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 $(p \rightarrow d)$ 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 methyl-silanes; $J(^{13}CH_3)$ 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
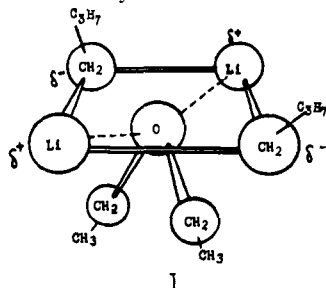
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some general way, our evidence is that only one Et_2O is specifically associated with it, probably because when this one is on one side of the four-membered ring of the dimer, alkyl groups (C_3H_7 in I) on the other side of the ring shield it from 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**.
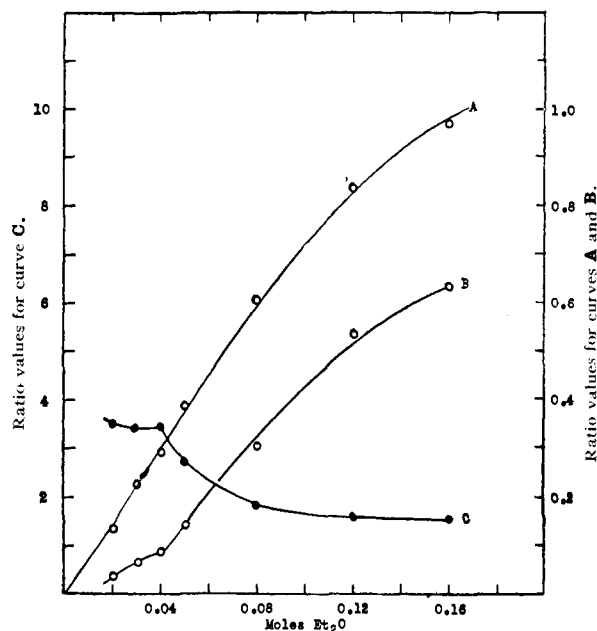

Fig. 1.—Curve **A** shows mole ratio of ether to hexane in vapor over 50 ml. of hexane at 25° to which increments of ether were added. Curve **B** shows same except 0.08 mole of BuLi was in the hexane. Curve **C** is the ratio of **A** to **B**.

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
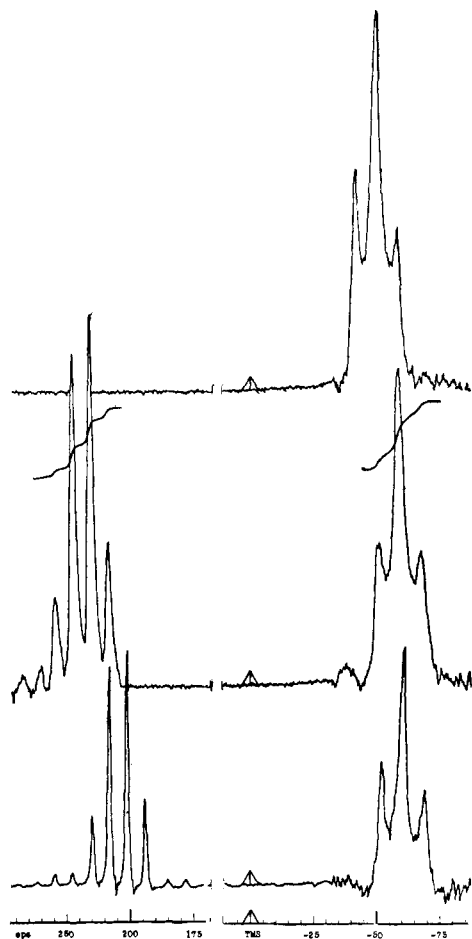
Fig. 2.—Methylene p.m.r. signals in hexane solutions. Upper curve from 1.6 mmoles of BuLi; center curve is the same, with 0.76 mmole of Et_2O; lower curve is the same, with 5.3 mmoles of ether and lower spectrum amplitude in 200-c.p.s. region.

of the BuLi methylene triplet is the properly weighted average between -50 and -59 c.p.s. Finally, and of greatest significance, *no amount of Et_2O in excess of that necessary to complex the organometallic causes any further change in the BuLi methylene signal;* the signal is -59 c.p.s. for dilute solutions of BuLi in Et_2O alone.

This fact, that the chemical shift does not change for the complexed BuLi methylene signal as the solvent changes from hexane to ether, must mean that the 1:2 complex persists in ether. This persistance is corroborated by an earlier observation that the change in BuLi chemical reactivity is slight in going from hexane solvent to Et_2O solvent, so long as sufficient Et_2O is always present to form a 1:2 complex.[1]

Freezing point depressions by Et_2O and BuLi and their mixtures were determined in cyclohexane. For example, when Et_2O and BuLi were mixed in the 1:2 mole ratio in cyclohexane to give 0.75 total stoichiometric molality, the freezing point depression was 5°, indicating only 0.25 actual molality. Ether itself causes a normal 20° molal freezing point depression of cyclohexane, while BuLi causes a depression of only one fourth that, indicating a tetramer for BuLi in the pure hydrocarbon.[3] We propose that *a symmetrical tetramer is formed by quadrapole association of two dimers,* i.e., two $(BuLi)_2$ units from structure I, face-to-face, with the Li–Li axis of one orthogonal to that of the other. Ether unsymmetrically solvating the dimer, as in I, should result in significant dielectric character for the complex. Indeed, so great is the rise in dielectric constant of BuLi in hexane when just 0.5 mole equivalent of Et_2O is added (and so little the influence

of additional ether), one can titrate butyllithium in hexane to a sharp end point with ether by simple high frequency methods.[4]

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The Hydrogen–Graphite Reaction between 360 and 800°

Sir:

The thermal reaction of hydrogen with graphite has been one of the least investigated heterogenous reactions.[1,2] This is due principally to the very low reaction rates involved. Packed column gas chromatography in conjunction with a flame ionization detector[3] has enabled us to study this reaction at temperatures as low as 360°. Although methane remained the principal product, the formation of five higher hydrocarbons below 650° provides a new insight into the reaction mechanism.

The experiment was conducted with a quartz tube reactor charged with 66 g. of spectroscopic grade graphite rods (United Carbon Products Co., ash content <10 p.p.m.). Ultrapure hydrogen (California Oxygen Co.) was further purified over a palladium catalyst and passed through a liquid nitrogen trap before entering the reactor. A Wheelco regulator controlled the furnace temperature within 3°.

After initially outgassing the graphite under vacuum for 24 hr. at 1000°, hydrogen was passed over the material an additional 6 hr. at 90 cm. pressure. This technique[4,5] has been found effective in removing any surface oxide which would interfere with the reaction. The reactor next was cooled to a predetermined temperature and, after allowing 1 hr. for thermal equilibrium, sealed off under pressure. These static runs lasted from 1 min. to 100 hr. The reaction products were analyzed on a 2-m. silica gel column, operated at 190° in series with a flame ionization detector.

Below 580° the reaction was zero order with respect to hydrogen at pressures of 90 to 180 cm. In this pressure-independent region, two distinct Arrhenius activation energies were measured. The inflection point was 515°, where the activation energy dropped from 70 to 12 kcal. per mole. Corney and Thomas,[6] working with a different grade of graphite, observed this inflection at about 600°. The reaction order gradually increased above 580° and reached 0.6 at 800°. This transition region probably extends to 1000°, where the reaction is first order[2] with an activation energy of 85.5 kcal. per mole. The rate constant for methane production varied from 2.0×10^{-16}

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