molecule in the present case is the long chain molecule and that the vacancy effect is compensated by a maintenance force of surrounding regular canals, or any monomer in the mother liquid immersed in the canals filling the vacancies and participating in the polymerization. It may be supposed that this is one of the reasons why the mole ratios in the monomer–thiourea complex and the polymer–thiourea complex are not in accord. A schematic representation of the polymerization is shown in Figure 6.

It is an interesting subject for future study to correlate the structures of the thiourea complexes with the monomer and the polymer. Structural studies along this line may be able to elucidate characteristics of many stereospecific polymerizations in urea or thiourea canal complexes.

Model Butadiene Polymerizations. I. An Investigation of 2:1 and 1:1 Ratios of *sec*-Butyllithium to Butadiene

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ABSTRACT: The reaction of *sec*-butyllithium with 1,3-butadiene in 1:1 or 2:1 molar ratios produced principally monolithio- and dilithiooctenes along with small amounts of 3,8-dimethyldecane, 3,4,7-trimethylnonane, and butadiene oligomers. Hydrolysis of the product mixture produced the corresponding olefins and alkanes from the lithio compounds. The relative amounts of 1- and 2-olefins produced from the lithiooctene were dependent on hydrolysis conditions. Further reaction of the octenyllithium adduct with *sec*-butyllithium also gave product distributions dependent upon hydrolysis conditions and led to the conclusion that the lithiooctene adduct was an allylic complex (B in Scheme I). The nuclear magnetic resonance spectrum of the monolithiooctenes in cyclohexane and perdeuteriobenzene supported the proposal of an allylic-type complex. The lithio product mixture was also hydrolyzed with D_2O and the deuterium-labeled positions and compounds were identified by glc–mass, infrared, and nuclear magnetic resonance. Dideuteriooctenes were observed which indicated that metallation of the octenyllithium complex occurred.

The steric course of the polymerization of 1,3-butadiene by alkyllithium has been thoroughly studied. The amount of pendant vinyl unsaturation is affected by polar additives, temperature, and concentration of the alkyllithium initiator, but unaffected by the organic moiety of the alkyllithium.[1] The course of the butadiene addition reactions as affected by experimental conditions has been previously determined by characterization of the resulting butadiene polymers or oligomers and necessarily has been related to the polymer or oligomer macrostructure.[2] In the current studies, the emphasis of reaction conditions *vs.* structure is placed upon the resulting microstructure through specific identification of reaction products and sequence distributions in oligomers. The products from a 1:1 and 2:1 molar ratio of *sec*-butyllithium and 1,3-butadiene have been characterized in this manner. The sequence distributions of oligomers formed from 1:2 and 1:3 product ratio are reported in parts II and III of this series.[3,4] By an extensive examination of the initiation, early propagation, and termination reactions of 1,3-butadiene and *sec*-butyllithium, we have obtained information concerning the mechanism of polymerization *vs.* incipient structure.

Experimental Section

The 1:1 and 2:1 reaction of *sec*-butyllithium and 1,3-butadiene were conducted in both polar and nonpolar media and for periods of time that depended upon depletion of the alkyllithium. The lithioolefins that formed precipitated slowly at 25° and quite rapidly at elevated temperatures. *sec*-Butyllithium was used instead of *n*-butyllithium because of a larger rate of initiation with butadiene which would minimize polymer or oligomer formation.[5] After hydrolysis of the product mixtures with water or deuterium oxide, the products were separated by preparative gas chromatography and identified by infrared, nuclear magnetic resonance, and mass spectrometry. A Perkin-Elmer Model 900 with flame ionization detector and a Silicone GE-Versilube F-50 liquid phase 150 ft × 0.01 in. i.d. column was used for the glpc measurements. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer (at 60 MHz). A Perkin-Elmer Model 21 spectrometer was used for the infrared investigations. Mass spectra were obtained on a combination Perkin-Elmer F-11 glpc–cec Model 21-130 mass spectrometer.

