Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

3-NEOPENTYLALLYLLITHIUM

I. THE 1,4-ADDITION PRODUCT OF TERT-BUTYLLITHIUM AND 1,3-BUTADIENE*

WILLIAM H. GLAZE**, JOHN E. HANICAK, MICHAEL L. MOORE and J. CHAUDHURI
Department of Chemistry, North Texas State University, Denton, Texas 76203 (*U.S.A.*)

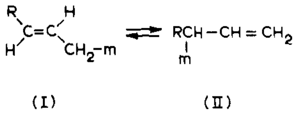
(Received March 31st, 1972)

SUMMARY

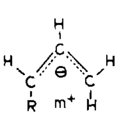
tert-Butyllithium and 1,3-butadiene react in hydrocarbon solvents in 1/1 molar ratio to yield *cis*- and *trans*-neopentylallyllithium (NpALi). Proton NMR data indicate that the ratio of *trans* to *cis* isomers of NpALi [(IVa)/(IVb)] is approximately 3/1 under the conditions used, and that the isomers do not equilibrate up to 70°. No evidence for the secondary isomer 1-NpALi (V) is observed. The upfield chemical shift of the 3-proton in NpALi is interpreted in terms of partial delocalization of charge within the allyl system, and is consistent with IR and UV absorption data.

INTRODUCTION

Several recent studies have focused on the nature of allyl derivatives of the non-transition metals and the mechanisms of their reactions. These reagents may exist as localized forms of the primary or secondary type [(I) and (II)] or as delocalized carbanion-cation pairs(III).



(I) (II)



(III)

Allylic magnesium systems have been studied quite extensively and, with few exceptions[1], workers in this area seem to regard these substances as mixtures of types (I) and (II) in rapid equilibrium[2], at least in ether solvents***. The precise composition of the allyl Grignard reagent probably depends on the nature of the substituent R,

---

* Portions of this work were reported at the Symposium on the Coordination and Organometallic Chemistry of the Alkali Metals, 161st National Meeting, American Chemical Society, Los Angeles, Calif. (1971).

** To whom inquiries should be addressed.

*** Our work on bis(neopentylallyl)magnesium in hydrocarbon solvents will be reported shortly.

the solvent, and the temperature. With R=CH_3 and m=MgBr, greater than 99% of the species are estimated to have structure (I)[2a]. Examples of σ-allyl→dynamic allyl transformations have been reported for aluminum[3], zinc[1,4,5], and boron[6] compounds.

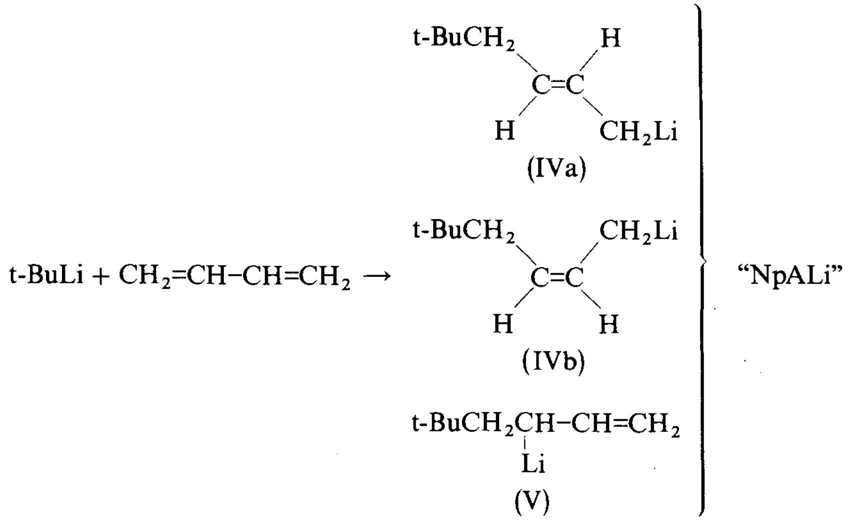
Allyllithium in diethyl ether and THF[7], allylsodium in the solid state[8], phenylallyllithium[9], and 1,3-diphenylallyllithium[10] have been characterized as ionic. The degree of intimacy of the cation and the allyl anion varies considerably from one system to another as evidenced by variations in the optical and magnetic resonance spectra[11].

