Fig. 1.—Plot of eq. 1 for various trial values of $\Delta G°$ (kcal./mole).

A variation of R_0^T with temperature can also be found in situations where rigidity of the molecular framework would seem to preclude the possibility of radical conformational changes. For example, we have observed such temperature variations for R_0^T in camphor and norcamphor. In these cases, no temperature-independent value for $\Delta G°$ would yield a straight line

TABLE I

| | | % Diequatorial conformer | | |
Solvent	$R_0{}^{298} \times 10^{40}$	Present C.D. data	Ultra-violet[a]	O.R.D.[a]
Methanol	+1.40	97 ± 2	100	99
Dioxane	+0.89	96 ± 2	88	100
EPA	+0.42	95 ± 2		
CCl₄	−1.21	90 ± 3		
Isooctane	−1.87	89 ± 3	82	82

[a] From J. Allinger, N. L. Allinger, L. E. Geller, and C. Djerassi, *J. Org. Chem.*, **26**, 3521 (1961). These authors indicate an accuracy of about ±10%.

in the plot suggested for eq. 1, and these results are indicative of nonnegligible $\Delta S°$ values, such as one might expect in the case of asymmetric solvation.[9] The analysis of these data in terms of this hypothesis and the problems posed by a multiplicity of conformers will be treated in a later paper.

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Nuclear Magnetic Resonance Spectroscopy and (p → d) π-Bonding in Silicon Compounds

Sir:

In several studies of the n.m.r. spectra of substituted methylsilanes, it has been concluded that the results can best be explained in terms of (p → d) π-bonding between silicon and electronegative atoms or groups.[1-5]

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The evidence cited includes the "small" low-field shifts of the proton resonances in hexamethyldisiloxane[1] and tris(trimethylsilyl)amine[2] as against tetramethylsilane; the smaller low-field shifts with increasing n in the series $(CH_3)_{4-n}MCl_n$ and $(CH_3)_{3-n}MHCl_n$ when M is Si than when M is $C^{3,4}$; the decrease in shielding along the series $(CH_3)_3SiX$, X = F, Cl, Br, I[5]; and the increase in $J(^{13}CH_3)$ in $(^{13}CH_3)SiX(^{12}CH_3)_2$ and in $J(^{29}SiH)$ in $(^{12}CH_3)_3{}^{29}SiX$ along the series CH_3 < F < Cl < Br < I.[5] We have recently studied several substituted methylsilanes and related alkanes; from the results, taken with published work, we conclude that many of the so-called anomalies in the spectra of silicon compounds are also to be found in the spectra of similar derivatives of carbon, and that it is at present unjustified to use these effects as evidence in favor of the occurrence of π-bonding in silicon compounds.

The β-proton shieldings in the series of compounds CH_3SiH_2X decrease along the series X = H, N, O, F (which is consistent with increasing inductive deshielding), but increase along the series X = I, Br, Cl, F[6]; a similar effect is observed both in the dimethylsilyl[7] and trimethylsilyl[5] halides, and has been explained for the last named derivatives in terms of increasing (p → d) π-bonding between silicon and the halogen atoms in the order I < Br < Cl < F. The same effect, however, has been observed in ethyl,[8,9] isopropyl,[8,9] *t*-butyl,[8] and cyclohexyl[10] halides. At present there is no satisfactory explanation for this, but since it occurs in compounds in which the α-atom is carbon, it is unlikely to be caused by (p → d) π-bonding.

