

METAL—DOUBLE BOND INTERACTIONS

IV. A STUDY OF LITHIUM— π -ELECTRON INTERACTIONS IN 3-BUTENYLLITHIUM BY ^7Li AND ^1H NMR SPECTROSCOPY

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Summary

3-Butenyllithium was prepared in an ether- and halide-free state by cleavage of di(3-butenyl)mercury with lithium metal. This product was shown to be hexameric in hydrocarbon solvents. A series of studies were carried out using ^1H and ^7Li NMR, infrared, and ultraviolet spectroscopy. The results of these studies indicate a perturbation of the π system of the butenyl moiety by the lithium aggregate, an interaction which also was supported by a calculation of the total energy of the system as a function of the conformation. This effect can be accounted for in terms of an intramolecular interaction.

This direct observation of a lithium—olefin interaction in a non-dissociated lithium aggregate supports earlier postulations of a similar interaction based on kinetics for ethylenation reactions in ether.

Also discussed are the role of aggregation states in accounting for differences in stereospecific addition in hydrocarbon vs. ether solvents.

Introduction

The importance of the reaction of organolithium reagents with carbon—carbon multiple bonds has been recognized both in polymerization reactions and for simple addition processes. It has been shown that the rate and mechanism of reaction depend on the solvent, the nature of the organolithium derivative, and on the substrate [1 - 4]. Results for ether solutions may be interpreted in terms of an anionic process with *trans* addition to the multiple bond

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[5]. This proposed carbanionic mechanism seems to hold true for carbonyl additions but does not explain ethylenation reactions [6]. The kinetics of the latter addition have been discussed in detail by Bartlett et al. [3]. The results indicate a direct metal-olefin interaction between ethylene and tetrameric (undissociated) alkyllithiums in ether. Since in the previous study the alkyllithiums were prepared by the action of an alkyl halide on lithium metal, the values of the rate constants will be somewhat lower than the reported values due to the presence of $\text{Li}_4\text{R}_{4-n}\text{X}_n$ species. It has been shown by Smith et al. that while the presence of lithium halides depressed the rate, the overall order of reaction was not affected [7].

Less definitive data have been presented with regard to the reactions of lithium derivatives in hydrocarbon media. It has been established that the reaction path differs from that in ether solvents, giving rise to *cis* addition, and it has been shown that the nature of the organic moiety influences the rate of addition to the double bond [5]. It has been postulated previously that in hydrocarbon solutions of 3-butenyllithium interactions occur between the double bond and the lithium core without disruption of the hexameric lithium aggregate [8]. This is in contrast to the suggested path for polymerization reactions.

In this present study a number of physical measurements are reported on 3-butenyllithium which lend support to this non-dissociative mechanism and also infer that the unique hexameric structure found only in hydrocarbon solutions may be responsible, in part, for determining the stereochemistry of addition.

Experimental

Preparation of compounds

1-Hydroxy-3-butene was obtained from Beacon Chemical Company or by the reaction of the Grignard of allyl chloride with formaldehyde [9]; b.p. 112.5 - 113.5°/748 mmHg [10]. 1-Chloro-3-butene was prepared by the chlorination of the alcohol with thionyl chloride using the procedure of Roberts [11]; b.p. 75.5° (lit. [10] 73 - 75°). 1-Bromo-3-butene was prepared by the bromination of the alcohol with PBr_3 [10]; b.p. 96.9° (lit. [10] 97°). 3-Butenylmercuric chloride was prepared by reaction of the Grignard reagent with mercuric chloride. In a typical synthesis, 0.17 mol of 1-chloro-3-butene was added dropwise to 0.2 g-atom of magnesium turnings in 200 ml of THF. The rate of halide addition was regulated to maintain gentle reflux. After all the halide had been added, the reaction mixture was refluxed for 2 h. Then 0.15 mol of mercuric chloride in 100 ml of THF was added and the reaction mixture was refluxed for 10 h. The mixture was hydrolyzed with concentrated ammonium chloride solution which resulted in precipitation of 3-butenylmercuric chloride. The crude product was collected by filtration and placed in a Soxhlet extractor for purification. The slight solubility of 3-butenylmercuric halide in cyclohexane allows an effective separation from unreacted mercuric halide to be made. The final product, obtained in a 74% yield, was collected from the filtration of the cyclohexane. The pure product appeared as fluffy white needles which decomposed at 130°. In a typical elemental analysis 0.685

mmol of 3-butenylmercuric chloride gave 0.690 mmol of chloride (as silver chloride) and 0.682 mmol of mercury (as mercuric sulfide). IR and NMR spectra confirmed the presence of the 3-butenyl skeleton, while the presence of ^{199}Hg satellites was evidence of mercury bonded to the organic moiety. Di(3-butenyl)mercury was prepared by the disproportionation of 3-butenylmercuric chloride using sodium stannite by the method of Nesmeyanov [12]. Typically, 0.014 mol of 3-butenylmercuric halide was dispersed in 50 ml hexane and 100 ml water and cooled to 0° . To this was added slowly (about 45 min) a mixture of 0.014 mol of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ in 40 ml of water mixed with 0.173 mol of NaOH dissolved in 30 ml of water at 0° . The mixture was stirred for 2 h, at which time free mercury was noted in the bottom of the flask. The hexane layer was separated and dried over CaCl_2 . The hexane layer was then fractionated in a high vacuum system. The di(3-butenyl)mercury remained in a 0° trap. It is a clear, colorless liquid with an apparent vapor pressure of 10^{-2} mmHg at 25° and moves very slowly at this temperature at a pressure of 10^{-6} mmHg. The final product was obtained in an 87% yield. The presence of the 3-butenyl moiety was confirmed by IR and NMR spectra. The mass spectrum at 70 eV shows ions at m/e 55 (butene), 214 (HgCH_2^+), 228 [$\text{Hg}(\text{CH}_2)_2^+$], 255 [$\text{Hg}(\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2)^+$], and 310 [$\text{Hg}(\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2)_2^+$]. 3-Butenyllithium was obtained in quantitative yield by the exchange of di(3-butenyl)mercury and excess lithium metal chips in cyclopentane at room temperature. The lithium was added to a specially constructed reaction vessel in an oxygen and water free drybox. The vessel was then transferred to a vacuum line where dried, degassed solvent and di(3-butenyl)mercury were distilled in. (Because of the low volatility of the mercury compound, it is more efficient to transfer the mercury compound to the vessel in the drybox when more than 1 ml of reactant is desired.) The vessel was then sealed off from the line and stirred with a magnetic stirrer for 18 - 24 h after which time the shiny lithium had become black and pitted. The reaction mixture was then filtered through a medium frit into an NMR tube or storage vessel attached to the reaction vessel. This final solution is pale yellow. The NMR and mass spectra indicated the absence of any starting product. 3-Butenyllithium obtained in this manner is free of contamination by lithium halides [13,14], etherates, and mixed organolithium compounds [15 - 17]. High vacuum techniques also minimized the contamination of the product by alkoxide formation [18]. Hydrolysis of the product with water gave 1-butene and lithium hydroxide. The 1-butene was identified by its IR, NMR, and mass spectrum. Also, VPC showed only one gas was present from the hydrolysis (after separation of the water). The lithium hydroxide was titrated with HCl and the number of moles of butene evolved was determined by the volume - pressure relation and by direct weighing of the gas. In a typical analysis, the lithium compound obtained from 0.35 mmol of di(3-butenyl)mercury gave on hydrolysis 0.71 mmol of 1-butene and 0.71 mmol of lithium titrated as lithium hydroxide.