Butadiene was Phillips Special Purity dried by vapor phase passage through a 3-ft activated alumina column at 50°. Tetrahydrofuran was Eastman White Label dried at room temperature over 4A molecular sieves and stored under nitrogen. The *sec*-butyllithium was purchased as 1.4 *N* cyclohexane solutions from Foote Mineral. Solvent standards were obtained by hydrolysis of the alkyllithium solutions followed by the same separation and drying procedure used for the various reaction mixtures.

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* To whom correspondence should be addressed.

[1] H. L. Hsieh, *J. Polym. Sci., Part A*, 3, 181 (1965).

[2] H. S. Makowski, M. Lynn, and A. N. Bogard, *J. Macromol. Sci., Chem.*, 2 (4), 665 (1968).

[3] J. C. Randall, F. E. Naylor, and H. L. Hsieh, *Macromolecules*, 3, 497 (1970).

[4] J. C. Randall and R. S. Silas, *ibid.*, 3, 491 (1970).

[5] H. L. Hsieh, *J. Polym. Sci., Part A*, 3, 163 (1965).

A. Reaction of *sec*-Butyllithium with Butadiene at 1:1 Molar Ratio. With minor variations the reactions were conducted (in duplicate) as follows. Dry, nitrogen-filled 7-oz beverage bottles were capped with crown caps over self-sealing gaskets. The *sec*-butyllithium (0.05 mol) was added to each bottle from a calibrated hypodermic syringe. When employed, tetrahydrofuran or triethylamine (0.025 mol) was also added at this point. Butadiene (0.05 mol) at −10° was finally added and the bottles were placed in a 70° constant-temperature water bath and tumbled for 15 min–2 hr. The mixtures were cooled to room temperature. Reaction mixtures, while still in the beverage bottles, were evaporated to dryness without heating, or hydrolyzed with the requisite diluent still present at 25 or 0°. Water was added dropwise from a syringe through a 20-gauge needle during 8 hr to prevent, as much as possible, local overheating. An excess of water was then added to dissolve the lithium salts and form two liquid phases. The water layers were removed and additional water (10 ml) was added. The mixtures were shaken and the water was again removed. The hydrocarbon layer was then transferred to clean bottles and dried over 4A molecular sieves. Accurate yields could not be obtained, but the reactions were assumed to be quantitative since no butane was produced during hydrolysis. The products were resolved into three octenes and two dodecanes by glpc through a Silicone GE-Versilube F-50 column programmed from 70 to 150° at 5°/min. Structure assignments were made on the basis of retention times in comparison with the products from the reaction of *sec*-butyllithium with butadiene at 2:1 molar ratio.

B. Reaction of *sec*-Butyllithium with Butadiene in 2:1 Molar Ratio. Reactions were conducted by the previous procedure. After addition of triethylamine (0.05 mol) or tetrahydrofuran (0.05 mol) to selected bottles, butadiene (0.05 mol) at −10° was added from a calibrated syringe. The bottles were quickly placed in a constant-temperature bath at 70° and tumbled for 2 hr. The reaction mixtures were cooled to room temperature and the products were evaporated to dryness under vacuum. Hydrolysis of solutions or of dry products was accomplished with D_2O or water.

The hydrolysis and work-up were as previously described. Recoveries were about 90% but the reactions were assumed to be quantitative since no unreacted *sec*-butyllithium or butadiene could be detected by glpc. A portion of reaction product was hydrogenated and passed into a glpc unit. Three major peaks were obtained. The products, from boiling point and comparison of retention times of authentic samples, were 3-methylheptane, 3,8-dimethyldecane, and 3,4,7-trimethylnonane. Portions of the products were examined by a glpc–mass spectrometer combination. The methylheptenes in one sample found by various methods are given in Table I. The nuclear magnetic resonance results were calculated by assuming the following three olefins were present: 5-methyl-1-heptene, *trans*-5-methyl-2-heptene, and *cis*-5-methyl-2-heptene. The hydrogen distribution by nuclear magnetic resonance is given in Table II.

The infrared data were derived from measurements of bands at 908, 970, and 700 cm^{-1} and the absence of absorption bands at 890 and 833 cm^{-1}.