It is now clearly established that SiHXYZ resonance chemical shifts are less sensitive than are CHXYZ shifts to changes in the rest of the molecule[6,7]; this is true not only when the substituents are potentially strongly π-bonding groups, such as –OR or –Cl, but also for others (like –I, –Br, and –SR) which are unlikely to be involved in strong π-bonds. It is therefore not surprising that CH₃SiXYZ resonances are less sensitive than CH₃CXYZ resonances to changes in X, Y, and Z. Substitution of –I (or –Br) for (Si)H in the three methylsilanes, for instance, shifts the β-proton resonance 0.7 (or 0.5) p.p.m. to low field, while in alkanes the analogous substitution shifts are about 0.9 and 0.7 p.p.m., respectively.[9] For polar, potentially strongly π-bonding groups, the shifts follow the same pattern: –F or –OR substitution shifts in the methylsilanes are about 0.15 and 0.05 p.p.m. to low field, respectively,[6] as against substitution shifts for the same substituents in alkanes of some 0.3 and 0.1 p.p.m.[9] There is no reason to conclude from these data that there is any unusual bonding in the silicon compounds.

Rather more convincing evidence indicating (p → d) π-bonding comes from the high-field shifts of the SiH proton resonances of fluorosilane (0.05 p.p.m.),[11] difluorosilane (0.20),[11] and methylfluorosilane (0.03)[7]; and of the β-proton resonances of methylfluorosilane (0.05)[7] and dimethylfluorosilane (0.02)[7] on substitution of one of the (Si)H atoms by –F. Even this, however, is by no means decisive. It is very dangerous to draw conclusions from changes in SiH chemical

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shifts when it is still not known why SiH_4 gives a resonance to low field of CH_4.[12] The high-field shifts of the β-protons are very small. In unsaturated carbon compounds the high-field shifts produced by –F or –OR substituents, which are likely to be due at least in part to π-bonding effects, are much greater, being some 0.5 p.p.m. (–F substitution) in acetylene,[13] 1.0 (–F) and 1.3 (–OR) in ethylene,[14,15] and 0.9 (–OR) in thiophene.[16]

We have previously drawn attention to the rough correlation between increasing $J(^{13}CH)$ in CH_3MXYZ and decreasing $\tau(CH_3)$ in $^{12}CH_3MXYZ$, which appears to hold whether M is C or Si.[6] It therefore seems as unreasonable to invoke (p → d) π-bonding to explain changes in $J(^{13}CH_3SiXYZ)$ as it is to explain the β-proton chemical shifts in the same way. Moreover, although the available data are not very precise, it seems that $J(^{13}CH_3)$ in substituted ethanes may change with substituent in much the same way as in methylsilanes; $J(^{13}CH_3)$ in CH_3CHBr_2, for instance, is 131.0 $\pm$ 0.3 c.p.s. as against 128.1 $\pm$ 0.5 in CH_3CHF_2.[10] These values may be compared with $J(^{13}CH_3)$ of 118.8 $\pm$ 1 c.p.s. in $(CH_3)_3SiF$, and of 121.0 $\pm$ 1 in $(CH_3)_3SiBr$.[5]

Finally, it must be emphasized that in molecules of formula $^{12}CH_3{}^{29}SiXYZ$ neither the sign of $J(^{29}SiH)$ nor the coupling mechanism is yet known. At present it is by no means established that this coupling constant [or the analogous $J(H-^{12}C-^{13}C)$ in carbon compounds] must depend only on the s-character in the intervening bonds.

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The Structure of Butyllithium in Ether. A Solvated Dimer[1]

Sir:

Reported here are data which establish beyond reasonable doubt that *n*-butyllithium (BuLi) exists in ether (Et_2O) solution as a solvated dimer, $Et_2O:(BuLi)_2$. The concept, favored by some,[2] of lithium alkyls as carbanions would seem to be incomplete at best, but the concept, rejected by others,[3] of three-center bonding would seem to be applicable. Hence, we propose structure I for the complex of butyllithium with ether. While excess ether may cluster about the complex in

I
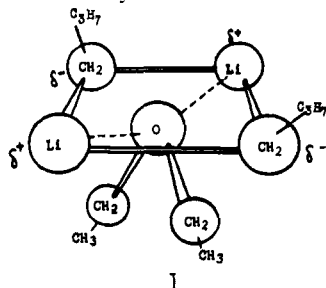
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some general way, our evidence is that only one Et_2O is specifically associated with it, probably because when this one is on one side of the four-membered ring of the dimer, alkyl groups $(C_3H_7$ in I) on the other side of the ring shield it from association of solvent there.

