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NEOPENTYLALLYLLITHIUM

III. EFFECTS OF ETHER SOLVENTS ON PMR AND UV SPECTRA

WILLIAM H. GLAZE*, JOHN E. HANICAK, J. CHAUDHURI, MICHAEL L. MOORE and DON P. DUNCAN

Department of Chemistry, North Texas State University, Denton, Texas 76203 (U.S.A.)

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SUMMARY

Neopentylallyllithium (NpALi), the 1,4-addition product of t-butyllithium and 1,3-butadiene, has been studied by PMR and UV methods in several ether solvents. The spectral results indicate that NpALi is more completely delocalized than in hydrocarbon solvents. *Cis–trans* isomerization occurs slowly in THF on the PMR time scale up to 30°, but is rapid on the laboratory time scale. In diethyl ether, isomerization is considerably slower. No difference in the UV absorption maximum in THF, DME, and triglyme is observed, indicating either that the same form of ion pairs are present in these solvents, or that the absorption maxima for various forms are not significantly different. An anomalously high λ_{max} value in ether is also reported.

In previous papers of this series, we have described the preparation and properties of 3-neopentylallyllithium (NpALi), which may be prepared conveniently by the addition of t-butyllithium to 1,3-butadiene in a non-donor solvent[1,2].

(I) (II) (III)

In aromatic and aliphatic solvents, NpALi apparently exists as aggregated, σ-bonded forms (I) and (II). The fact that we observed no *cis-trans* isomerization was taken to indicate the absence of a dynamic equilibrium involving species (III). These results are in agreement with similar work on the isoprene adduct by Bywater, Schué and Worsfold[3,4], and with the work of Morton and coworkers[5].

We now report more data on the effect of ethers on the spectra of NpALi. In the subsequent paper, we will contrast the chemical behavior of NpALi in different solvent systems.

Donating solvents such as diethyl ether, THF, and the glymes would be expected to coordinate strongly with the lithium ion, and thereby to facilitate the transfer of

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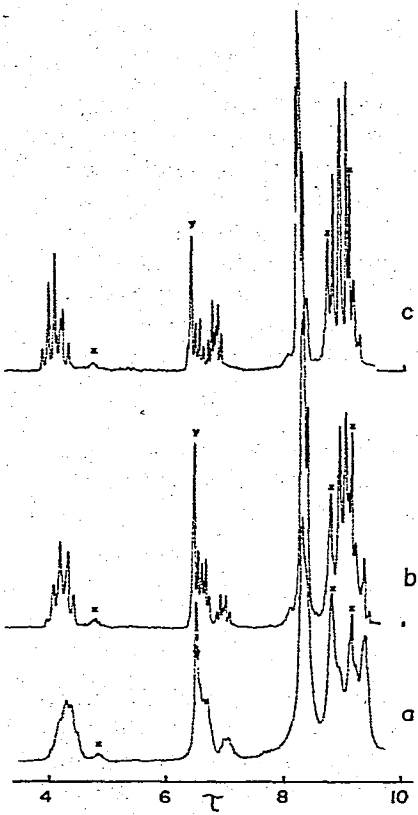
* To whom correspondence should be addressed.

charge density to the organic portion of NpALi. This increase in charge would be expected to concentrate on the γ and α carbon atoms[6], and to cause several spectral perturbations. A red shift of the $\pi \rightarrow \pi^*$ transition from its position in hydrocarbon solvents (270 nm)[1] would be expected*. The shift would probably be more pronounced the greater the separation of cation and carbanion, at least if other cation–carbanion pairs can be used as guides[7–10]. The decrease in β–γ bond order and concomitant increase in α–β bond order would be expected to decrease the so-called C=C stretching vibration from its value of 1595 cm^{-1} in hydrocarbon solvents[1,11]. Finally, the increase in charge density at the γ-carbon atom, combined with the change in bond order, would be expected to result in upfield and downfield shifts of the γ and α proton resonances respectively.

The results which are reported here largely confirm these expectations.