C. Reaction of 5-Methylheptenyllithium with *sec*-Butyllithium. Reactions were conducted according to the standard procedure using 0.10 mol of *sec*-butyllithium and 0.10 mol of butadiene. The reaction mixture was then cooled to room temperature. Half of the solution was removed with a calibrated syringe and evaporated to dryness under vacuum. To the remaining half of the solution was added 0.05 mol of 1.6 *N* *sec*-butyllithium in cyclohexane. The bottle was returned to a 70° constant-temperature bath and tumbled for 2 hr after which the reaction mixture was evaporated to dryness under vacuum. Both samples were then hydrolyzed and recovered as before. The products were separated by glpc and identified by comparison of retention times with the products from the reaction of 2 mol of *sec*-butyllithium with 1 mol of butadiene.

TABLE I

Olefin type	Per cent Glpc	 Nmr	 Ir
Terminal	42.5	44	43
trans-Internal	46.0	56	45
cis-Internal	11.5		12

TABLE II

Hydrogen type	Per cent Calcd	 Found
Olefinic	15	15
Allylic to double bond	26	26
CH, CH_2	22	22
CH_3	37	38

TABLE III
REACTION OF *sec*-BUTYLLITHIUM WITH BUTADIENE AT 1:1 MOLAR RATIO

	Weight per cent of product					
	25° hydrolysis					0° hydrolysis
Hydrolysis product	*a*	*b*	*c*	*d*	*e*	*f*
5-Methyl-1-heptene	6	5	7	11	13	13
cis-5-Methyl-2-heptene	32	34	26	30	32	23
trans-5-Methyl-2-heptene	50	42	60	50	54	60
3,8-Dimethyldecane	4	13	2	2	<1	4
3,4,7-Trimethylnonane	9	6	4	2	<1	1
Butadiene oligomer				5		

[a] Cyclohexane reaction solvent removed before hydrolysis. [b] Cyclohexane plus 0.5 mol of tetrahydrofuran reaction solvent removed before hydrolysis. [c] Cyclohexane reaction solvent. [d] Cyclohexane reaction solvent. Tetrahydrofuran (0.5 mol) added before hydrolysis. [e] Cyclohexane plus 0.5 mol of tetrahydrofuran reaction solvent. [f] Cyclohexane reaction solvent.

Results and Discussion

Products from 1:1 Molar Ratio of *sec*-Butyllithium–Butadiene. The principal reaction products from the 1:1 mixture were octenes. The reaction conditions and product distributions after hydrolysis are given in Table III for six product mixtures. The mono addition products were 5-methyl-1-heptene (5–13%) and *cis*- and *trans*-5-methyl-2-heptene (76–86%). The relatively small variations of the product distributions in spite of various reaction conditions which are known to affect polymer macrostructure, *i.e.*, solvent polarity and temperature, suggest that the product distributions are determined primarily by hydrolysis. The identification of C_{12}-alkanes in the olefin mixture indicates that *sec*-butyllithium addition as well as metallation reactions may also occur. Further evidence for metallation products was obtained upon examination of the reaction mixtures after hydrolysis with deuterium oxide.

Products from a 2:1 Molar Ratio of *sec*-Butyllithium–Butadiene. The product distributions for the various C_8's, C_{12}'s and oligomers are given for the 2:1 reaction

TABLE IV
PRODUCTS FORMED BY REACTION OF BUTYLLITHIUM WITH BUTADIENE AT 2:1 MOLAR RATIO IN CYCLOHEXANE

Hydrolysis product	Weight per cent of product —*sec*-Butyllithium— *a*	*b*	*c*
5-Methyl-1-heptene	30	28	22
cis-5-Methyl-2-heptene	14	13	23
trans-5-Methyl-2-heptene	26	25	45
3,8-Dimethyldecane	26	25	4
3,4,7-Trimethylnonane	5	5	7

[a] Cyclohexane solvent only. [b] Triethylamine (0.5 mol) added to reaction. Unidentified products 4%. [c] Tetrahydrofuran (0.5 mol) added to reaction.

