the *trans* proton is at lower field and this is the only compound in this series which has reversed the *cis-trans* order. On the basis of this plot, the assignments in propylene by the previous workers were considered to be in error. However, in a recent communication, Bothner-By[21] made the assignments in propylene from its complete analysis and according to his results the *cis* proton is at lower field which is in complete agreement with these predictions.

No attempt has been made to correlate the shifts of the α-proton since, besides anisotropy, other effects will be large and difficult to evaluate. Further work is being carried out for similar correla-

tions between Hammett's σ-constant, bond moments and other bond properties in related systems.

The Nuclear Resonance Spectra of Allyllithium and Vinyllithium[1]

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Nuclear magnetic resonance has been used to investigate the structures of allyllithium and vinyllithium in diethyl ether solution. Preparation of solid allyl- and vinyllithium by the lithium–tin exchange reaction in pentane is described. and the results of spectral analysis are reported and discussed.

Nordlander and Roberts[4] have reported that the n.m.r. spectrum of allylmagnesium bromide in diethyl ether consists of a doublet and a quintet, consistent with a structure in which all four methylene hydrogen atoms are magnetically equivalent: that is, the spectrum is of the AX_4 type.[5] We have observed the spectrum of a dilute ether solution of the related compound allyllithium and found a similar result. We also wish to report the spectrum of the simpler compound vinyllithium, which shows no such time-average symmetry.

Experimental

Vinyllithium[6] and allyllithium[7] can be prepared conveniently by the exchange reaction between phenyllithium and tetravinyltin and tetraallyltin in ether solution. However. the resulting solutions of these reagents contain significant amounts of lithium bromide (from the preparation of phenyllithium from bromobenzene) and low concentrations of tetraphenyltin. In order to obtain uncontaminated vinyl- and allyllithium solutions. a modification of our method was used.

In the system

$$(CH_2{=}CH)_4Sn + BuLi \xrightarrow{\text{pentane}}$$
$$CH_2{=}CHLi + BuSn(CH{=}CH_2)_3$$
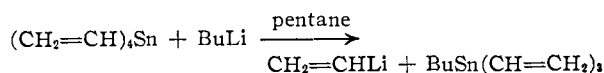
vinyllithium is the least soluble species. all organotin compounds, as well as butyllithium, being quite soluble.[8] This

allowed the preparation of an ether solution containing only vinyllithium by the procedure to be described.

To a solution of 2 g. (0.0088 mole) of tetravinyltin in 2 cc. of pentane under an atmosphere of prepurified nitrogen was added 25 cc. of 0.35 N solution of butyllithium in pentane. The resulting solution was concentrated by blowing a brisk stream of prepurified nitrogen across the surface of the solution. After the mixture had been left standing for several minutes. solid vinyllithium precipitated as an amorphous white powder. The solid was filtered under nitrogen using a sintered glass filtering apparatus and washed well with pentane. Dry vinyllithium is violently pyrophoric in air. and its properties and an alternate method of preparation will be reported elsewhere.[9] The sample of vinyllithium prepared as described above was dissolved in 2 cc. of diethyl ether immediately after its isolation.

Solid allyllithium was prepared in the same manner by the reaction of tetraallyltin and butyllithium (1:1 molar ratio) in pentane at room temperature.

Samples of the ether solutions of both compounds were sealed in 5 mm. Pyrex sample tubes and spectra were taken using a Varian Associates V-4300B spectrometer. Spectra of vinyllithium were obtained and analyzed at both 40 mc. and 60 Mc. Only 60 Mc. spectra were taken with allyllithium. The spectra were calibrated by the use of audiofrequency sidebands.

Results and Discussion

The spectrum of allyllithium showed the well-separated doublet and quintet typical of spectra of the AX_4 type, from which the parameters were derived by a first order analysis.

$$\delta_A = -5.52 \pm 0.05 \text{ p.p.m.}$$
$$\delta_X = -1.35 \pm 0.05 \text{ p.p.m.}$$
$$|A_{AX}| = 12 \pm 1 \text{ c.p.s.}$$

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(3) Alfred P. Sloan Fellow.

(4) J. E. Nordlander and J. D. Roberts. *J. Am. Chem. Soc.*, **81**, 1769 (1959).

(5) J. A. Pople. W. G. Schneider and H. J. Bernstein. "High Resolution Nuclear Magnetic Resonance Spectroscopy." McGraw-Hill Book Company. New York. N. Y.. 1959, Chapter 6.

(6) D. Seyferth and M. A. Weiner. *Chem. and Ind. (London)*. 402 (1959).

(7) D. Seyferth and M. A. Weiner. *J. Org. Chem.*. **24**. 1395 (1959).

(8) A complete discussion of the exchange reaction which gives vinyl- and allyllithium will be given in later publications. It should be pointed out. however. that while practically complete exchange between tetravinyltin and butyllithium (1:1 molar ratio) is observed in ether. in pentane these reagents in 1:4 molar ratio react to give a mixture of Bu₃SnCH=CH₂ and Bu₂Sn(CH=CH₂)₂ and a correspondingly lower yield of vinyllithium.

(9) E. C. Juenge and D. Seyferth. *J. Org. Chem.*. **26**, 563 (1961).