Alkyl-substituted allyllithiums represent a very important sub-class of these reagents since they are often soluble in hydrocarbon solvents and therein play an active role in the polymerization of dienes[12]. Bywater, Schué, and coworkers have examined the adducts of isoprene and sec- or tert-butyllithium[13]. Similarly, our group[14] and two others[15,16] have reported some evidence relating to the structure of similar adducts with butadiene. Seyferth and Jula[17], and more recently, a Russian group[18], have published some structural information concerning 2-butenyllithium in basic solvents. Nonetheless, the description of alkyl-substituted allyllithiums, particularly in hydrocarbon solvents is still incomplete, and there is no apparent agreement regarding interconversions between the various isomeric forms.

The present paper is the first of several in which we hope to describe alkyl-substituted allyl metals of this type in some detail, and also to examine some of their important and interesting chemistry.

RESULTS AND DISCUSSION

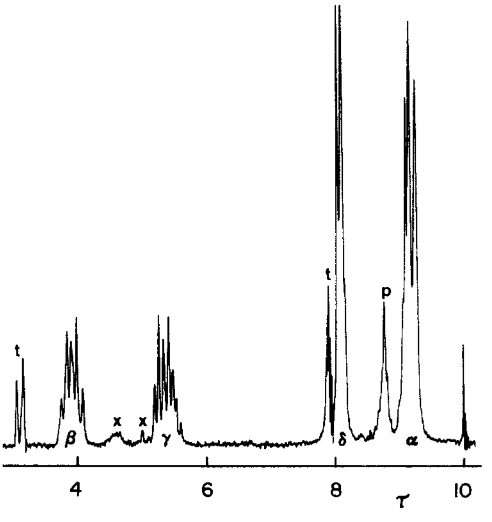
Neopentylallyllithium (NpALi) may be conveniently prepared by the addition of tert-butyllithium to 1,3-butadiene in any hydrocarbon solvent. The reaction proceeds in high yield (~95%) at 20° in approximately 20 min and is moderately exothermic. In order to prevent formation of higher molecular weight addition products, the ratio of tert-butyllithium to the diene should be no less than unity. In this work we generally employ a ten percent excess of the lithium alkyl. This method has



been utilized by other workers to prepare adducts of very reactive alkyllithiums with butadiene[16] and isoprene[13]. However, the method is not general, as indicated by our failure to prevent the oligomerization of 1,3-cyclohexadiene and 2,4-hexadiene using the conditions described above. Higher addition products were also observed using isoprene and a less reactive alkyllithium (n-butyllithium)[13].

NpALi is moderately soluble in hydrocarbon solvents, and its solutions remain clear for several hours at room temperature if kept in an inert atmosphere. In the presence of excess tert-butyllithium, however, a yellow tinted solid precipitates from these solutions on long standing*. NpALi reacts with ether solvents, presumably cleaving the ether in the usual fashion[19]. The solutions are sufficiently stable to be handled below room temperature for brief periods, however.

The 100 MHz proton NMR spectrum of NpALi (prepared from tert-butyllithium-d_9) in toluene-d_8 is shown in Fig. 1. The spectrum consists of two one-proton multiplets centered near τ 4 and 5.5, and two two-proton doublets at τ 8.1 and 9.2. Closer inspection shows that the low field multiplets are unsymmetrical (Fig. 2b) and that the two high field doublets also show structure which cannot be attributed to residual solvent or tert-butyl protons. After a careful analysis, including spin decoupling experiments, we have concluded that the spectrum is that of a mixture of *trans*-



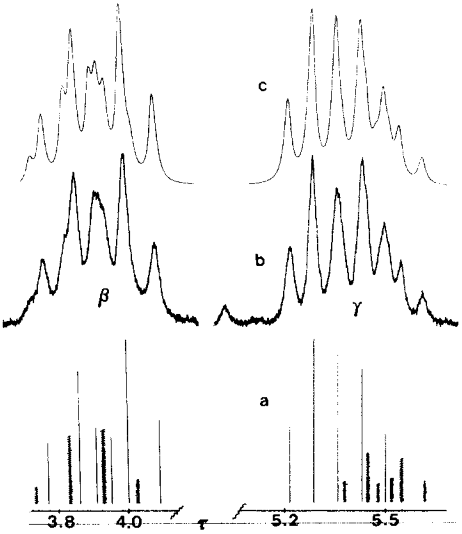


Fig. 1. 100 MHz PMR spectrum of NpALi prepared from 1,3-butadiene and tert-butyllithium-d_9; toluene-d_8 solvent, 30°. p = residual pentane protons; t = residual toluene protons; x = 2/1 adduct. See Table 1 for assignments of α, β, γ and δ protons.

