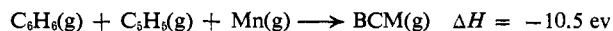


Several methods are available for the determination of appearance potentials. The vanishing current<sup>9</sup> and extrapolation<sup>10</sup> methods and Honig's<sup>11</sup> procedure were all applied to the molecular ion. The results, shown in Table II, are similar, with respect to argon as a reference, for all these methods. The extrapolation method, which is relatively straightforward to apply, was therefore used for the other ions.

With the usual qualification that the appearance potential may well include excess energy over the true ionization potential, we can deduce an upper limit for the energy of formation of BCM. This is given by the difference in the spectroscopic first ionization potential of manganese (7.43 eV) and the appearance potential of this ion in the mass spectrometer (Table II). We obtain



The mean metal-ring bond energy is then 5.25 eV, somewhat higher than the value of 4.60 eV found for the iron-cyclopentadienyl bond in ferrocene.<sup>3</sup> Since the product ions in the mass spectrometer may be in any of a number of electronic excited states this increase is probably not significant.

### Experimental Section

**Preparation of Benzene(cyclopentadienyl)manganese(I).** With continuous stirring, bromobenzene (1.15 moles) was added slowly to 30 g of magnesium turnings (1.25 g-atoms) under a nitrogen atmosphere. After formation of the Grignard reagent, 41 ml of

(9) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).

(10) R. H. Vought, *ibid.*, **71**, 93 (1947).

(11) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

cyclopentadiene (0.6 mole) was added during 15 min, whereupon 70 g of anhydrous manganese chloride (1.8 moles) and 100 ml of benzene were added rapidly and the reaction was allowed to proceed at 65° for 20 min followed by boiling under reflux for 30 min. The reaction was cooled in ice, hydrolyzed with 300 ml of methyl alcohol and 500 ml of water, and allowed to stand overnight. The organic layer was then separated and evaporated to dryness. The residue was extracted with cyclohexane and purified by chromatography on alumina. The pink solution from the column was evaporated to dryness and the residue sublimed under vacuum. The product forms large deep red crystals which are easily separated by hand from the white crystals of biphenyl, mp 205° (with decomposition *in vacuo*), yield 0.45 g, *d* 1.45 (floatation in aqueous KI solution).

*Anal.* Calcd for  $\text{MnC}_{11}\text{H}_{11}$ : Mn, 27.72; C, 66.68; H, 5.60. Found: Mn, 27.26; C, 67.02; H, 5.67.

Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 521 infrared spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer from benzene solutions prepared *in vacuo*. TMS was present as an internal standard. The mass spectra of ferrocene and benzene(cyclopentadienyl)manganese were obtained on an Atlas CH-4 mass spectrometer at an ionizing potential of 70 eV. The mass spectrum of dibenzene(chromium) was obtained on a Bendix time-of-flight mass spectrometer at an ionizing potential of 50 eV, the sample reservoir containing the solid being maintained at approximately 60°. The appearance potentials were obtained on the latter instrument by a comparison of the ion current of argon and the molecular ion at suitable voltage intervals between 30 and 0 eV, and subsequently by a comparison of the ion current of the other species with that of the molecular ion. The relative abundances of the manganese-containing fragments are therefore correct. The data were corrected for trap current and pressure variations.

**Acknowledgments.** We wish to acknowledge our indebtedness to the late Professor T. S. Piper. We thank Mr. George Sanzone for help and advice in the mass spectral measurements, and Mr. J. Nemeth for microanalyses. This research was supported by a grant from the National Science Foundation.