The dimethyl etherate of 3-butenyllithium was prepared in two ways: (i), by using a mixed solvent, with dimethyl ether as one of the components, in the reaction flask and proceeding in the same fashion as outlined in the synthesis of 3-butenyllithium, or (ii), by equipping the second vessel with a break seal, and after the mixture had been filtered from the reaction vessel into the second

vessel and sealed, this vessel could in turn be attached to a vacuum line, opened, and the dimethyl ether added. Either procedure gave identical results.

Di-n-butylmercury was prepared and purified in a manner similar to that used for di(3-butenyl)mercury, and was identified by its NMR and IR spectra.

n-Butyllithium and its etherate were formed in the same manner as used for 3-butenyllithium and its etherate. The compound was identified through its hydrolysis products and its NMR and infrared spectra.

Spectroscopic studies

The high resolution PMR spectra were obtained on a Varian DP - 60 IL NMR spectrometer. Line positions were measured by synchronizing the output of a Hewlett - Packard 211A square wave generator to the frequency difference between the locking and sweep frequency and counting multiple frequencies using a Hewlett - Packard 5245L counter. Chemical shifts and coupling constants for the vinyl regions of all the 3-butene derivatives with the exception of the chloro and tin compounds were obtained from exact analysis of the spectra using UEANMR [19]. These will be reported later in more detail [20]. ^7Li NMR were obtained on a Jeol - JNM - 4H - 100 spectrometer. A proton probe was built which fits inside the ^7Li probe so that the two detection coils were concentric. This modification allowed the internal proton lock required to accurately measure the small ^7Li chemical shifts [21]. Proton, lithium, and sideband frequencies were determined with a Hewlett - Packard 5245L counter with a (5251A) 20 - 100 MHz frequency converter plug-in unit.

Infrared spectra were determined on either a Perkin - Elmer 237B or 621 spectrometer. The values obtained are good to $\pm 2\text{ cm}^{-1}$ in the region of $625 - 2000\text{ cm}^{-1}$, and to $\pm 4\text{ cm}^{-1}$ in the region $2000 - 4000\text{ cm}^{-1}$. In order to obtain satisfactory IR spectra of the organolithium derivatives, samples were prepared in an argon-filled drybox in which sodium - potassium alloy was used as a scavenger. After the initial spectrum had been obtained the samples were allowed to stand open to the air for a few minutes and then redetermined in order to identify absorptions due to decomposition products. Dilution studies were also utilized to determine absorptions due to impurities.

The ultraviolet absorption spectra were obtained on Cary 14 and Hitachi model EPS - 3 recording spectrophotometers using nitrogen flushing. Cells and solvent were transparent down to 180 nm. The mass spectra were determined with an Atlas Werk CH4 mass spectrometer with an ionizing potential of 70 eV and ionization current $18\text{ }\mu\text{A}$.

Molecular weight determination

The degree of association of 3-butenyllithium was determined from its molecular weight in solution by the vapor pressure lowering of cyclopentane solutions assuming Raoult's law (Table 1). The procedure was carried out completely under high-vacuum conditions. The lithium compound was prepared in the usual way in cyclopentane and then filtered into a vessel fitted with a stirring bar and break seal. This vessel then was sealed and attached to a manometer on the high-vacuum system. The vessel was opened to the manometer (after evacuation) through the break seal, brought to 21.0° , and the vapor pressure determined. Then some of the cyclopentane solvent was re-

moved (and weighed), the system allowed to come to equilibrium and the new vapor pressure recorded. This procedure was repeated several times. Finally all of the cyclopentane was distilled out, combined with the previous fractions and weighed. The organolithium compound was then hydrolyzed and the amount of butene gas evolved was determined. This value was then substantiated by titration of the lithium hydroxide (or ethoxide) formed. The volumes of the molecular weight vessel and the manometer were determined and the concentrations of the solutions were corrected for the amount of cyclopentane in the vapor phase. Molecular weights determined for standards by this method were within 4 - 7% of their actual values, which in light of previous work [22 - 24] was sufficient to establish the degree of association in hydrocarbon solvent. The method has the disadvantage of requiring a fairly high concentration of solute (5% in polymer), but this was outweighed by the advantage of maintaining high-vacuum conditions at all times.

Results and discussion

Physical and chemical properties

Halide-free 3-butenyllithium is a white to very pale yellow solid which melts at 22.4° and has a low vapor pressure as evidenced by the fact that it cannot be sublimed at 50° and 10⁻⁶ mmHg. Higher temperatures cause rapid decomposition yielding polymeric materials. It is extremely soluble in all solvents tried including TMS, ether, benzene, and cyclopentane. Above its melting point it appears to be miscible in all proportions with the solvents. All solutions observed were light yellow in color. 3-Butenyllithium decomposes slowly at room temperature either as the pure material or in hydrocarbon solutions, while addition of ether enhances the rate of decomposition. Solutions kept at -80° appear to be stable for long periods of time, regardless of solvent. In the presence of lithium metal, hydrocarbon solutions of the reagent appear to show little decomposition after several months at 25°. It was shown to be hexameric in cyclopentane solutions by vapor pressure lowering experiments. The results are summarized in Table 1. These results are consistent with findings for similar organolithium compounds [25 - 28].