Fig. 2. Observed and calculated 100 MHz spectra of β and γ proton regions of NpALi; toluene-d_8 solvent, 30°. (a) Line spectrum calculated from parameters shown in Table 1; 3/1 ratio of *trans*/*cis* transitions. (b) Observed spectrum. (c) Same as (a) but with Lorentz line shape added, 2.5 Hz line width.

---

* The yellow precipitate is soluble in ether solvents and yields two $C_8H_{14}D_2$ olefins upon reaction with deuterium oxide. The olefins were identified as *trans*-5,5-dimethyl-2-hexene and 5,5-dimethyl-1-hexene. The positions of the deuterium labels are unknown[16a].

TABLE 1

$(CD_3)_3C\overset{\delta}{C}H_2\overset{\gamma}{C}H{=}\overset{\beta}{C}H\overset{\alpha}{C}H_2Li$

100 MHz PMR PARAMETERS FOR 3-NEOPENTYLALLYLLITHIUM

Temp.: 30° ; solvent: toluene; reference: TMS.

Isomer	τ_α	τ_β	τ_γ	τ_δ	$J_{\alpha\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
Trans	9.225	3.941	5.363	8.065	9.4	14.5	7.0
Cis	9.199	3.888	5.505	8.114	10.0	10.0	6.9

and *cis*-3-NpALi [(IVa) and (IVb)]. The assignments of the chemical shifts and coupling constants for both species are shown in Table 1.

In order to test this hypothesis, we have synthesized the spectrum of the individual isomers using LAOCOON III[20]. The predicted transitions for (IVa) and (IVb) were mixed with an appropriate factor added to weight the intensities of the transitions due to the predominant isomer. The resulting lines were plotted and the line spectrum compared with the experimental spectrum. It was concluded that a 3/1 ratio of (IVa)/(IVb) represented the best fit of the data*. The observed and calculated lines were then matched and the least squares analysis of LAOCOON III was performed on the individual isomers. The final parameters are those shown in Table 1. The transition frequencies for the two isomers were again mixed with the proper weighting factor and the results plotted in the form of a line spectrum (Fig. 2a). The shaded lines in this figure illustrate transitions due to the *cis* isomer [(IVb)]. In order to dramatize the agreement between calculated and experimental spectra, a Lorentzian line shape was added to the computer calculated transitions. With a line width of 2.5 Hz, the resulting spectrum, shown in Fig. 2c, is very similar to the observed spectrum (Fig. 2b).

We therefore conclude that NpALi, as prepared here, consists of a mixture of (IVa) and (IVb) which *do not interconvert on the NMR time scale.* It is possible, of course, that *cis–trans* isomerization may occur at an appreciable rate on the laboratory time scale; however, except in the fortuitous case where the enthalpies of the isomers are identical, this would lead to a changing *cis/trans* ratio as the temperature of the sample is varied. *No such change is seen over the range from* −70° *to* +70°. The transitions at τ 5.223 and 5.625 due to the *trans* and *cis* isomers respectively are particularly useful in monitoring the ratio of the isomers, and no change in the relative intensities of these peaks is observed over the full temperature range studied**. Moreover, the chemical shifts of the various protons do not vary more than 2 Hz over the same temperature range.

The same data also speak against the occurrence of the secondary form 1-NpALi(V), which various authors have postulated for similar systems in ether

---

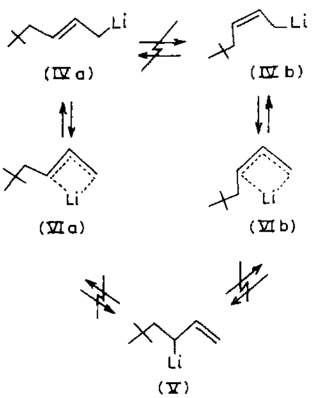
* The precise isomer ratio may not be determined by this method since the real line width is unknown and may vary for the two isomers. However, the ratio appears to be near 3/1 as indicated in Fig. 2. Reaction of NpALi solutions in hydrocarbon solvents with ethanol gives 5,5-dimethyl-1-hexene (2%), *trans*- and *cis*-5,5-dimethyl-2-hexene (75% and 23%) (for further details, *cf.* following paper).