## The Nuclear Magnetic Resonance and Microwave Spectra of Some Deuterio Derivatives of 2,4-Dicarbocloheptaborane(7)

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**Abstract:** In spite of the known structure of 2,4-dicarbocloheptaborane(7), ambiguous nmr assignments were obtained for both the <sup>11</sup>B and <sup>1</sup>H nmr spectra of this molecule. Deuterium exchange was expected to aid in the nmr analysis of this molecule. Although deuterium exchanges completely at high temperatures (400°), at lower temperatures (100°) deuterium exchanges in only three definite positions. A determination of these deuterium atom locations by microwave spectroscopy for the partially deuterated isotopic species allows an unequivocal assignment to be made for both the <sup>11</sup>B and <sup>1</sup>H nmr spectra. For the partially deuterated molecule, the three deuterium atoms are preferentially substituted on the boron atoms in the base plane. These results are compatible with the nmr spectra for related boron compounds.

The structure of the dicarbocloheptaborane(7) prepared from pyrolysis of 2,3-dicarboclohexaborane(8)<sup>2</sup> has been determined to be that of a pentagonal

(1) (a) California State College; (b) University of Southern California; (c) Jet Propulsion Laboratory.

(2) (a) T. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963); (b) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

bipyramid with the two carbon atoms in the 2,4 positions<sup>3</sup> (Figure 1). Although the structure is known, an unambiguous assignment of certain <sup>11</sup>B and <sup>1</sup>H nmr resonance lines has not, heretofore, been possible.

(3) R. A. Beaudet and R. L. Poynter, *J. Am. Chem. Soc.*, **86**, 1258 (1964).

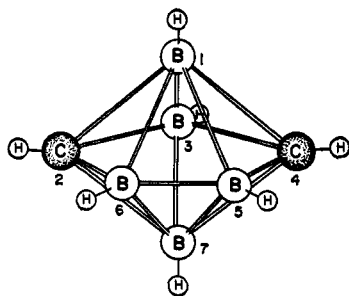


Figure 1. Molecular structure of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>.

The <sup>11</sup>B nmr spectrum consists of three sets of doublets with an area ratio of 1:2:2 (Figure 2). Either one of the two doublets of equal area ( $\delta -2.0$  or  $+23.5$ ) may arise from proton coupling to the two apical boron atoms and the remaining doublet may arise from proton coupling to the two equivalent basal borons. There is no *a priori* reason to select one assignment over the other. For although apical boron resonances in the higher boron hydrides (e.g., B<sub>5</sub>H<sub>9</sub>, B<sub>6</sub>H<sub>10</sub>) are generally found at high fields,<sup>4</sup> the apical boron resonances of B<sub>10</sub>H<sub>10</sub><sup>2-</sup>, a compound isoelectronic with the hypothetical C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> carborane, are found at lower fields than the frequencies of the equatorial borons.<sup>5</sup>

The <sup>1</sup>H nmr spectrum poses a similar assignment problem. Proton resonances at  $\tau$  6.00 and 9.85 are assigned to the apical hydrogens and to the two equivalent boron-attached equatorial hydrogens, but not necessarily in that order.<sup>2b,6</sup>

Early studies on the deuteration of other small carboranes, 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> and 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>,<sup>7,8</sup> suggested that some or all of the boron-attached hydrogens of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> might exchange with deuteriodiborane. With appropriate deuterium substitution it was expected that a solution to the nmr assignments would result from an unambiguous structural assignment provided by microwave analysis coupled with changes in the <sup>11</sup>B and <sup>1</sup>H nmr spectra.

### Experimental Section

**Deuteriodiborane** was prepared by adding boron trifluoride ethyl etherate dropwise to a diglyme solution of lithium aluminum deuteride (98% D)<sup>9</sup> using a standard work-up and purification scheme.<sup>10</sup> **2,4-Dicarbaloheptaborane(7)** was prepared by the pyrolysis of 2,3-dicarbaheptaborane(8).<sup>2</sup>

The observed infrared bands for C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> are given in Table I. The C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> mass spectrum exhibits a sharp cut-off at *m/e* 86 which corresponds to the <sup>12</sup>C<sub>2</sub><sup>11</sup>B<sub>5</sub>H<sub>7</sub><sup>+</sup> ion.