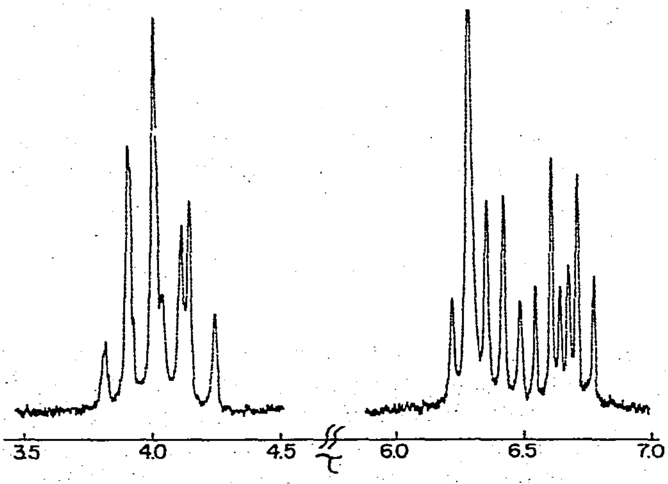


Fig. 1. 100 MHz PMR spectrum of NpALi in THF-d_8. a. −78° ; b. −45° (both before isomerization at 0°); c. −18° (after isomerization). x=$C_{12}H_{21}Li$ (diadduct of butadiene and t-BuLi); y=residual THF α-protons; z=residual pentane.

Fig. 2. 100 MHz PMR spectrum of β-γ region in THF-d_8· −4°C. (See Table 1 for chemical shifts and coupling constants.)

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* The transition may not necessarily be identified with a $\pi \rightarrow \pi^*$ transition. A σ(C–Li)$\rightarrow \pi^*$ designation may be more appropriate, particularly in non-donor solvents[7].

RESULTS AND DISCUSSION

PMR results in THF. NpALi was prepared from t-C_4D_9Li using greaseless vacuum-line techniques[1]. After removal of the pentane solvent, addition of THF-d_8 was carried out keeping the sample below $-70°$. The solution was then sealed in an NMR sample tube. Without allowing the sample to warm appreciably, the tube was inserted into the cooled probe at $-78°$ (Fig. 1a). Upon warming to $-45°$ (Fig. 1b), the spectrum sharpened and was found to be quite similar to that observed in toluene[1]. However, we noted that resonances for the *cis* and *trans* forms* were more separated in THF, particularly in the γ-proton region which has shifted upfield as compared to toluene solutions**. The more upfield γ-multiplet at τ 6.7 we have assigned to the *cis* form ($J_{\beta\gamma}$ 10.5) and the multiplet at τ 6.4 to the *trans* form ($J_{\beta\gamma}$ 13.6). The sample was then allowed to stay at 30° briefly, and lowered again to $-18°$. As shown in Fig. 1c, extensive *cis–trans* isomerization has apparently occurred. The *cis*-γ-multiplet has increased in intensity at the expense of the *trans*-γ-multiplet and is now predominant. Integration of the β and γ regions at this temperature indicated a *cis/trans* ratio of 1.35. Figure 2 is an expansion of the β and γ regions (at $-4°$). It should be noted that coalescence of the *cis* and *trans* multiplets was not observed up to 30°.

Analysis of the spectra using the computer synthesis procedure described by us previously[1a] has yielded the parameters shown in Table 1.

It is clear from a comparison of these data with those obtained in hydrocarbon solvents that NpALi is substantially more delocalized in THF***. The upfield shift of the γ-protons (>1.3 ppm) is paralleled by a smaller downfield shift of the α-protons (>0.2 ppm).

TABLE 1

PMR PARAMETERS FOR NpALi IN THF AND DIETHYL ETHER $[(CD_3)_3C\overset{\delta}{C}H_2\overset{\gamma}{C}H\overset{\beta}{C}H\overset{\alpha}{C}H_2]^-, Li^+$

Trans									*Cis*						
t(°*C*)	*Solvent*	τ_α	τ_β	τ_γ	τ_δ	$J_{\alpha\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$	τ_α	τ_β	τ_γ	τ_δ	$J_{\alpha\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
+30	THF	8.71	4.02	6.37	8.15	10.5	13.4	6.5	8.81	3.90	6.65	8.12	9.9	9.7	6.4
−18	THF	8.78	4.04	6.38	8.16	10.2	13.6	6.9	8.90	3.92	6.71	8.11	10.2	9.3	6.2
−35	THF	8.85	4.13	6.48	8.27	10.0	13.8	7.2	9.02	4.01	6.84	8.22	9.6	9.0	6.0
+21	Et_2O	8.96	4.03	5.94	8.22	10.1	14.3	6.7	8.99	3.92	6.11	8.17	10.0	10.5	6.5
−10	Et_2O	8.68	4.02	6.02	8.11	10.5	14.2	6.5							
−20	Et_2O	8.66	4.02	6.02	8.12										
−45	Et_2O	8.60	4.02	6.10	8.11	(10)	(13)								