** Bywater *et al.* also observed no change in the isomer ratio of the isoprene adduct over a similar temperature range[13].

solvents[17,18]. Again, we would expect that the existence of (V) for more than a rotational lifetime would result in *cis–trans* isomerization[2b]. The absence of isomerization either indicates that (V) is not a species to be considered, or as mentioned earlier, that the enthalpy difference between (IVa) and (IVb) is negligible. We are more inclined to accept the first alternative.

The unusual character of the bonding in NpALi is reflected in some of the parameters shown in Table 1. The most striking is the large upfield shift of the γ-proton (τ 5.5). On the surface, this would seem to indicate an unusually high charge density at this position and therefore to indicate some degree of delocalization of charge from the α-position to the γ-position. However, the effect is not as pronounced as that observed in ether solvents. For example. NpALi in diethyl ether and THF shows γ-proton resonances near τ 5.9 and 6.4 respectively[21]. In the isoprene adduct of tert-butyllithium[13], the τ value of the corresponding proton is approximately 6.5 in THF.

The upfield shift of the γ-proton is paralleled by a corresponding *downfield* shift of the α-protons from their expected position[*]. Both of these effects may be attributed to "partial delocalization" of charge within (IVa) and (IVb). Alternately, we may postulate a rapid equilibrium between these covalent forms and some ionic species, ***provided no cis–trans isomerization is allowed.*** However it seems very unlikely that quantities of the ionic forms (VIa) and (VIb) sufficient to cause the observed shifts are present in hydrocarbon solutions.



The IR spectrum of NpALi in benzene shows a band of medium strength at 1594 cm^{-1} with a shoulder at 1574 cm^{-1}. In cyclohexane the shape of the band is nearly the same as in benzene, the values of the maxima being 1597 cm^{-1} and 1579 cm^{-1} respectively. IR data of this type have been interpreted in terms of decreased C=C bond order[2d,7]. The values for NpALi are somewhat higher than that for 2-butenyllithium in ether[17] (1540 cm^{-1}), but are substantially lower than that reported for (2-butenyl)trimethyltin[23] (1670 and 1658 cm^{-1} for *trans* and *cis* forms). The frequency difference between the main absorption and the shoulder in the spectrum of NpALi,

---

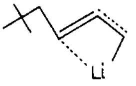
[*] One can estimate from the spectrum of ethyllithium in benzene (τ 10.75) and from the shielding constant of the C=C group[22], that the α-protons in NpALi should occur at approximately τ 9.9. The observed value shown in Table 1 is approximately 70 Hz downfield from this value.

combined with PMR results suggests that these two bands may be attributed to the *trans* and *cis* forms [(IVa) and (IVb)] respectively[23].

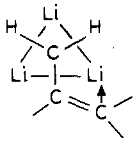
The UV spectrum of NpALi in n-pentane shows in addition to strong absorption near 210 nm, a broad band at 270 nm ($\varepsilon = 1 \times 10^4$ mol^{-1} cm^{-1}) which may be attributed to the allyllithium system. Although the band is observed at shorter wavelengths than the corresponding band in allyllithium in THF (310–320 nm)[7], the transition is markedly red shifted in comparison to $\pi \rightarrow \pi^*$ transitions in isolated carbon–carbon double bonds[22].

Clearly then, some perturbation of the C=C system is evident from the various spectra of NpALi, even in hydrocarbon solvents. The upfield shift of the γ-proton, the corresponding downfield shift of the α-protons, the UV and the IR data all indicate some type of π-component in the α–β bond. We may simply refer to this effect as "σ–π conjugation", and represent the structure of NpALi as shown in (VII)[16]. Similar effects have also been noted for allylic derivatives of several metals[1–7,13–16], and the magnitude of the spectral shifts are roughly proportional to the electropositivity of the metal. In the case of allylic lithium compounds, however, we feel that the structures such as (VII) omit an essential feature, namely, the geometry of the electron deficient aggregate. Molecular models indicate that interaction of the γ-carbon atom with the lithium atom would be very weak in a monomeric species such as (VII). On the other hand, in a dimer or tetramer the distance between the γ-carbon atom and a lithium atom is substantially decreased.

For example, in the tetramer of NpALi, shown in one perspective in (VIII), the vacant lithium orbitals may be properly disposed so that charge transfer from the γ-position can take place as shown. Thus, the aggregate structure contains a mechanism for the stabilization of negative charge density at the gamma position which is not available to other metal allyls. The observation that 3-butenyllithium shows spectral perturbations[24] even in the absence of π-delocalization, is evidence for the type of structure shown in (VIII).