**Hydrogen-Deuterium Exchange between Deuteriodiborane and 2,4-Dicarbaloheptaborane(7). (A) Ambient Temperature. Preparation of B<sub>3</sub>B<sub>2</sub>B-Trideuterio-2,4-dicarbaloheptaborane(7).** An

(4) (a) T. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959); (b) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 320 (1959); (c) R. E. Williams, S. G. Gibbins, and I. Shapiro, *ibid.*, **30**, 333 (1959).

(5) E. L. Muettterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(6) All previously reported <sup>1</sup>H chemical shifts for C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> have been converted to the  $\tau$  reference system in order to avoid negative values where TMS is selected as the zero reference.

(7) I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(8) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

(9) Metal Hydrides, Inc., Beverly, Mass.

(10) (a) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolmik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952); (b) W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

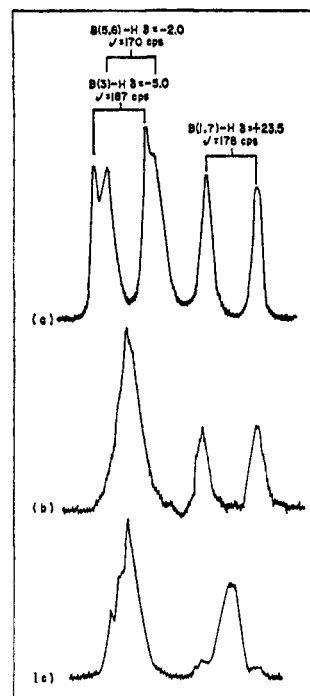


Figure 2. <sup>11</sup>B nmr spectra of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>: (a) undeuterated; (b) 3,5,6-deuterated; (c) 1,3,5,6,7-deuterated. All spectra chemical shifts were measured using BF<sub>3</sub> etherate as the <sup>11</sup>B reference compound. The spectra were measured at 12.8 Mc.

initial H,D exchange between a 1:1 mixture of B<sub>2</sub>D<sub>6</sub> and 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> at ambient temperature was followed by infrared spectrometry. Minor changes in the B-H and B-D stretch vibrational frequency regions as well as other regions of the spectrum were evident within 2 hr. After 24 hr the infrared spectrum of the mixture had changed quite significantly. Very little additional exchange occurred over longer periods of time. For other physical

Table I. Infrared Bands of 2,4-Dicarbaloheptaborane(7)<sup>a</sup>

2620 (vs) (B-H stretch)	1064 (s)	888 (mw)
2055 (vw)	1053 (s)	877 (mw)
1295 (vw)	1042 (s)	866 (mw)
1285 (vw)	993 (w)	814 (mw)
1220 (s)	982 (w)	803 (m)
1213 (s)	951 (mw)	792 (mw)
1204 (s)	944 (mw)	688 (mw)
1178 (m)	931 (mw)	682 (mw)
1165 (m)	916 (m)	677 (m)
1158 (m)	902 (mw)	667 (mw)
1075 (sh, s)		

<sup>a</sup> Frequencies are in cm<sup>-1</sup>. Line intensities are given in parentheses.

measurements a 0.20-mmole quantity of the deuterated carborane was prepared by three 24-hr exchange reactions with equimolar quantities of B<sub>2</sub>D<sub>6</sub>. After each exchange, the deuterium-enriched carborane was separated from the partially protonated deuteriodiborane by vacuum fractionation through traps at -110 and -190°. The contents of the -110° trap were mixed with fresh deuteriodiborane for the next exchange reaction. The infrared spectrum of the carborane fraction after the final exchange exhibited absorption frequencies at 2630 (s) (B-H stretch), 1990 (vs) (B-D stretch), 1190 (m), 1162 (m), and 1060 cm<sup>-1</sup> (s) and additional weak peaks. The mass spectrum exhibited a sharp cut-off at *m/e* 89 which corresponds to <sup>12</sup>C<sub>2</sub><sup>11</sup>B<sub>5</sub><sup>1</sup>H<sub>4</sub><sup>2</sup>D<sub>3</sub><sup>+</sup>. An infrared analysis<sup>10b</sup> of the deuteriodiborane from the final exchange indicated ca. 90% D enrichment of all equilibrated positions in the carborane.