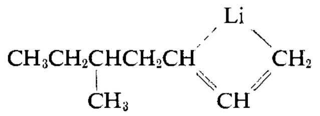
TABLE V
REACTION OF 5-METHYLHEPTENYLLITHIUM WITH *sec*-BUTYLLITHIUM

Hydrolysis product	Weight per cent of product Step one (1:1)	Step two (2:1)
5-Methyl-1-heptene	6	31
cis-5-Methyl-2-heptene	32	8
trans-5-Methyl-2-heptene	50	33
3,8-Dimethyldecane	4	18
3,4,7-Trimethylnonane	9	10

mixture in Tables IV and V. Similar product ratios for the C_8's were obtained for these mixtures also, although the results do not appear as definitive as in the 1:1 case. Hydrolysis conditions could be expected to affect the product distributions; thus it is surprising to find reasonably uniform product distributions in spite of reaction and hydrolysis conditions.

Higher order addition and/or metallation reactions were indicated by a yellow precipitate which formed. Runs A and B gave quite similar results; however, run C differed substantially with less secondary products. A stepwise reaction is reported in Table V; step one is a 1:1 ratio and equivalent to run A in Table I. An additional mole of *sec*-butyllithium was added in step two. Analysis of the product mixture following hydrolysis showed definitively that the product distribution of the octenes had changed without further butadiene addition reactions.

Collectively, the data from the sets of product mixtures indicate that the C_8 product distributions are determined primarily by the mode of termination rather than reaction conditions. A few correlations appear feasible concerning the product distributions and reaction conditions, *e.g.*, the amount of 1-olefin appears to increase with alkyllithium–butadiene ratio; likewise, the secondary reactions apparently increase with alkyllithium–butadiene ratio. However, the principal conclusion is that the incipient configuration of the butadiene unit in the 5-methylheptenyllithium complex is determined only after reactions involving the lithium atom, *i.e.*, addition of butadiene, addition or metallation with *sec*-butyllithium, or hydrolysis with active hydrogen compounds. Such circumstances suggest that the olefin configurations or polybutadiene configurations are the result of a two-step process: (A) addition of butadiene to an alkyllithium or living polymer end unit to form an alkenyllithium complex, and (B) removal of the lithium through further addition or termination reactions which then result in a particular configuration. For *sec*-butyllithium–butadiene adducts, a 5-methylheptenyl complex of an allylic type (A) appears reasonable in which lithium is σ bonded to the 1 position and back-bonded to the number 3 carbon. This, of course, does not preclude subsequent aggregate formation in hydrocarbon solution. Presumably, the 1-olefin and 2-olefin would be produced by hydrolysis at the 3 or 1 position, respectively; likewise, 1,4 or 1,2 addition in the polymer would occur by 1,3-butadiene addition to the 1 or 3 position. Supporting evidence for such an allylic complex was obtained after examination of the nuclear magnetic resonance spectrum of the 1:1 *sec*-butyllithium–butadiene reaction products in perdeuteriobenzene part of which is reproduced in Figure 1,[6] as well as from an investigation of the octene D_2O hydrolysis products.


A

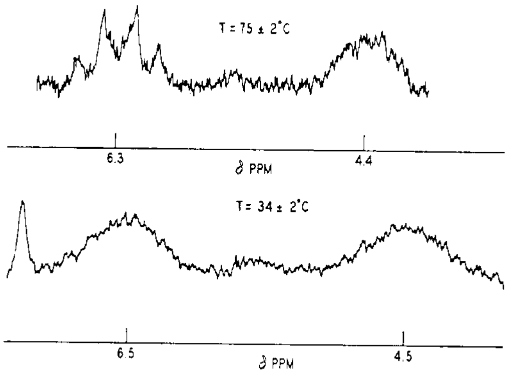


Figure 1. Effect of temperature on olefinic resonance frequencies of octenyl *sec*-butyllithium–butadiene adduct.