TABLE 1

MOLECULAR WEIGHT FROM VAPOR PRESSURE DEPRESSION MEASUREMENTS OF 3-BUTENYL-LITHIUM IN CYCLOPENTANE

Molarity		Molecular weight	Degree of association
Monomer	Hexamer		
5.06	0.84	369	6.0
4.10	0.68	355	5.7
3.25	0.54	432	7.0
2.14	0.36	377	6.1
1.56	0.26	339	5.5
1.34	0.22	379	6.1
1.15	0.19	385	6.2
1.06	0.18	432	7.0
0.95	0.16	386	6.2
0.77	0.13	328	5.3

Approximate Molecular Orbital calculations

As noted in the Introduction, various postulates have been presented regarding the nature of addition and interaction of double bonds with lithium alkyls. In order to provide some basis for the development of experiments to test these hypotheses and in an attempt to determine whether an intramolecular interaction of the double bond with lithium core in this hexameric species stabilizes or destabilizes a particular conformation, a series of INDO calculations [29] were performed. $\text{Li}_6(\text{CH}_3)_5(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ was used for the calculation rather than the butenyllithium hexamer to simplify the calculation by decreasing the number of atoms and eliminating steric interactions between butenyl groups.

The general description of the model and justification for its choice have been described previously [30]. The structure is composed of six lithium atoms located at the corners of a regular octahedron with Li—Li distances of 2.55 Å. Six of the eight faces of the octahedron are occupied by carbon atoms while the two remaining vacant faces have been placed opposite one another. The single C—C bond, the C=C double bond, and the C—H bond have been assigned the values 1.54, 1.35, and 1.09 Å, respectively, as shown in Fig. 1a.

Each of the methyl groups was in the lower energy pseudo-eclipsed conformation, (a dihedral angle formed by the hydrogen, the carbon, and a point in the center of a lithium face, and by the same hydrogen, the carbon and a lithium atom was zero degrees) as shown in Fig. 1b. To facilitate close approach of the empty face of the octahedron and the double bond, the hydrogen on the butenyl α -carbon was in the pseudo-*gauche* conformation (Fig. 1c). In this series of calculations, the only parameter varied was the dihedral angle, ω , formed by the center of the lithium aggregate and the α -, β - and γ -carbons.

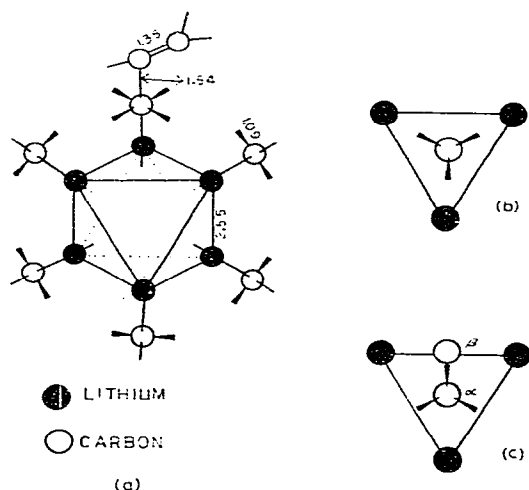
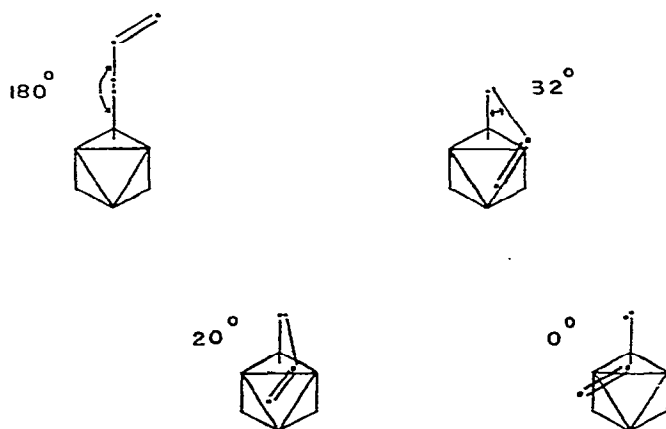


Fig. 1. (a) Geometry of the model used for the INDO calculations. (b) Configuration of each of the methyl groups over its respective face. (c) Configuration of the α -carbon of the 3-butenyl group with respect to the aggregate face.



BUTENYLLITHIUM ROTAMERS

Fig. 2. Change in position of the vinyl group with respect to the open face as a function of rotation about the α - β carbon bond in 3-butenyllithium.

Changes in ω correspond to a simple rotation about the bond between the α - and β -carbon atoms. Four of these rotamers are diagrammed in Fig. 2. In each figure, the nodal plane of the π system is parallel to the paper. When ω equals 180° , the double bond is well removed from the lithium framework in that the minimum lithium-vinyl carbon distance is $4.09 \text{ \AA}$. If ω equals 32° , the π orbital points along one edge of the empty face and brings the δ -carbon only $2.13 \text{ \AA}$ from one of the lithium atoms. As ω decreases to zero, the double bond sweeps across the empty face. Figure 3 shows the relative changes in the total energy of the molecule as ω is varied. The most stable molecular configurations are those which permit the interaction of the vinyl system with the lithium framework through one of the empty faces.

This is not to imply that the strength of interaction between the vinyl group and the open face is 90 kcal as indicated in Fig. 3. This would certainly result in differentiation of two of the butenyl groups which is contradictory to our observed data. The reason for this large calculated interaction is due to the fact that in the model the five other groups are methyls which cause little steric interaction as the butenyl group sweeps over the open face. In the actual compound, these steric interactions would certainly cause the magnitude of the interaction to be reduced to a more reasonable value.

The above information suggests that the addition mechanism of an olefin to an alkylolithium may also be dependent on the structural differences between hexamer and tetramer as well as usual effects like solvent polarity.

Figure 4 depicts two possible mechanisms based on differences in aggregation state. The hexamer shown in Fig. 4a can initially interact with the olefin via the open face. As stated, calculations indicate that this will stabilize the molecule. In the tetramer (Fig. 4b), however, the olefin must either interact initially with the lithium atoms, followed by displacement of the alkyl group