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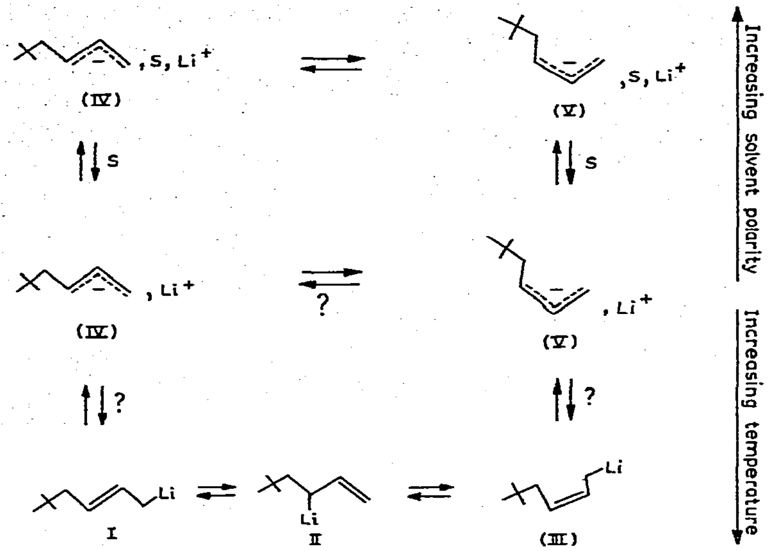
* We will continue to utilize the terms *cis* and *trans* for the two forms of NpALi observed by PMR in THF, even though the *syn* and *anti* designations used for the ionic forms may be more appropriate[11].

** The *cis* and *trans* γ-proton resonances in toluene were found at τ 5.50 and 5.36 respectively. The α-protons were at τ 9.20 and 9.22[1].

*** More delocalization in THF is supported by the IR spectrum of NpALi. The rather sharp band which is observed in hydrocarbon solvents at 1595 cm^{-1} broadens upon the addition of THF and the maximum shifts to 1540 cm^{-1}. In ether, an intermediate value of 1545 cm^{-1} is observed.

It is also clear that a mechanism for *cis–trans* isomerization of NpALi exists in THF which was not available in hydrocarbon solvents[1,3]. However, the rate of isomerization is still slow on the NMR time scale, since individual *cis* and *trans* resonances are observed as high as 30°.

Unfortunately, on the basis of these data we are still unable to describe the nature of NpALi in THF in more detail. Ionic delocalized forms such as IV and V would appear to be most reasonable, but covalent forms cannot be excluded, since they provide a very reasonable route for *cis–trans* isomerization[4,5].



It is known that ionic forms such as (IV) and (V) may exist as solvent separated ion-pairs or with intimate contact between the anion and cation[7–10]. Only indirect evidence concerning the participation of such forms is available from the PMR data. We refer to a general upfield shift of all chemical shifts which is observed as NpALi/THF solutions are decreased in temperature (see Table 1). Young and coworkers have observed similar behavior for the delocalized sodium salt of 1,3-diphenylpropene[12]. The effect was interpreted in terms of increased charge on the allyl ion at lower temperatures due to the formation of more solvent separated ion pairs. By analogy, we may postulate that solvent separated ion pairs of NpALi play a more important role at lower temperatures but we are still unable to describe that role more quantitatively.

Several spectra of NpALi were taken below −50°, both before and after isomerization at room temperature. In each case, collapse of the α-proton signals was observed, which at higher temperatures consist of two sharp doublets. Apparently, C_α–C_β rotation, which is rapid at high temperatures, is slowed at lower temperatures★. Similar behavior has been observed for 3-phenylallyllithium[13], 1,3-diphenylallyl-