To make definitive nuclear magnetic resonance assignments it was necessary to examine a nuclear magnetic resonance spectrum unobscured by overlap with cyclohexane. Inspection of the nuclear magnetic resonance spectrum of a similar product mixture in cyclohexane instead of perdeuteriobenzene showed no differences for those spectral regions that were free of the cyclohexane overlap. Thus, we assumed that the spectrum of the reaction mixture in perdeuteriobenzene was representative of that in cyclohexane. Of particular interest were the downfield multiplets in the nuclear magnetic resonance spectrum at 6.4 and 4.4 ppm. As illustrated in Figure 1, both sharpened upon warming to 60–70°; the 6.4-ppm multiplet resolved into a quartet with a separation of 10–11 Hz and is assigned to the proton in the 2 position. The multiplet at 4.4 ppm is assigned to the proton in the 3 position. The relative intensities of the two multiplets were exactly

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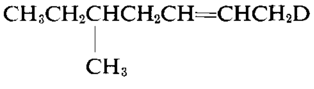
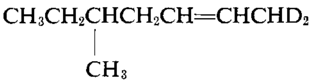
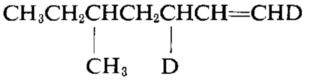
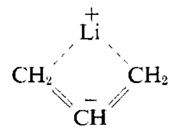
[6] Similar nmr studies have been made at the authors' request by Professor W. H. Glaze and P. Jones at North Texas State University.

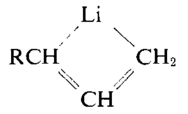
TABLE VI

DEUTERIUM OXIDE HYDROLYSIS PRODUCTS FROM 1:1 AND 2:1 *sec*-BUTYLLITHIUM–BUTADIENE REACTION MIXTURES

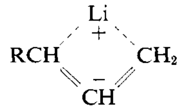
Hydrolysis product	1:1 reaction mixture	2:1 reaction mixture
 $CH_3CH_2\underset{CH_3}{CH}CH_2CH{=}CHCH_2D$	Major *trans* >50% *cis* ~30%	Major − *trans* ~50% *cis* ~5%
 $CH_3CH_2\underset{CH_3}{CH}CH_2CH{=}CHCHD_2$	Minor	Major +
 $CH_3CH_2\underset{CH_3}{CH}CH_2\underset{D}{CH}CH{=}CHD$	Major ~15%	Major ~40%

1:1. A methyl resonance at 0.9 ppm corresponded to approximately eight to nine protons instead of six. The enhancement of the methyl area is best explained by overlap with the resonances from the protons α to the lithium atom. No higher field resonance frequencies were detected above that observed at 0.9 ppm from tetramethylsilane. The nuclear magnetic resonance spectrum of allyllithium reported as an AB_4 system at 37° with chemical shifts at 6.38 and 2.24 ppm, respectively, and $J_{AB} \approx 12$ Hz, provided evidence that allylithium in tetrahydrofuran existed as a delocalized π complex.[7] The upfield shift observed for the 3 proton in the 5-methylheptenyllithium adduct also suggests a delocalized complex. In addition, the nuclear magnetic resonance spectra of allyllithium and the 5-methylheptenyllithium complex showed similar temperature effects[8] and resonance frequencies for the 2-protons. However, the lithium–carbon bonds in the 5-methylheptenyl complex are not equivalent as in allyllithium since the 1 proton is shifted upfield and the 3 proton downfield from the corresponding positions in allyllithium. Thus, the 5-methylheptenyllithium in a nonpolar solvent may be better represented by





rather than a delocalized π complex of the type[9]



The absence of any resonance frequencies at 0.9 ppm above tetramethylsilane, where the 2 proton absorbs in *sec*-butyllithium, indicates that addition occurred to the *sec*-butyllithium moiety in support of either of the above structures. The fact that no resonance frequencies corresponding to the dilithium alkanes were detected is not surprising since the solubility of these compounds in cyclohexane + perdeuteriobenzene is exceedingly poor.

Hydrolysis of the 1:1 and 2:1 *sec*-Butyllithium–Butadiene Reaction Mixtures with D_2O. Further evidence supporting the proposed structure of the 5-methylheptenyllithium complex was obtained from an investigation of the reaction products hydrolyzed with D_2O. Aliquots from the 2:1 and 1:1 mixtures were hydrolyzed separately with D_2O and H_2O and then separated by preparative gas chromatography into samples of *cis*-5-methyl-2-heptene, *trans*-5-methyl-2-heptene, and 5-methyl-1-heptene. The H_2O hydrolysis products provided reference materials for investigations by infrared, nuclear magnetic resonance, and mass spectrometry. In addition, the D_2O hydrolyzed product mixture was examined by glc–mass and the major deuterio derivatives were determined.