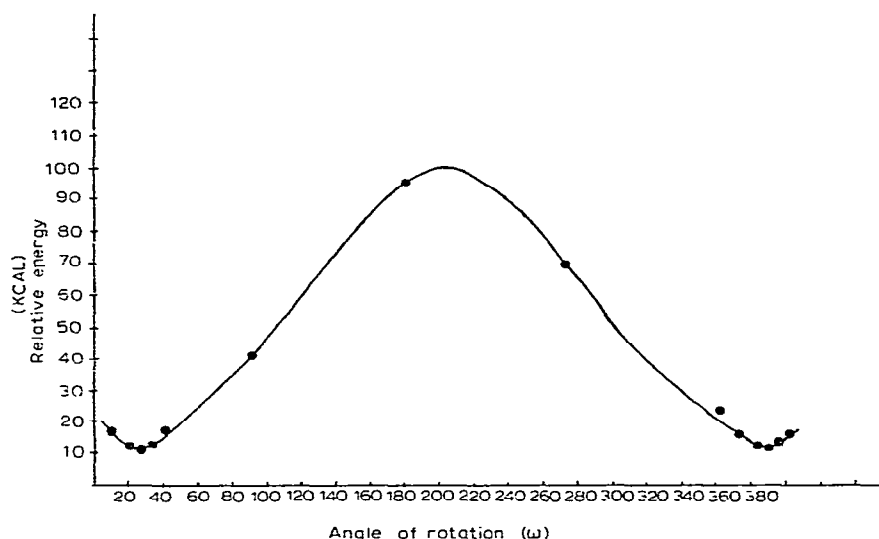


Fig. 3. The total energy of the molecule, calculated from INDO methods, is plotted versus the angle of rotation about the α - β carbon bond (ω).

by the olefin, or interact through a concerted mechanism in which there is a direct displacement of the alkyl group by the olefin. Each of the mechanisms would have different stereochemical implications. The mechanism shown in Fig. 4a would lead to *cis* products, while the mechanism shown in Fig. 4b would lead to *trans* products. While it may not be valid to extend these arguments to conjugated dienes, the mechanisms postulated to suggest that the

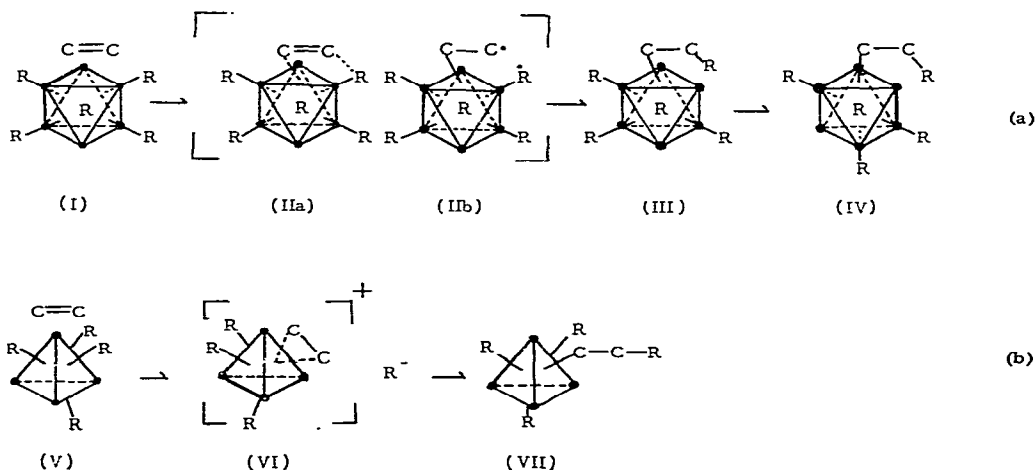


Fig. 4. (a) Proposed mechanism for the addition of olefin to a hexameric lithium species in non-polar solvent. (b) Proposed mechanism for the addition of olefins to tetrameric species in polar solvents.

TABLE 2

PMR PARAMETERS FOR SELECTED 3-BUTENYL DERIVATIVES

Compound	δ_1 (ppm)	δ_2 (ppm)	δ_3 (ppm)	δ_4 (ppm)	δ_5 (ppm)	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	J_{45}
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{Cl}^a$	-5.12	-5.09	-5.81	-2.47	-3.50							
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{Br}^a, b$	-5.090	-5.061	-5.765	-2.563	-3.349							
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{I}^a, b$	-5.086	-5.081	-5.738	-2.600	-3.130							
$\text{CH}_2 = \text{CHCH}_2\text{CH}_3^a, b$	-4.939	-4.86	-5.780	-2.05	-0.98							
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{OH}^a, b$	-5.057	-5.000	-5.788	-2.266	-3.572							
$[\text{CH}_2 = \text{CH}(\text{CH}_2)_2]_2\text{Hg}^a, b$	-4.976	-4.873	-5.888	-2.551	-1.117							
$[\text{CH}_2 = \text{CH}(\text{CH}_2)_2]_2\text{Cd}^b, c$	-4.947	-4.851	-5.937	-2.399	-0.682							
$[\text{CH}_2 = \text{CH}(\text{CH}_2)_2]_3\text{Bc}$	-4.89	-4.83	-5.83		-1.33							
$[\text{CH}_2 = \text{CH}(\text{CH}_2)_2]_2\text{SnPh}_2^e$	-4.94	-4.88	-5.82									
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{Li}^b, c$	-5.068	-4.908	-6.035	-2.483	+0.851	2.331	17.298	-1.456	9.984	-0.876	7.016	7.580
$\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{Li}^b, c$	-4.827	-4.623	-5.291	-2.225	+0.935	2.565	16.953	-1.569	9.917	-1.140	6.308	8.964
$\text{CH}_3(\text{CH}_2)_3\text{Li}^e$					+0.85							8.14

^aIn CCl_4 . ^bChemical shifts were determined by exact analysis techniques using LAOCN III [19]. Chemical shifts obtained in this manner are accurate to ± 0.002 ppm. ^cIn C_5H_{10} . ^dIn $(\text{CH}_3\text{CH}_2)_2\text{O}$. ^eIn CCl_4 , see ref. 36.

differences in mode of addition with changing solvent polarity may also be due, in part, to concurrent structural changes in the lithium aggregate.

Spectroscopic studies

The ^7Li chemical shift (δ) of butenyllithium was found to be concentration dependent above 1 *M*. Below this concentration a constant value of δ -1.44 ppm was obtained which should be compared with δ values of -1.52 and -1.53 ppm for ethyl- and n-butyllithiums, respectively. Neither of the latter compounds shows a concentration dependence for the ^7Li resonance in cyclopentane when measured relative to an internal proton lock [21]. In ether, the ^7Li chemical shift of 3-butenyllithium was -0.74 ppm while the chemical shifts of ethyl- and n-butyllithium were -0.77 and -0.74 ppm, respectively.

Within a particular solvent system, it has been observed that the principle factor in determining differences in chemical shifts between two alkyllithiums is the substituent anisotropy term [21]. In this respect, the 3-butenyl and n-butyl substituents' anisotropy terms should be similar and, as predicted, the ^7Li chemical shifts of the n-butyl- and 3-butenyllithium are identical in diethyl ether. In cyclopentane, however, the 3-butenyl derivative is shifted 0.1 ppm upfield. This upfield shift is attributed to the interaction of the unsaturated portion of the alkenyl group with the lithium core causing a deshielding of the lithium nucleus. This is not observed in diethyl ether, however, because the ether is a more effective base than the double bond and thus prevents the interaction from occurring.