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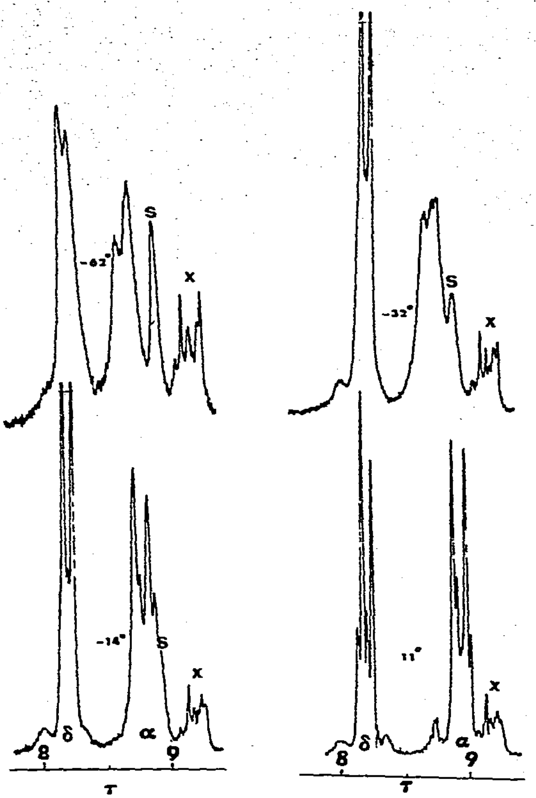
★ C_α–C_β bond rotation may occur either through the intermediary of covalent forms such as (I) and (II), or because of a lowered barrier in the allylic anion[13–15].



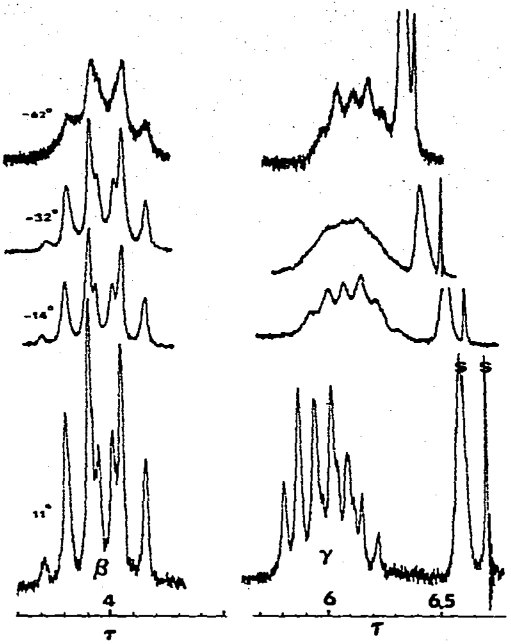


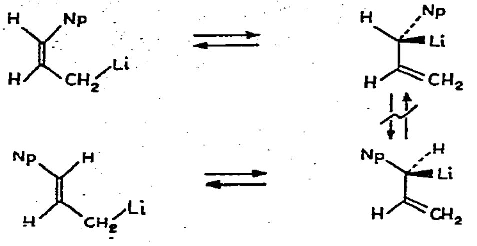
Fig. 3. 100 MHz PMR spectrum of NpALi [1.0 *M*] in diethyl ether-d_{10}; δ-CH_2 and α-CH_2 region. x = residual t-butyl and pentane protons; s = residual ether protons.

Fig. 4. Same as Fig. 3; β-CH and γ-CH region. s = residual ether protons.

lithium[14], allyllithium[15], crotyllithium[16], and for the isoprene adduct of t-butyllithium[3].

PMR results in Et_2O. Spectra of NpALi in diethyl ether-d_{10} were obtained in a manner similar to that described above. The results are shown in Figs. 3 and 4 and the parameters are listed in Table 1. As expected, NpALi shows proton shifts in ether which indicate a degree of ionic delocalization intermediate between that observed in hydrocarbon solvents. Most surprising is the γ-proton resonance which is a relatively well defined quintet at −62°, goes through a coalescence near −30°, and finally sharpens to a multiplet at 11° which is highly reminiscent of the γ-multiplet in toluene[7]. The multiplet is skewed to the high field side due to the overlap of *trans* and *cis* =CH multiplets in a ratio of approximately 3/1. Moreover, this ratio did not appear to change as the temperature of the sample was varied from 30° to −20° over a period of approximately one hour. Two situations would account for this behavior: (a) a dynamic equilibrium between forms (I), (II) and (III) consisting primarily of the first two in a 3/1 ratio, with little enthalpy difference between the two; or (b) a static mixture of (I) and (II), [or (IV) and (V)] in the same 3/1 ratio as they existed in toluene.