VII



(VIII)

To obtain some evidence in favor of aggregation, we have carried out cryoscopic molecular weight measurements on NpALi solutions in benzene. Unfortunately, our method of preparation makes it extremely difficult to obtain NpALi solutions free of tert-butyllithium. The data shown in Table 2 refer to solutions in which the ratio of NpALi/t-BuLi was approximately 9/1. Notwithstanding this difficulty, it is clear that NpALi exists in benzene as some form of aggregate. The apparent change in the degree of aggregation over the concentration range studied may be due to the presence of mixed tert-butyllithium aggregates of various types. More likely, the effect is due to increased dissociation of the higher aggregates, probably tetramers, into lower aggregates, probably dimers, as the concentration decreases[25]. It should be noted that Morton and coworkers obtained a degree of aggregation of two for polyisoprenyllithium and polybutadienyllithium[26]. In each of these two cases, however,

TABLE 2

ASSOCIATION OF NpALi IN BENZENE

Molality (RLi)	$\Delta T/K_f$	*i*	*Run. No.*
0.330	0.0891	3.70	1
0.272	0.0836	3.25	2
0.246	0.0782	3.15	1
0.163	0.0565	2.88	1
0.115	0.0470	2.45	2
0.0928	0.0412	2.25	2
0.0495	0.0231	2.14	2

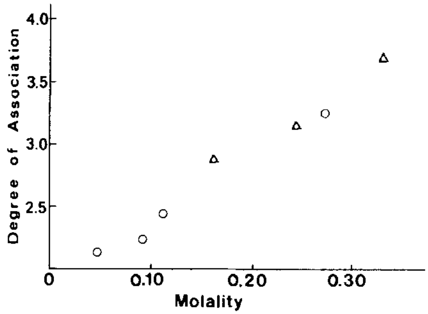


Fig. 3. Degree of aggregation of NpALi in benzene determined from freezing point depression measurements. △ Run number one; ○ run number two.

the actual concentration of the lithium compound was lower than the range shown in Table 2, and only lower aggregates (dimers) would be expected.

The data in Table 2, combined with Morton's work[26], is confirming evidence that the degree of association of "living" polydienyllithium compounds changes as the degree of polymerization (*DP*) increases. Makowski and coworkers[27,28] first reported evidence to this effect and suggested that the dependence of polymer stereochemistry on *DP* was related to the changing states of aggregation. Bywater and coworkers[13] observed that *cis–trans* isomerization of polyisoprenyllithium, though absent in the unit with *DP* 1.2, occurred rapidly on the laboratory time scale in polymers with higher *DP* values. It is conceivable that such isomerizations proceed only through dissociation to the monomeric unit, and that this is a more favorable process when oligomers with high *DP* values are involved. Perhaps the most important deduction to be drawn from this reasoning is that the stereochemical course of allyllithium reactions may depend on the aggregation of the reactive species[29,30].

In summary, the present data indicate that NpALi consists of the primary forms [(IVa) and (IV)] with no evidence found to support the existence of the secondary form [(V)]. Exchange between various aggregates, probably dimers and tetramers, but possibly monomers occurs without isomerization of (IVa) and (IVb). The existence of minute quantities of ionic forms such as (VIa) and (VIb) cannot be excluded, although it is safe to say that these species are not thermodynamically important.

In the subsequent paper we will examine some typical reactions of NpALi with particular attention to the conditions which lead to allylic rearrangement.

EXPERIMENTAL SECTION

Materials

n-Pentane (Phillips Pure Grade) was shaken repeatedly with sulfuric acid and distilled. Final distillation from a sodium mirror was carried out on a vacuum line immediately prior to use. Benzene (Phillips Pure Grade) was first distilled from $LiAlH_4$ and then from a sodium mirror. Deuterated solvents (Stohler Isotope Chemicals) were distilled from sodium mirrors into break-seal ampoules and stored in a freezer prior to use. Butadiene (Phillips Special Purity Grade) was treated similarly. tert-Butyllithium (Foote Mineral) was resublimed on the vacuum line and stored in n-pentane in break-seal ampoules. Analysis[31] of solutions showed that the percentage of non-carbon-bound lithium was generally less than 5%. tert-Butyllithium-d_9 was prepared from tert-butyl chloride-d_9 (Merck Sharp and Dohme, Canada) and lithium metal in n-pentane on the vacuum line. The product was resublimed and stored in n-pentane as described above.