In additional studies ^1H NMR was used to examine a variety of 3-butenyl derivatives. The data are collected in Table 2. The ^1H chemical shifts, as a function of concentration in cyclopentane solvent (Table 3), show no effect over a 17-fold change in concentration. The more dilute samples were also studied as a function of temperature between -40 and 50° and again showed no variation either in chemical shift or in linewidth. The interpretation of data of this type is complicated by solvent, magnetic anisotropy, and other effects. It has been shown, however, that by use of the internal chemical shifts in the ethyl halides these effects can be minimized and a reasonable correlation of the chemical shift with the electronegativity of the substituent can be obtained [23,31]. This approach has been extended to the study of addition compounds where correlation between the internal chemical shift and the heat of formation has been observed [24].

Using these data, Fig. 5 was constructed in which the internal chemical

TABLE 3
CHEMICAL SHIFTS OF 3-BUTENYLLITHIUM IN CYCLOPENTANE AT VARIOUS CONCENTRATIONS

Molarity	δ_1 (ppm) ^a	δ_2 (ppm)	δ_3 (ppm)	δ_4 (ppm)	δ_5 (ppm)
2.19	-5.08	-4.91	-6.05	-2.50	+0.84
1.97	-5.08	-4.89	-6.05	-2.50	+0.85
1.96	-5.07	-4.92	-6.04	-2.51	+0.84
1.06	-5.08	-4.89	-6.06	-2.49	+0.85
0.50	-5.07	-4.91	-6.04	-2.50	+0.85
0.13	-5.07	-4.92	-6.04	-2.51	+0.85

^aThe proton designations are as follows: $\overset{2}{\text{H}}\text{C}=\overset{3}{\text{C}}-\overset{4}{\text{C}}-\overset{5}{\text{C}}-\text{Li}$ and are relative to internal TMS.

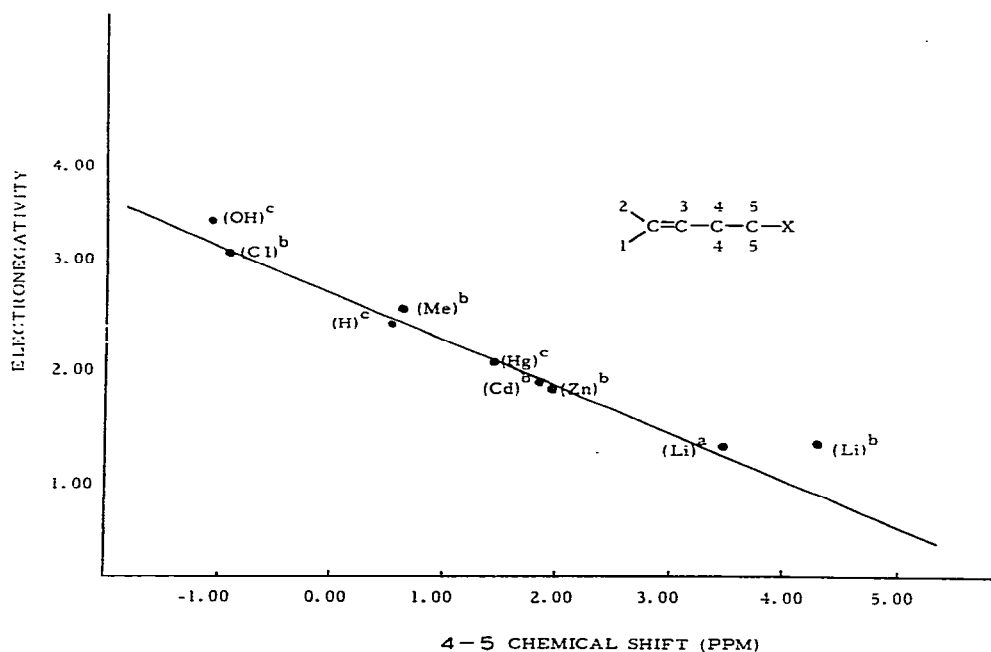


Fig. 5. A least-squares fit (correlation coeff = -0.98938) of the internal chemical shifts of a series of butenyl derivatives versus electronegativity. Spectra were obtained in (a) diethyl ether, (b) cyclopentane and (c) carbon tetrachloride.

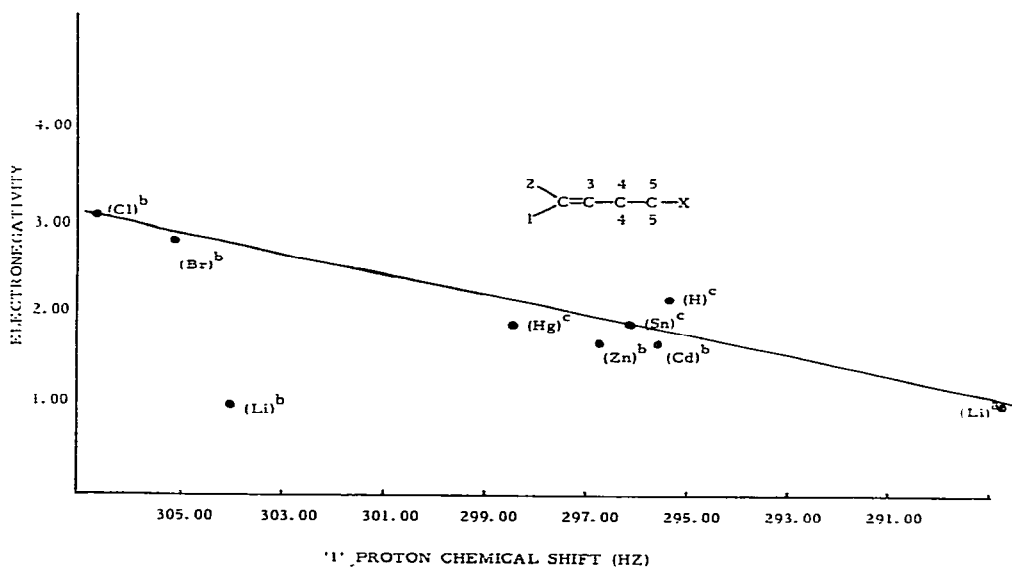


Fig. 6. A least-squares fit (correlation coeff = $+0.82460$) of the chemical shift of the "1" proton versus electronegativity for a series of butenyl derivatives. Spectra were obtained in (a) diethyl ether, (b) cyclopentane and (c) carbon tetrachloride.