**(B) Exchange at 100°. Preparation of B<sub>3</sub>B<sub>2</sub>B<sub>2</sub>B-Pentadeuterio-2,4-dicarbaloheptaborane(7).** A mixture of 1.0 mmole of

Table II. Observed and Calculated Microwave Transitions for  $C_2B_5H_4D_3^a$ 

Transition	All $^{11}B$ species		$1-^{10}B$ species		$5-^{10}B$ species	
	$\nu_{obsd}$	$\nu_{calcd}$	$\nu_{obsd}$	$\nu_{calcd}$	$\nu_{obsd}$	$\nu_{calcd}$
3 <sub>03</sub> -2 <sub>02</sub>	20882.75	...	20934.39	...	21126.19	...
3 <sub>13</sub> -2 <sub>02</sub>	20729.30	20729.18	20779.38	20779.09	20975.07	20974.82
3 <sub>12</sub> -2 <sub>11</sub>	22790.70	...	22958.40	...	23025.23	...
3 <sub>22</sub> -2 <sub>21</sub>	22054.77	22054.92	22188.49	22188.38	22294.60	22294.96
3 <sub>21</sub> -2 <sub>20</sub>	23226.79	...	23442.38	...	23463.73	...
4 <sub>04</sub> -3 <sub>03</sub>	27437.82	27437.90	27487.66	27487.65	27765.70	27765.55
4 <sub>14</sub> -3 <sub>13</sub>	27395.14	27395.25	27445.95	27445.81	27723.44	27723.83
4 <sub>13</sub> -3 <sub>12</sub>	29618.34	29618.16	29780.99	29781.32	29931.58	29931.60
4 <sub>23</sub> -3 <sub>22</sub>	29065.45	29065.44	29215.83	29215.95	29385.40	29385.86
4 <sub>22</sub> -3 <sub>21</sub>	30978.25	30978.04	31249.67	31249.76	31290.52	31290.54
4 <sub>32</sub> -3 <sub>31</sub>	29932.27	29932.29	30148.64	30148.24	30251.55	30251.29
4 <sub>31</sub> -3 <sub>30</sub>	30679.58	30679.74	30963.32	30962.69	30999.73	30999.73

<sup>a</sup> All frequencies are given in Mc/sec. The observed transitions are accurate to within  $\pm 0.10$  Mc/sec.

2,4- $C_2B_5H_7$  and 1.0 mmole of  $B_2D_6$  was sealed in a 500-ml flask and heated at 100° for a 5-hr period. Using the procedure given in section A, the partially deuterated carborane was separated from the mixture and treated with fresh deuteriodiborane. After a fourth exchange an infrared analysis<sup>10b</sup> of the deuteriodiborane fraction indicated ca. 90% D enrichment of all equilibrated positions in the carborane. The carborane fraction contained small amounts of deuterated higher boron hydride impurities (probably formed from the pyrolysis of the deuteriodiborane) which were conveniently removed by gas-liquid chromatography. The infrared spectrum of the purified deuterated carborane had major absorption peaks at 2630 (relative intensity = 0.45), 1990 (3.0), 1180 (0.35), and 1050  $cm^{-1}$  (1.0). The mass spectrum exhibited a cut-off at  $m/e$  91 which corresponds to the  $^{12}C_2^{11}B_5^1H_2^2D_3^+$  ion.

**Microwave Spectrum of B,B,B-Trideuterated 2,4-Dicarba-cloheptaborane(7).** The microwave spectrum of the trideuterated species was studied in the region from 18 to 36 Gc with a conventional Stark modulated microwave spectrometer. Frequencies were measured by the interpolation technique using a Collins 51S-1 receiver. The standard frequencies were generated by a Hewlett-Packard Model 104AR quartz oscillator which was calibrated against WWV.

The carborane sample was studied in a 12-ft absorption cell cooled to Dry Ice temperature. The sample pressure was kept between 20 and 40  $\mu$ . No decomposition was observed under these conditions.