Preparation of NpALi

Butadiene was measured volumetrically as the gas into a break-seal ampoule. This ampoule was attached to the apparatus shown in Fig. 4 along with ampoules containing a measured amount of tert-butyllithium (typical amount of 1 mmole in 10 ml of n-pentane), one containing 0.5–1.0 ml of deuterated NMR solvent, and one with tetramethylsilane. After evacuating the apparatus and leak testing at $< 10^{-4}$ mmHg pressure, it was sealed off at point a. The ampoule containing the tert-butyllithium solution was broken with a hammer and the contents transferred to the reservoir. The butadiene ampoule was then broken and the contents condensed onto the tert-butyllithium with a liquid nitrogen bath. The mixture was then allowed to warm to room temperature for approximately 30 min after which the reaction was complete. The pentane then was transferred into the trap cooled with liquid nitrogen, leaving

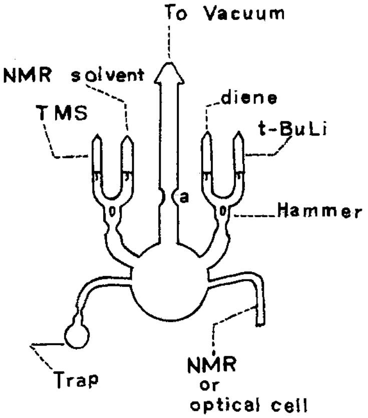


Fig. 4. Apparatus used for preparation of NpALi.

NpALi as white crystals in the reservoir. The trap then was sealed off with a torch. Deuterated solvent (or non-deuterated solvent for UV work) was then transferred from a break-seal ampoule to the reservoir and the resulting solution of NpALi was transferred to the NMR tube (or UV cell) by tilting the entire apparatus. The NMR cell then was sealed off, or in case of UV measurements, the entire apparatus was taken to the spectrometer. A special optical Dewar was constructed to allow UV measurements below room temperature, but the spectrum of NpALi showed no temperature dependence.

Spectral measurements

Spectral measurements were carried out on JEOLCO Model PS-100 and MH-60-II NMR spectrometers and a Cary Model 14 UV spectrophotometer. Temperature control of the PS-100 variable temperature accessory is at least ±2°. IR measurements were made on a Perkin–Elmer Model 621 spectrophotometer. Cesium iodide fixed-thickness cells were loaded with NpALi solutions in a dry box whose atmosphere was continually purified by circulation through beds of Molecular Sieve and Dow Q Catalyst. The cells were transferred to the nitrogen-flushed spectrometer in desiccators and were exposed to the atmosphere for only a few seconds in transit.

Molecular weight measurements

Mol. wt. determinations were carried out in the dry box described above. Solutions of NpALi in benzene were transferred to the box in a glass apparatus directly from the vacuum line where they were prepared. The apparatus was fitted with a rubber septum so that aliquots could be removed with a gas-tight syringe. Freezing point measurements were made in a closed vessel cooled in a brass block which itself was cooled by chilled glycol-water solution circulated through the block from an external temperature regulated bath. Cooling curves were measured with a thermistor thermometer in conjunction with a simple bridge circuit. The bridge unbalance was measured continuously with a potentiometric recorder. The thermistor was previously calibrated with a Beckmann thermometer and was reproducible to ±0.001°. Freezing points of NpALi solutions were made alternately with pure benzene from the same batch used to prepared the NpALi solution. Reproducibility of freezing points was at least ±0.006°. The data in Table 2 refer to two runs on two different batches of NpALi wherein the amount of 1/2 addition product ($C_{12}H_{21}Li$) was shown to be present in less than 5% of the amount of NpALi.

ACKNOWLEDGEMENTS

We are grateful to the Robert A. Welch Foundation and the N.T.S.U. Faculty Research Fund for generous support of this work.

REFERENCES

1 P. West and M. C. Woodville, *Progress in Organometallic Chemistry, Proceedings of the Fourth International Conference on Organometallic Chemistry*, C15 (1969).