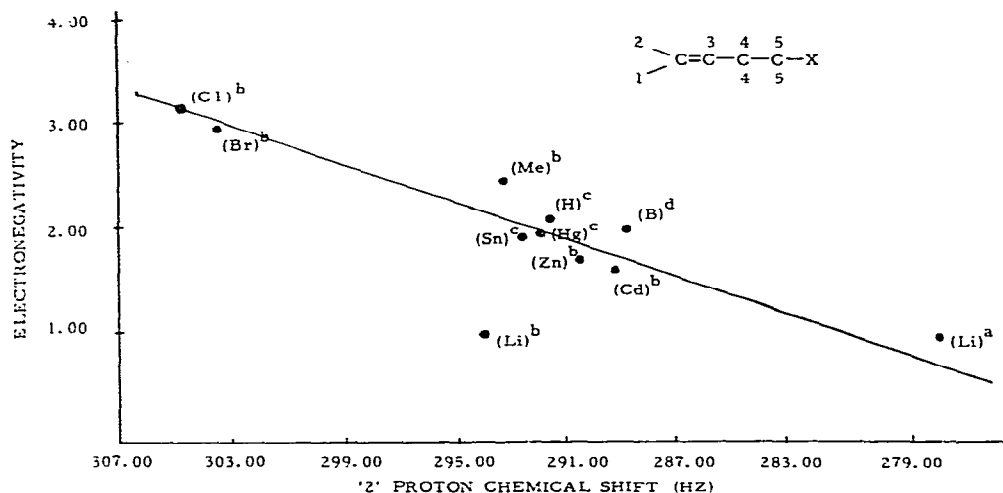


Fig. 7. A least-squares fit (correlation coeff = 0.85013) of the chemical shift of the "2" proton versus electronegativity for a series of butenyl derivatives. Spectra were obtained in (a) diethyl ether, (b) cyclopentane and (c) carbon tetrachloride.

shift ($\delta_5 - \delta_4$) is plotted versus Pauling electronegativity of the substituent. The line was determined using a least-squares fit and had a correlation coefficient of -0.989 . Examination of Fig. 5 reveals that butenyllithium in hydrocarbon falls off an otherwise linear plot and that the deviation is to higher field. A deviation in this direction can be rationalized by examination of the metal-carbon dipole: $M^{\delta+}-C-C=C^{\delta-}$.

The ^7Li chemical shift indicated an upfield shift on complexing with the double bond. This indicates the lithium ion is becoming more positive*; thus an increased negative charge should also reside on the adjacent 5 carbon. This increased shielding would cause the upfield deviation observed. The proton region of the double bond was also examined and the results are shown in Figs. 6 and 7. In both the 1 and 2 protons, the 3-butenyllithium derivative deviates significantly from the straight line in cyclopentane solvent. This perturbation of the double bond region is taken as additional evidence of interaction between the double bond and the lithium core. Figures 5, 6 and 7 also indicate that when the solvent is changed to diethyl ether the values of the chemical shifts of the 5 - 4, 1 and 2 protons return to "normal" values. Again, this is the result of adding a stronger Lewis base, ether, to disrupt the metal-olefin interaction.

A more detailed study of the effects of varying ether concentrations on 3-butenyllithium chemical shifts was made and the results are shown in Table 4. The largest effect on the chemical shifts is obtained when the dimethyl ether/3-butenyllithium ratio is 2/3. The observed shifts of the 1 and 2 protons are -4.81 , -4.61 ppm, respectively. These values are in much closer agreement with those predicted from Figs. 6 and 7. The 5 proton resonance is shifted upfield by 0.13 ppm in these samples while the ether resonance decreases from

* Alkylolithiums have chemical shifts in the range -0.8 to -1.5 ppm when 70% aqueous LiBr is taken to be 0 ppm and lithium metallate derivatives show chemical shifts up to $+3.0$ ppm.

TABLE 4

CHEMICAL SHIFTS FOR DIMETHYL ETHER AND 3-BUTENYLLITHIUM WITH DIFFERENT ETHER/LITHIUM RATIOS

$\text{O}(\text{CH}_3)_2/\text{LiR}^a$	$\text{O}(\text{CH}_3)_2(\text{ppm})^b$	$\delta_1(\text{ppm})$	$\delta_2(\text{ppm})$	$\delta_3(\text{ppm})$	$\delta_4(\text{ppm})$	$\delta_5(\text{ppm})$
	-3.19					
0.38	-3.34	-4.89	-4.70	-5.99	-2.30	+0.93
0.40	-3.34	-4.89	-4.68	-5.96	-2.25	+0.97
0.65	-3.33	-4.81	-4.61	-5.93	-2.18	+0.99
0.67	-3.32	-4.81	-4.61	-5.94	-2.18	+0.98
2.85	-3.25	-4.78	-4.55	-5.92	-2.16	+0.98

^aAll samples were in cyclopentane solvent. ^bAll chemical shift values are relative to TMS.

-3.19 ppm for pure dimethyl ether to -3.34 ppm for samples with an ether to lithium ratio of less than 2/3. For samples with ether/lithium ratios greater than this, the ether resonance moves upfield toward that for the pure dimethyl ether sample. In all cases, only a single set of resonance lines are observed for these protons and for the 3-butenyl group.

This behavior is in full accord with the known behavior of simple hexameric organolithium compounds which have been shown to undergo dissociation to tetrameric units which are complexed by from 2 to 4 moles of ether per aggregate [3,32 - 34]. It has also been noted that the complexed ether is in rapid equilibrium with excess ether present in the system as observed.