No attempt was made to improve the accuracy of these measurements. The chemical shifts are referred to the central peak of the ether triplet, and the difference between them is known more accurately than their individual magnitudes. The allylmagnesium bromide spectrum reported by Nordlander and Roberts[4] shows much smaller chemical shifts and leads us to suspect that the spectrum was run at 40 Mc. and that the 60 Mc. appearing in the caption of their figure is a typographical error.

The apparent magnetic equivalence of the four methylene protons suggests the same interpretations as does the similar situation in the allyl Grignard compound.[4] Over times of the order of 0.1 sec. or less, one or more of the following must occur:

(a) internal rotation in the allyl anion,

(b) intramolecular hydrogen exchange among the methylene protons in that ion, or

(c) intra- or intermolecular lithium exchange involving the allyllithium molecule.

We are in accord with Nordlander and Roberts in feeling that the last of these is the most plausible.

In order to investigate further such phenomena in organometallic compounds, we obtained the spectrum of vinyllithium (Fig. 1). We have analyzed this spectrum, which is of the ABC type, by iterated solution of the "high resolution" Hamiltonian,[10] and obtained the chemical shifts and coupling constants

$$\delta_A = 0$$
$$\delta_B = 0.511 \pm 0.005 \text{ p.p.m.}$$
$$\delta_C = 1.190 \pm 0.005 \text{ p.p.m.}$$

$$A_{AB} = 19.3 \pm 0.5 \text{ c.p.s.}$$
$$A_{AC} = 23.9 \pm 0.5 \text{ c.p.s.}$$
$$A_{BC} = 7.1 \pm 0.5 \text{ c.p.s.}$$

No reference compounds were employed. The computations were carried out on an IBM 704 computer using a program modified from one kindly supplied by Dr. A. A. Bothner-By of the Mellon Institute. The modification consisted primarily of the addition of a display program which permits observation and photographing of the calculated spectrum on a cathode ray tube. Figure 1 includes a photograph made in this way using the parameters listed above.

No time average symmetry of the three hydrogen atoms of vinyllithium was evident, and the lifetime of this unsymmetrical state must be greater than ~1/40 sec. However, this study allows no conclusions regarding the exact nature of the species present in solution, i.e., whether vinyllithium is present in covalent or ionic form.

Structural assignment of the protons denoted by A, B and C is difficult. Banwell and Sheppard[11] have noted a strong correlation between vinylic chemical shifts and Taft's resonance parameter σ_R, which permits such an assignment in many cases. In the absence of an experimental value or a means of theoretical prediction of σ_R for lithium, however, we are obliged to forego this method. Instead, we

(10) R. W. Fessenden and J. S. Waugh. J. Chem. Phys., 31, 996 (1959).

(11) C. N. Banwell and N. Sheppard. Molecular Physics; C. N. Banwell. N. Sheppard. J. J. Turner; Spectrochim. Acta, 16, 794 (1960).
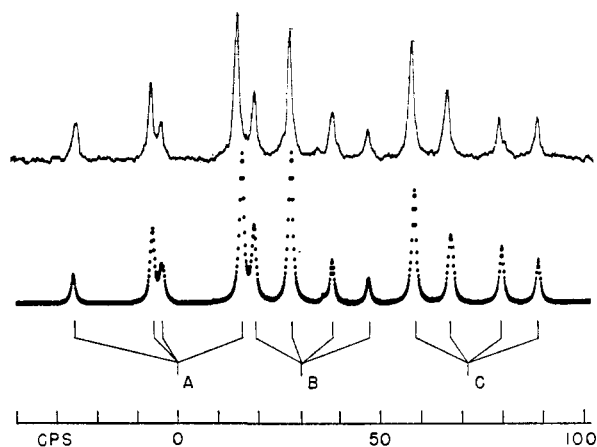
Fig. 1.—Nuclear magnetic resonance spectrum of vinyllithium in diethyl ether solution (60 Mc.); applied magnetic field increases toward the right.

make use of the same authors' observation that gem-, cis- and trans-coupling constants for vinyl groups show a clear linear decrease with increasing electronegativity of the substituent, down to their minimum E_n of 2.5. The slopes of all three plots are nearly the same, but the intercepts are different. Over the relatively small range of E_n appropriate to common organic compounds, the coupling constants tend to fall into the well known regions

$$A_{gem} \approx 1 \text{ c.p.s.}$$
$$A_{cis} \approx 10 \text{ c.p.s.}$$
$$A_{trans} \approx 17 \text{ c.p.s.}$$

A long extrapolation of these plots to $E_n = 1.0$, appropriate to Li, agrees remarkably well with our results if and only if we make the assignment

(B) H　　　H (A)
　　　　C=C
(C) H　　　Li
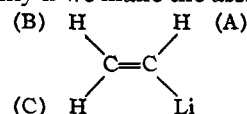
It may be noted that this assignment associates the smallest electronic shielding with the proton closest to the strongly electron-donating lithium atom. While this fact is perhaps surprising, it should be remembered that chemical shifts result from differences in induced electronic currents and not from differences in local charge density, as inferred chemically or from simple molecular orbital theory, themselves.

The parallel changes of all three coupling constants of the vinyl group with changing electronegativity of the substituent, noted by Banwell and Sheppard[11] and extended here, seem difficult to reconcile with the view[12] that variation in such coupling constants is mainly a matter of changes in bond angles. An investigation of this question is now in progress.

(12) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).