At the present time, we are inclined to accept the second alternative*. However, we propose that the term "static", as used in the second alternative, be interpreted to mean that no equilibrium exists whose net effect is rotation about the C_β–C_γ bond. This does not rule out the existence of a "semi-dynamic" equilibrium** in which the individual *cis* and *trans* isomers are each in equilibrium with a different conformationally fixed α-neopentylallyl isomer***. The coalescence near −20° is apparently due to retardation of these equilibria.



One more piece of evidence from Table 1 is relevant to this discussion. We note that the α and γ proton resonances shift downfield and upfield respectively as the temperature is lowered. This is in the direction one would predict if NpALi were becoming more delocalized. Moreover, we note that the spectrum at −62° in Figs. 3 and 4 consists of near collapsed resonances in all regions shown. Therefore, we suggest that at lower temperature in ether NpALi consists of the near-rigid ion pair, which is predominantly in the *trans* form. It will also be noted that the value of $J_{\beta\gamma}$ at the low temperature is in line with the values observed for the *trans* form in THF****.

UV Absorption spectra. In view of the many successful applications of ultraviolet-visible absorption spectroscopy in the study of ion pairs[7-9], we hoped that a similar investigation of NpALi would also be revealing. As reported earlier[7], NpALi in hydrocarbon solvents shows a strong absorption at 270 nm ($\varepsilon = 1.0 \times 10^4\ M^{-1}\cdot$

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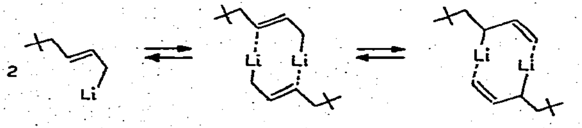
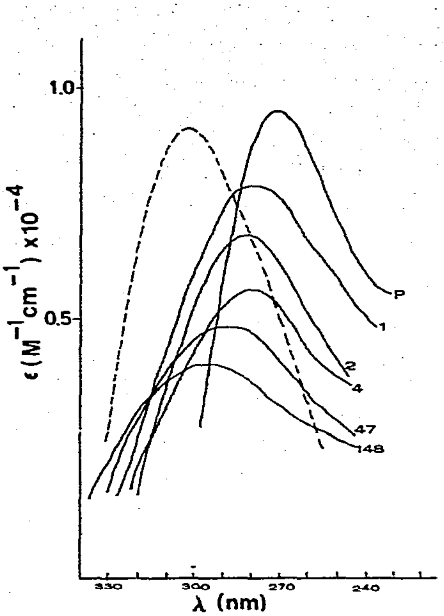
* The second alternative is supported by the spectrum of 2-butenyllithium[16] and by a comparison of the hydrolysis products of NpALi in ether with those of "dynamic" bis(neopentylallyl)magnesium[17] in the same solvent. The yields of the lithium and magnesium compound are as follows: *trans*-5,5-dimethyl-2-hexene (Li 68 %, Mg 18 %); *cis*-isomer (Li 21 %, Mg 12 %), and 5,5-dimethyl-1-hexene (Li 11 %, Mg 70 %). Apparently, covalent-dynamic allylmagnesium compounds yield predominant amounts of the rearranged 1-olefin in all cases which have been investigated. For further references and discussion of this point, see the following paper[17].

** See the following paper on bis(neopentylallyl)magnesium for further discussion and spectra relating to another proposed "semi-dynamic" allyl system.

*** Lithium exchange between the α and γ positions is shown in the figures above as a unimolecular process. There is no evidence to rule out other possible exchange processes such as those below involving monomer and dimer NpALi. However, the net effect of the exchange may not include *cis*–*trans* isomerization.