Additional support for these arguments comes from an examination of J_{45} and a comparison of the coupling constant in 3-butenyllithium, 3-butenyllithium etherate and n-butyllithium. In hydrocarbon solvent, the coupling constant in ethyllithium is 8.4 Hz [27] and for n-butyllithium the same coupling constant is 8.14 Hz (Table 2). 3-Butenyllithium exhibits a coupling constant of 7.58 Hz, for these same two protons (5 and 4). Addition of ether changes these values to 8.9 Hz for the ethyl- and n-butyllithium and to 8.96 Hz for the 3-butenyllithium compounds respectively. The change in coupling constant for the latter compound is at least twice as great as that observed in either of the others. If one can interpret the difference here as being due to an averaging of conformers, then the ether adduct of 3-butenyllithium provides more con-

TABLE 5

THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME SELECTED BUTENYL DERIVATIVES

Compound	Solvent	Maxima(nm)
C_4H_8	Vapor	187 ^a
$\text{C}_4\text{H}_7\text{Br}$	Isopentane	187
$\text{C}_4\text{H}_7\text{Br}$	Vapor	187
$\text{C}_4\text{H}_7\text{Cl}$	Isopentane	192
$\text{C}_4\text{H}_7\text{Cl}$	Vapor	188
$\text{C}_4\text{H}_7\text{OH}$	Isopentane	194
$\text{C}_4\text{H}_7\text{OH}$	Vapor	188
$(\text{C}_4\text{H}_7)_2\text{Hg}$	Isopentane	187, 210 (br)
$(\text{C}_4\text{H}_7)_2\text{Hg}$	Vapor	208, 210, 213, 216
$(\text{C}_4\text{H}_7\text{Li})_6$	Hexane	194, 215, 235, 260
$(\text{C}_4\text{H}_7\text{Li})_6$	Isopentane	208, 212, 218, 225, 251

^aSamson et al. observed the absorption maxima at 176 nm with a shoulder at 187 - 180 nm at 0.2 mm Hg pressure [37]. High pressure samples show a maximum at 187 nm.

TABLE 6

INFRARED SPECTRA OF 3-BUTENYL LITHIUM, 3-BUTENYL LITHIUM · METHYL ETHERATE, DI(3-BUTENYL)MERCURY AND 1-BROMO-3-BUTENE

$\text{CH}_2\text{CH}(\text{CH}_2)_2\text{Br}^a$	$\text{CH}_2\text{CH}(\text{CH}_2)_2\text{Br}^b$	$[\text{CH}_2\text{CH}(\text{CH}_2)_2]_2\text{Hg}^d$	$\text{CH}_2\text{CH}(\text{CH}_2)_2\text{Li}^a$	$\text{CH}_2\text{CH}(\text{CH}_2)_2\text{Li}^c$
3045 s	3100	3038 s	3035 s	3020 s
	2950 s			
2640 w	2850 s	2772 m	2683 s	2690 s
1981 w		1977 w		
1841 m	1850 w	1824 m	1841 w	1842 w
			1790 (sh)	1791 w
1730 w				
1700 w				
1643 s	1650 s	1640 s	1620 s	1626 s
1501 (sh)	1440 s	1509 (sh)		
1414 s		1409 s	1387 s	1386 s
1302 m	1320 (sh)	1335 w		
	1295 s	1303 m		
		1284 m	1283 s	1287 s
1261 s				
	1240 (sh)	1241 s		
1204 s	1175	1179 m	1179 w	1186 s
				1151 w
1097 w		1115 w		
			1068 s	
1057 w	1035 (sh)	1035 w		1049 s
983 s	985 s	983 s	995 s	997 s
			949 s	952 s
907 s	925 vs		902 s	
		891 s		
874 w			859 s	879 s
				824 s
789 w	790			780 s
	760 vs			
757	755 vs			
	680 vs			
668		715	659	664
597		650		
575				
		568		
		516		
			481	462

^aCyclopentane solvent. ^bGas phase. ^cCyclopentane + ether.

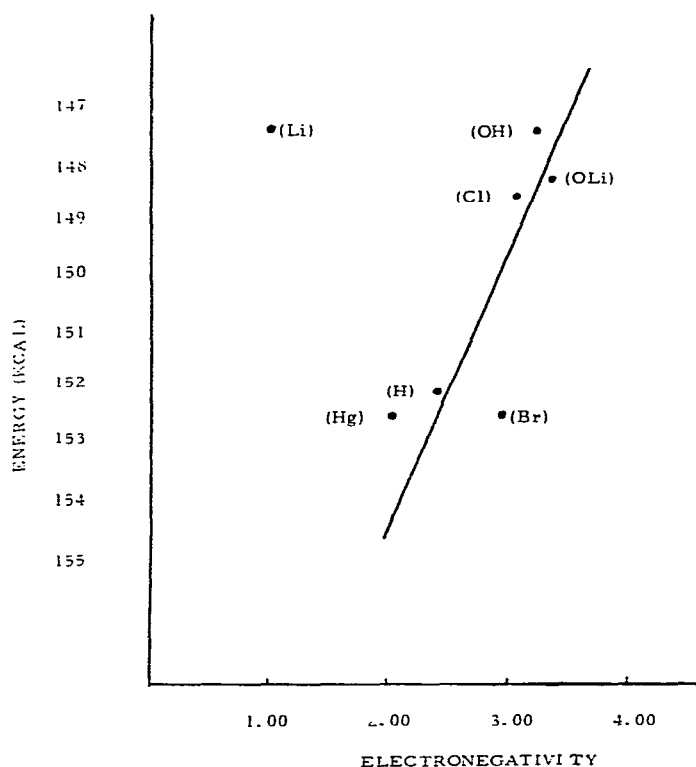


Fig. 8. A plot of the $\lambda_{\max}$ of the $\pi \rightarrow \pi^*$ transition in a series of butenyl derivatives versus electronegativity. All samples were run in isopentane.

formers similar to the ethyl- and n-butyllithium compounds. This would also be consistent with a tying down (through adduct formation) of the vinyl region with the lithium moiety which is then "freed" by the stronger base, ether.

The UV studies also showed a perturbation of the double bond in 3-butenyllithium. The $\pi \rightarrow \pi^*$ transitions for several butenyl derivatives are collected in Table 5. If these data are plotted against electronegativity, as shown in Fig. 8, then it is observed that as the electronegativity of the substituent increases, the energy of the $\pi \rightarrow \pi^*$ transition decreases. While this relationship is not linear enough to predict an exact value for the $\pi \rightarrow \pi^*$ transition in 3-butenyllithium, it does allow us to predict that based on an electronegativity value of 1 on the Pauling scale for the lithium aggregate that the $\pi \rightarrow \pi^*$ transition should occur at higher energy than any of the other butenyl derivatives in this study. The opposite, however, is observed with a transition in the range 200 - 230 nm, lower in energy than any of the other butenyl derivatives studied. The assignment of $\pi \rightarrow \pi^*$ transition is complicated in the lithium derivative because it has been shown that the lithium framework transition also occurs in this region [30] which caused broad bands with a number of inflections (see Fig. 9). Upon hydrolysis, gross changes took place in the 200 - 230 nm region and a new peak (at 185) corresponding to the 1-butene appeared. A

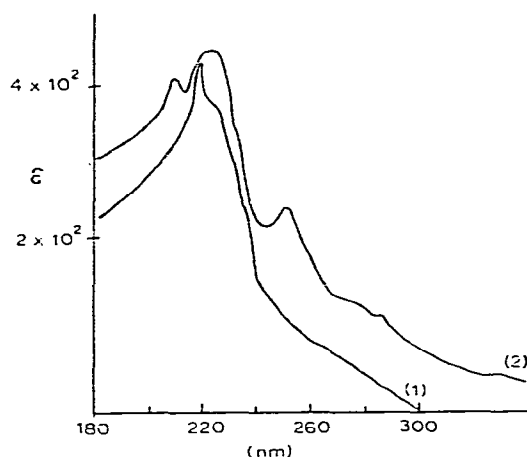


Fig. 9. The UV spectrum of (1) butyl and (2) 3-butenyllithium in isopentane.

similar observation was made by Lyle et al. [35] who postulated similar interactions in 3-butenylboron.

