly increase the rate of tetramer dissociation, but this effect cannot account for the observed low sensitivity of the initiation rate to alkyl group structure. Possibly the rate-determining step involves formation of a high-energy transient species such as occurs in the intramolecular exchange. The nmr exchange results lend support to the contention[17] that dissociation of alkyllithium species to monomer is not required for reaction with a substrate such as a diene or styrene.

Acknowledgments. The authors are grateful to Mr. O. W. Norton for assistance in obtaining the ^7Li nmr spectra.

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(15) S. Bywater, *Advan. Polymer Sci.*, 4, 66 (1965).

(16) H. L. Hsieh, *J. Polymer Sci.*, A3, 163 (1965).

(17) T. L. Brown, *J. Organometal. Chem.*, 5, 191 (1966).