1:1 *sec*-Butyllithium–Butadiene Reaction Mixture. Comparison of the nuclear magnetic resonance spectra of the deuterated and nondeuterated heptenes revealed that deuteration occurred at the 1 and 3 positions in 5-methyl-1-heptene but only at the 1 position in both the *cis*- and *trans*-5-methyl-2-heptenes. The glpc–mass investigation indicated that a dideuterio derivative was the major product among the deuterio-5-methyl-1-heptenes and monodeuterio products were predominant among the *cis*- and *trans*-5-methyl-2-heptenes. The relative extents of deuteration as determined by nuclear magnetic resonance for 5-methyl-1-heptene at the 1 and 3 positions were within experimental error of 1:1; thus, the dideuterio-1-heptene must result from either an equimolar mixture of the 1,1- and 3,3-dideuterio derivatives or the 1,3-dideuterio-5-methyl-1-heptene. The absence of a detectable $=CH_2$ wagging vibration at ~910 cm^{-1} in the infrared spectrum indicated that the latter was the case. The products obtained after D_2O hydrolysis of the 1:1 reaction mixture are summarized in Table VI.

2:1 *sec*-Butyllithium–Butadiene Reaction Mixture. The nuclear magnetic resonance spectra of the 2:1 reaction products were similar to those of the 1:1 mixture in that once again deuteration was observed only at the 1 position for the 2-heptenes and at the 1 and 3 positions for the 1-heptenes. Interestingly, extensive dideuteration as well as monodeuteration occurred for the 2-heptenes since parent ions of both *m/e* 113 and 114

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[7] P. West, J. T. Purmont, and S. V. McKinley, *J. Amer. Chem. Soc.*, **90**, 797 (1968).

[8] The olefinic resonance frequencies in alkenyllithium complexes have been generally observed to sharpen upon heating; this effect of temperature has been attributed to changes produced in the conformational averaging process.

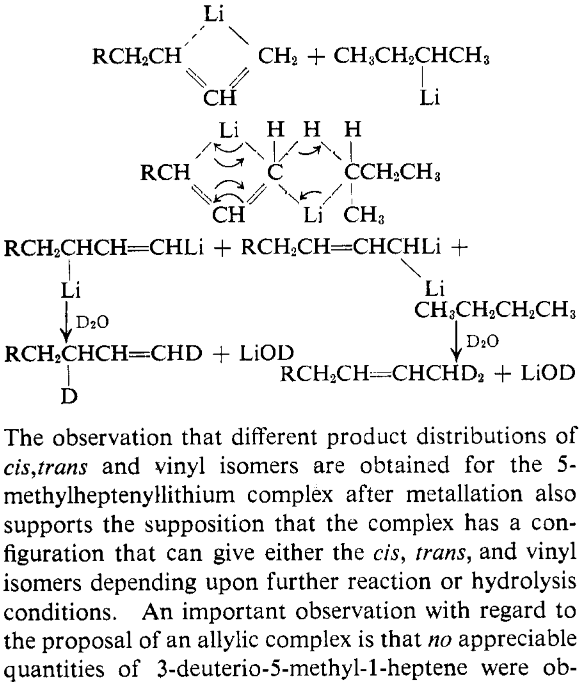
[9] K. F. O'Driscoll, T. Yonezawa, and T. Migashimura, *Div. Polym. Chem., Polym. Prepr., Amer. Chem. Soc.*, **6** (2), 876 (1965); K. F. O'Driscoll and T. Yonezawa, *Rev. Macromol. Chem.*, **1**, 1 (1966).

were observed in the mass spectrum. Since only 1-deuteration was indicated by nuclear magnetic resonance, the dideuterio derivative must have the structure $CH_3CH_2CH(CH_3)CH_2CH{=}CHCD_2H$. Supporting evidence for the above dideuterio derivative was obtained from the infrared spectrum since three CD stretching bands were observed near 2200, 2165, and 2125 cm^{-1}. The 2165-cm^{-1} band has been previously assigned to a CD stretching vibration in $-CH_2D$ units.[10]