IR data for a series of butenyl derivatives are collected in Table 6. Examination of this Table shows that the double bond stretching frequency is shifted to lower energy (1620 cm^{-1}) in the lithium derivative and also the vinyl C—H stretch at 3035 cm^{-1} , again is shifted to lower energy. If our earlier postulates about the nature of the double bond—lithium interaction are correct, then only two of the six alkenyl groups may be complexed at one time. Only one band attributable to the double bond stretch is observed, however, in 3-butenyllithium and this band demonstrates only a slight upfield shift (6 cm^{-1}) upon the addition of diethyl ether. These data leads us to conclude that lithium—double bond interaction is very weak, perhaps, of a dipole—dipole nature. This type of interaction would still be consistent with the results. Perturbation of the π cloud of the double bond would cause substantial modification of the NMR and UV spectra but would have little effect on the IR spectrum because the bulk of the force constant for the double bond stretch lies in the σ bond.

References

- 1 H. Hsieh, D.J. Kelly and A.V. Tobolsky, *J. Polym. Sci.*, **26** (1957) 240.
- 2 H. Hsieh and A.V. Tobolsky, *J. Polym. Sci.*, **25** (1957) 245.
- 3 P.D. Bartlett, C.V. Goebel and W.P. Weber, *J. Amer. Chem. Soc.*, **91** (1969) 7425.
- 4 D.J. Worsfold and S. Bywater, *Can. J. Chem.*, **38** (1960) 1891.
- 5 M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience, New York, N.Y., 1968, Ch. VIII.
- 6 P.D. Bartlett, S.J. Tauber and W.P. Weber, *J. Amer. Chem. Soc.*, **91** (1969) 6362.
- 7 S.G. Smith, L.F. Charbonneau, D.P. Novak and T.L. Brown, *J. Amer. Chem. Soc.*, **94** (1972) 7059.
- 8 J.B. Smart, M.T. Emerson and J.P. Oliver, *J. Amer. Chem. Soc.*, **88** (1966) 4101.
- 9 M.G. Ettlinger and J.E. Hodgkins, *J. Amer. Chem. Soc.*, **77** (1955) 1831.
- 10 D.J. Patel, C.L. Hamilton and J.D. Roberts, *J. Amer. Chem. Soc.*, **87** (1965) 5144.
- 11 M.C. Caserio, W.H. Graham and J.D. Roberts, *Tetrahedron*, **11** (1960) 171.
- 12 A.N. Nesmeyanov, A.E. Borisov and N.V. Novikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1959) 1216.

- 13 R. West and W. Glaze, *J. Amer. Chem. Soc.*, **83** (1961) 3580.
- 14 T.V. Talalaeva, A.N. Rodinov and K.A. Kocheshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1961) 1990.
- 15 T.V. Talalaeva, A.N. Rodinov and K.A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **154** (1964) 174.
- 16 D. Seyferth and H.M. Cohen, *Inorg. Chem.*, **2** (1963) 625.
- 17 M.A. Weiner and R. West, *J. Amer. Chem. Soc.*, **85** (1963) 485.
- 18 T.L. Brown, J.A. Ladd and G.N. Newman, *J. Organometal. Chem.*, **2** (1965) 1.
- 19 Delos F. Detar (ed.), *Computer Programs for Chemistry*, Vol. 1. W.A. Benjamin, 1968.
- 20 R. Hogan, P. Scherr, J. St. Denis, T. Dolzine and J.P. Oliver, in preparation.
- 21 R. Hogan, P. Scherr and J.P. Oliver, in preparation.
- 22 L.M. Seitz and T.L. Brown, *J. Amer. Chem. Soc.*, **88** (1966) 2174.
- 23 B.P. Dailey and J.N. Schoolery, *J. Amer. Chem. Soc.*, **77** (1955) 3977.
- 24 A. Leib, M.T. Emerson and J.P. Oliver, *Inorg. Chem.*, **4** (1965) 1825.
- 25 G.E. Coates, *Organo-metallic Compounds*, 2nd edn., Methuen, London, 1960, Ch. 1.
- 26 T.L. Brown and M.T. Rogers, *J. Amer. Chem. Soc.*, **79** (1957) 1859.
- 27 T.L. Brown, D.W. Dickerhoof and D.A. Bafus, *J. Amer. Chem. Soc.*, **84** (1962) 1371.
- 28 T.L. Brown, *Advan. Organometal. Chem.*, **3** (1966) 365; M. Morton and L.J. Fetters, *J. Polym. Sci., Part A*, **2** (1964) 3311; D. Margerison and J.P. Newport, *Trans. Faraday Soc.*, **59** (1963) 2058; M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, **1** (1962) 654.
- 29 J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
- 30 J.B. Smart, R. Hogan, P.A. Scherr, L. Ferrier and J.P. Oliver, *J. Amer. Chem. Soc.*, **92** (1972) 8371.
- 31 J.R. Cavanaugh and B.P. Dailey, *J. Chem. Phys.*, **34** (1961) 1099.
- 32 L.M. Seitz and T.L. Brown, *J. Amer. Chem. Soc.*, **88** (1966) 2174.
- 33 P. West and R. Waack, *J. Amer. Chem. Soc.*, **89** (1967) 4395.
- 34 L.D. McKeever, R. Waack, M.A. Doran and E.B. Baker, *J. Amer. Chem. Soc.*, **91** (1969) 1057.
- 35 R.E. Lyle, E.J. De Witt and J.C. Pattison, *J. Org. Chem.*, **21** (1956) 61.
- 36 H.C. Clark and R.C. Poller, *Can. J. Chem.*, **48** (1970) 2670.
- 37 J.A.R. Samson, F.F. Zanno and K. Watanabe, *J. Chem. Phys.*, **36** (1962) 783.