2 (a) J. E. Nordlander, W. G. Young and J. D. Roberts, *J. Amer. Chem. Soc.*, 83 (1961) 494;
(b) G. M. Whitesides, J. E. Nordlander and J. D. Roberts, *J. Amer. Chem. Soc.*, 84 (1962) 2010;

(c) G. M. Whitesides, J. E. Nordlander and J. D. Roberts, *Discussions Faraday Soc.*, 34 (1962) 185;
(d) H. E. Zieger and J. D. Roberts, *J. Org. Chem.*, 34 (1969) 1976;
(e) M. Gaudemar, *Bull. Soc. Chim. Fr.*, (1958) 1475;
(f) C. Prevost, M. Gaudemar, L. Miginiac, F. Bardone–Gaudemar and M. Andrac, *Bull. Soc. Chim. Fr.*, (1959) 679;
(g) C. Prevost and B. Grosse, *C.R. Acad. Sci., Paris*, 252 (1961) 1023.

3 H. Lehmkuhl and D. Reinehr, *J. Organometal. Chem.*, 23 (1970) C25.

4 G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 5 (1966) 161.

5 K. H. Thiele and P. Zdunneck, *J. Organometal. Chem.*, 4 (1965) 10.

6 B. M. Mikhailov, G. Yu. Pek, V. S. Bogdanov and V. F. Pozdner, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 1117.

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

8 E. J. Lanpher, *J. Amer. Chem. Soc.*, 79 (1957) 5578.

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

10 H. H. Freedman, V. R. Sandel and B. P. Thill, *J. Amer. Chem. Soc.*, 89 (1967) 1762.

11 (a) J. W. Burley and R. N. Young, *J. Chem. Soc. B*, (1971) 1018; *J. Chem. Soc. D*, (1969) 1127;
(b) J. W. Burley, R. Ife and R. N. Young, *J. Chem. Soc. D*, (1970) 1256.

12 L. E. Forman, in J. P. Kennedy and E. Tornqvist (Eds.), *Polymer Chemistry of Synthetic Elastomers*, Interscience, N.Y., 1969, Ch. 6.

13 F. Schue', D. J. Worsfold and S. Bywater, *J. Polym. Sci., Part B*, 7 (1969) 821; *Bull. Soc. Chim. Fr.*, (1970) 271; *Macromolecules*, 3 (1970) 509.

14 W. H. Glaze and P. C. Jones, *J. Chem. Soc., D*, (1969) 1434.

15 M. Morton, R. D. Sanderson and R. Sakata, *Polymer Letters*, 9 (1971) 61.

16 F. E. Naylor, H. L. Hsieh and J. C. Randall, *Macromolecules*, 3 (1970) 486; J. C. Randall and R. S. Silas, *Macromolecules*, 3 (1970) 491; J. C. Randall, F. E. Naylor and H. L. Hsieh, *Macromolecules*, 3 (1970) 4970.

17 D. Seyferth and T. F. Jula, *J. Organometal. Chem.*, 8 (1967) P13.

18 E. R. Dolinskaya, I. Y. Poddubnyi and I. U. Tserteli, *Dokl. Akad. Nauk SSSR*, 191 (1970) 862.

19 (a) K. Ziegler and H. Gellert, *Justus Liebigs Ann. Chem.*, 567 (1950) 185;
(b) H. Gilman, A. H. Haubein and H. Hartzfield, *J. Org. Chem.*, 19 (1954) 103;
(c) H. Gilman and B. J. Gah, *J. Org. Chem.*, 22 (1957) 1165.

20 S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41 (1964) 3863.

21 W. H. Glaze, J. E. Hanicak, D. J. Berry and D. P. Duncan, *J. Organometal. Chem.*, 44 (1972) 49.

22 R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, Wiley, N.Y., 1969, 2nd. ed.

23 H. G. Kuvila and J. A. Verdone, *Tetrahedron Lett.*, (1964) 119.

24 J. P. Oliver, J. B. Smart and M. T. Everson, *J. Amer. Chem. Soc.*, 88 (1966) 4101.

25 H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 92 (1970) 4664.

26 M. Morton, L. J. Fetters, R. A. Pett and J. F. Meier, *Macromolecules*, 3 (1970) 327.

27 H. S. Makowski and M. Lynn, *J. Macromol. Chem.*, 1 (1966) 443.

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

29 W. H. Glaze, J. Lin and E. G. Felton, *J. Org. Chem.*, 30 (1966) 248.

30 W. H. Glaze and C. H. Freeman, *J. Amer. Chem. Soc.*, 91 (1969) 7198.

31 H. Gilman and F. K. Cartledge, *J. Organometal Chem.*, 2 (1964) 447.