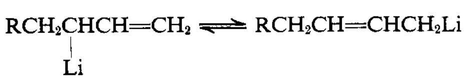
The 2200- and 2125-cm^{-1} bands are probably the asymmetrical and symmetrical CD stretching frequencies, respectively, of the $-CD_2H$ unit. Only a low percentage (estimated at ~7% by mass spectrometry) of the dideuterio-*trans*-5-methyl-2-heptene was observed in the 1:1 reaction mixture. The infrared spectrum gave, in this instance, an intense band at 2165 cm^{-1} with weak shoulders near 2200 and 2125 cm^{-1} in accord with the above assignment. The D_2O hydrolysis products from the 2:1 reaction mixture are also summarized in Table VI.

The presence of dideuterio derivatives among the octenyllithium hydrolysis products suggests that metallation has occurred prior to hydrolysis. In particular, the absence of other than trace amounts of any monodeuterio derivatives among the 5-methyl-1-heptenes may indicate that metallation is the major route for production of the 1-heptenes under these reaction conditions. A mechanism which could account for the observed dideuterio derivatives is given in Scheme I.

SCHEME I



The observation that different product distributions of *cis,trans* and vinyl isomers are obtained for the 5-methylheptenyllithium complex after metallation also supports the supposition that the complex has a configuration that can give either the *cis*, *trans*, and vinyl isomers depending upon further reaction or hydrolysis conditions. An important observation with regard to the proposal of an allylic complex is that *no* appreciable quantities of 3-deuterio-5-methyl-1-heptene were obtained which suggests that the 1-olefins obtained after hydrolysis did not result from tautomers

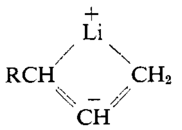


$$RCH_2\underset{\displaystyle Li}{CH}CH{=}CH_2 \rightleftharpoons RCH_2CH{=}CHCH_2Li$$

Hydrolysis of the monolithio derivatives under the conditions investigated thus give predominantly the 1,4-product as would be expected with the proposed complex.

Summary and Conclusion

An increase in vinyl or 1,2-butadiene addition units in polybutadine as a result of a more polar reaction medium has often been observed. The results from this investigation indicate that the lithium atom is bonded in the 1 position in the butadiene-*sec*-butyllithium adducts with association occurring at the 3 position in nonpolar solvent. An increase in polarity as a result of *sec*-butyllithium concentration does little to change this with the vinyl products resulting predominantly from subsequent metallation reactions. The presence of tetrahydrofuran in the reaction mixture may result in quite a different reaction mechanism. Polarization may be affected in the complex to the extent that a substantial lithium carbon bond is formed at the 3 position that may approach the delocalized π complex



Again, we emphasize the proposed structure does not preclude aggregation in hydrocarbon solvents. Support for such a charge delocation in the presence of tetrahydrofuran may be found in a comparison of the 3 proton resonance frequencies with and without tetrahydrofuran. A higher field resonance frequency was observed for the 3 proton in phenylallyllithium in perdeuteriotetrahydrofuran than in the *sec*-butyllithium adduct in perdeuteriobenzene.[11] A solvent effect does not offer a likely explanation for the differences since the 2 proton gave similar resonance frequencies in both solvents. Also, the 3 proton resonance frequencies were observed to shift upfield in the present study when tetrahydrofuran was added to the solvent system. An exact resonance frequency was not obtained since the position was obscured by overlap. The existence of a 5-methylheptenyllithium complex of the type described in this study can be readily extended to butyllithium initiated living polymers which will be more fully discussed in paper III of this series. Presumably, 1,4 or 1,2 addition in polybutadiene would occur by addition of butadiene to either the 1 or 3 positions. Interestingly, 2,1 addition would be precluded.

Acknowledgment. The authors wish to acknowledge the assistance of Dr. R. S. Silas and R. P. Zelinski for guidance and many useful discussions and Messrs. W. J. Hines and J. A. Favre for glc and mass spectral analyses.

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(10) C. Y. Liang, M. R. Lytton, and C. J. Boone, *J. Polym. Sci.*, **47**, 140 (1960).

(11) V. T. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968).