Boron, as it occurs in nature, consists of two isotopes,  $^{11}B$  and  $^{10}B$ , with relative abundances of 81 and 19%, respectively. Hence there are a variety of isotopic  $C_2B_5H_7$  molecules, distinguished from each other by the boron isotopic concentration ratio. The most abundant species (35%) contains all  $^{11}B$  atoms (normal species). Referring to Figure 1, the isotopic species with a  $^{10}B$  atom substituted at the 1 position and the species with a  $^{10}B$  atom substituted at the 5 position each make up 16% of the molecules. (In the future, we shall refer to these two isotopic species as the B(1) and B(5) species, respectively.) The isotopic species with a  $^{10}B$  atom substituted at the 3 position (designated as the B(3) species) accounts for only 8% of the molecules. All of the doubly and higher substituted species account for the remaining 10% of the molecules. In this analysis, the spectra of only the normal, the B(1), and the B(5) molecular species were assigned. The lines of the other isotopic species were much weaker and were not assigned in this study. The observed transition frequencies together with the calculated frequencies are given in Table II. The assignments were made by comparing the Stark effects of the lines with those of the undeuterated species.

Since the molecular structure of the undeuterated 2,4-dicarba-cloheptaborane(7) has already been accurately determined,<sup>3,11</sup> the rotational constants could be calculated for the two possible trideuterated species which are consistent with the nmr data. This substitution may occur at either the 1,3,7 or the 3,5,6 positions. The rotational constants were obtained by a two-step process. Using the molecular structure,<sup>3</sup> the moments of inertia were calculated for the undeuterated and the deuterated species. The differences between the moments of inertia of the deuterated and undeuterated species were then added to the observed moments of

inertia of the undeuterated species. This procedure minimized errors due to the zero-point vibrations.

The calculated rotational constants are compared with the experimentally determined constants in Table III. From an examination of this table it may be seen that deuteration has occurred in the 3,5,6 positions. The equatorial hydrogens appear to exchange more readily with deuterium.

Table III. Rotational Constants of  $B_2C_2H_4D_3^a$ 

Species		Estimated rotational constants		Obsd rotational constants
		3,5,6-Deuterated	1,3,7-Deuterated	
All B <sup>11</sup>	A	4601	4350	4590.93
	B	4031	3949	4047.09
	C	3296	3618	3304.50
5-B <sup>10</sup>	A	4634	4381	4622.46
	B	4068	3987	4085.35
	C	3337	3670	3346.30
1-B <sup>10</sup>	A	4659	4402	4648.87
	B	4074	3990	4091.81
	C	3296	3618	3304.32

<sup>a</sup> Mc/sec.

## Results and Discussion

From the above evidence all five of the boron-attached hydrogen atoms in 2,4-dicarba-cloheptaborane(7) undergo an exchange reaction with deuteriodiborane at 100°. To summarize: (1) the mass spectrum of the deuterated carborane exhibits a sharp cut-off at  $m/e$  91 which corresponds to the  $^{12}C_2^{11}B_5^1H_2^2D_3^+$  ion. (2) A strong infrared absorption at 1990  $cm^{-1}$  is present in the exchanged material and is assigned to the B-D stretching region. The absence of a C-D stretch is not significant because the C-H stretching frequency is infrared inactive; however, (3) the  $^1H$  nmr spectrum (Figure 3c) exhibits only a strong carbon-attached hydrogen resonance. (4) The collapse of all B-H doublets in the  $^{11}B$  nmr spectrum (Figure 2c) indicates that all five of the boron-attached hydrogen atoms have been exchanged.<sup>12</sup>

Under ambient temperature conditions, however, the exchange reaction does not proceed to the same extent as at the higher temperatures. This is evident from the mass spectrum, which shows a sharp cut-off corresponding to the  $^{12}C_2^{11}B_5^1H_4^2D_3^+$  ion. Further, only the low-field B-H doublets ( $\delta$  -2.0, -5.0)<sup>2a</sup>

(12) The  $^{11}B$ -D spin-spin coupling is not well resolved in the  $^{11}B$  nmr spectrum of the deuterated  $C_2B_5H_7$ .