Ordinate values in Fig. 1 show the mole ratio of Et_2O to hexane in the vapor phase at 25° in equilibrium with 50 ml. of hexane to which increments of Et_2O were added, curve **A** for ordinary hexane and curve **B** for hexane containing 0.08 mole of BuLi. It is seen that the vapor pressure of EtO_2 is depressed by the BuLi until a 1:2 respective molar ratio is reached, *i.e.*, curve **B** shows a discontinuity at 0.04 mole of Et_2O added. This discontinuity is even more distinct in curve **C**, which is Et_2O added *vs.* the ratio of ordinate values from **A** and **B**.
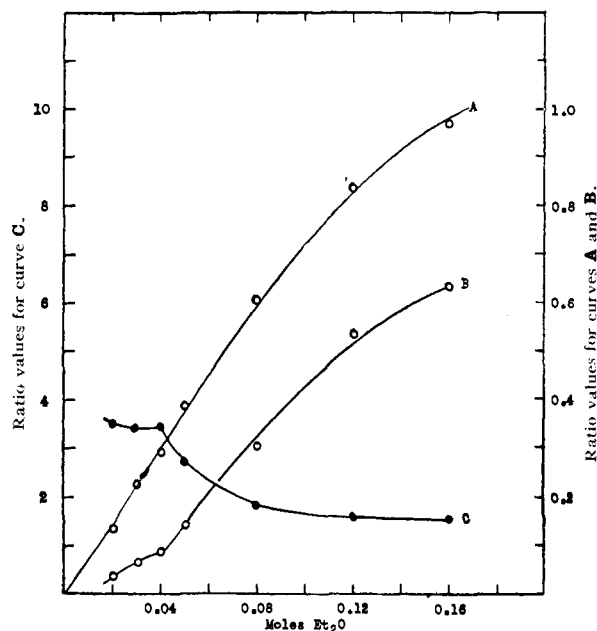

Fig. 1.—Curve **A** shows mole ratio of ether to hexane in vapor over 50 ml. of hexane at 25° to which increments of ether were added. Curve **B** shows same except 0.08 mole of BuLi was in the hexane. Curve **C** is the ratio of **A** to **B**.

Shown in Fig. 2 are representative traces of proton magnetic spectra (60 Mc.) from Et_2O, BuLi, and their mixtures in hexane. The methylene signal from Et_2O at any concentration in ordinary hexane is +204 c.p.s. (downfield from TMS), but with BuLi present (*cf.* center curve) the Et_2O methylene signal is +218.5 c.p.s., so long as the Et_2O–BuLi mole ratio is <0.5. The 14.5-c.p.s. downfield shift of the Et_2O methylene protons is a rational consequence of an increase in the electronegativity of adjacent oxygen when it is complexed with BuLi. The chemical shift of the Et_2O methylene quartet when the Et_2O–BuLi mole ratio is >0.5 (*i.e.*, Et_2O in excess of that needed to form the complex, *cf.* lower curve) is a single average value from complexed and uncomplexed ether, even at low temperatures, presumably because of rapid equilibration between the two forms.

The methylene signal from BuLi (protons α to Li) at any concentration in ordinary hexane is −50 c.p.s. (*cf.* upper curve), but with sufficient ether present to form the 1:2 complex, the BuLi methylene signal is −59 c.p.s. (*cf.* lower curve). The 9-c.p.s. upfield shift of the BuLi methylene protons is a rational consequence of a decrease in the electronegativity of adjacent lithium when it is complexed with Et_2O. When the Et_2O present is insufficient to convert all BuLi to the 1:2 complex (*cf.* center curve), the position