(11) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **43**, 2166 (1965).

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

The low-field doublet ( $\delta -5.0$ ) in the  $^{11}\text{B}$  spectrum and the low-field quartet ( $\tau$  5.25)<sup>13</sup> in the  $^1\text{H}$  spectrum of  $\text{C}_2\text{B}_5\text{H}_7$  may be assigned to the lone equatorial B-H group on the basis of area considerations alone. The two remaining doublets in the  $^{11}\text{B}$  nmr spectrum and the quartets in the  $^1\text{H}$  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  $\text{B}_5\text{C}_2\text{H}_4\text{D}_3$  the three deuterium atoms are attached to the equatorial borons (3,5,6). Hence the remaining doublet in the  $^{11}\text{B}$  nmr ( $\delta +23.5$ ) can be assigned to the apical borons at positions 1 and 7. The resonance at  $\delta -2.0$  belongs to the equatorial borons.

Similarly in the  $^1\text{H}$  nmr spectrum, the quartet centered at  $\tau$  9.85 can be assigned to the protons on the apical borons. The remaining unassigned quartet at  $\tau$  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

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

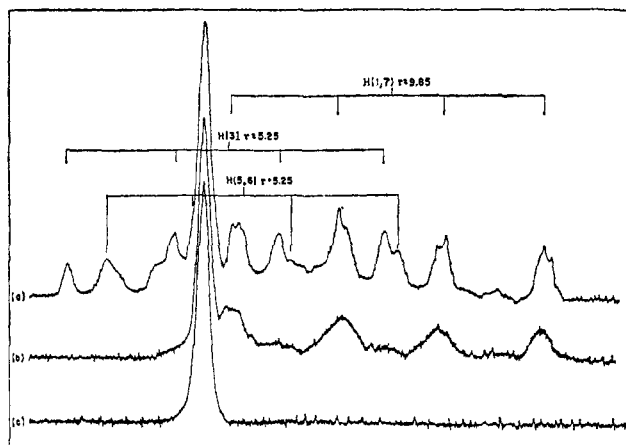


Figure 3.  $^1\text{H}$  nmr spectra: (a) undeuterated; (b) 3,5,6-deuterated; (c) 1,3,5,6,7-deuterated. All spectra chemical shifts were measured using tetramethylsilane as the reference compound. The spectra were measured at 60 Mc.

agreement with the corresponding resonances found in related systems, e.g.,  $\text{B}_5\text{H}_9$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{C}_2\text{B}_4\text{H}_8$ .

**Acknowledgments.** This work was supported in part by the Office of Naval Research, the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-849-55, the Jet Propulsion Laboratory, NASA Contract NAS7-100, and the Research Corp.

## Organometallic Exchange Reactions. IV. Lithiomethyltrimethylsilane and *t*-Butyllithium in Hydrocarbon Solvents<sup>1</sup>

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Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. Received May 19, 1966

**Abstract:** The  $^7\text{Li}$  and  $^1\text{H}$  spectra of mixtures of *t*-butyllithium and lithiomethyltrimethylsilane [ $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ ] 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:  $[\text{LiC}(\text{CH}_3)_3]_4 \rightarrow 2[\text{LiC}(\text{CH}_3)_2]_2$ . At temperatures in the range  $+10$  to  $+20^\circ$  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 alkyl lithium compounds in ether at temperatures on the order of  $-50^\circ$ . Intermolecular exchange between tetramers has been demonstrated,<sup>3</sup> and a quantitative assessment of the exchange rate for methyl lithium has been made. On the basis of rather sparse evidence<sup>4,5</sup>

it appears that intermolecular exchanges between alkyl-lithium 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,<sup>6,7</sup>

(1) This research was supported by a grant from the National Science Foundation.

(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).

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(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).