**** Alternately, we may assume that at low temperatures a more delocalized dimeric form exists such as shown above.



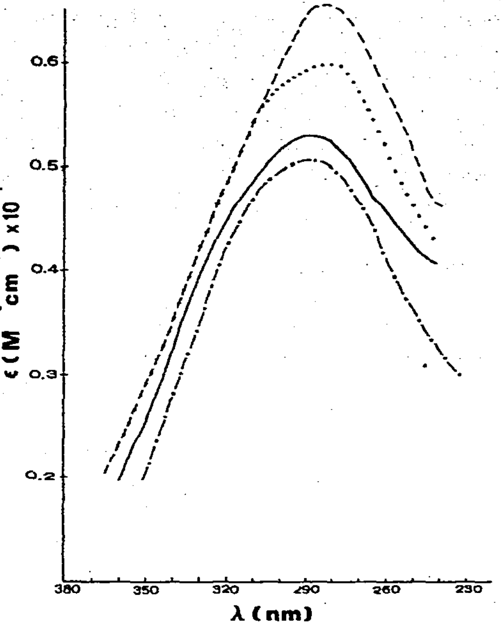


Fig. 5. Effect of THF on the absorption band of NpALi. P=pentane solvent; numbers refer to moles of THF added per mole of NpALi. [NpALi]=2.2×10^{-3} *M*, −10°. ---- Spectrum in diethyl ether.

Fig. 6. Effect of temperature and diglyme on the absorption band of NpALi in THF; [NpALi]=4.0×10^{-3} *M*. ---- −70° (before warming to room temperature); ..... −65° (after warming to room temperature); —— 25°; —·—·—·— diglyme+THF (1.0 vol. %).

cm^{-1})*. If the pentane is replaced with increments of THF, the spectra shown in Fig. 5 result. The band broadens considerably and shifts to longer wavelengths (λ_{max} 297 nm; $\varepsilon = 0.4 \times 10^4 \cdot M^{-1}$ cm^{-1}). This band is relatively insensitive to temperature changes as shown in Fig. 6. More surprising, the addition of DME and diglyme [$CH_3O(CH_2$-$CH_2)_{1-2}CH_3$] have little effect. We are led to conclude one of the following: (a) that contact and solvent-separated ion pairs of NpALi are not distinguishable by the UV method, (b) that only one form of NpALi ion pair exists under all conditions in THF/glyme solvents, or (c) a number of ionic forms exist with various degrees of solvent participation (and slightly different λ_{max} values). In view of the PMR results described above, we are inclined to accept either (a) or (c), with the further stipulation that more solvent separated forms prevail at lower temperatures and in glyme solvents. Unfortunately, more definite conclusions concerning this subject will require further data.

Finally, we note that the absorption maximum of NpALi in diethyl ether appears at 310 nm, *i.e.* at longer wavelengths, than that found in THF, THF/DME, or THF/diglyme. The band observed in ether appears to shift slightly to the blue as the temperature is lowered, and, perhaps more significant, the band is much more narrow than in THF. This suggests that only one type of species is present. However, we are unable to justify the obvious conclusion that this is a solvent separated ion pair.

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* In a preliminary communication[18], we reported erroneous absorption maxima for NpALi in hydrocarbon solvent due to our failure to anticipate the slow reaction rate of butadiene and t-butyllithium at high dilutions.

Rather, we anticipate that the explanation of this phenomenon will involve the effect of aggregation on the electronic levels of NpALi. Various theoretical treatments[19] indicate significant perturbation of the electronic energy levels of methyllithium upon formation of aggregates. However, to our knowledge, only one paper has appeared in which spectral shifts have been interpreted in terms of aggregate equilibria, and in this case the correlation was not quantitative[20]. Until more definitive data is available, we must leave unexplained the matter of the anomalous λ_{max} of NpALi in diethyl ether.

EXPERIMENTAL

The preparation of NpALi followed the procedure outlined previously[1a], and was carried out using greaseless vacuum-line techniques. Solvents were dried over sodium mirrors until a shiny surface remained, and measured into break-seal ampoules. In the case of PMR work, pentane was removed from NpALi by distillation under vacuum and replaced by the solvent of choice with TMS added. A JEOL PS-100 spectrometer with variable temperature control (±2°) was employed. UV spectra were obtained using a Cary 14 spectrometer. The solution to be studied was prepared in a closed system containing a side-connected 2 mm UV cell with 0.180 or 0.165 mm quartz spacer. The cell was cooled in the spectrometer cell compartment in a double-walled Dewar with quartz windows containing spectrograde methanol. Liquid nitrogen was added to the methanol to bring the temperature to the desired level. Control was ±2° during a run.

IR cells were loaded in a dry box as described earlier[1a].

ACKNOWLEDGEMENT

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Note added in proof. In a recent paper, Oliver *et al.* have described the UV spectra of several alkyllithium compounds[21]. Their results indicate a blue shift of twelve nm for the transition $(C_2H_5Li)_6 \rightarrow (C_2H_5Li)_4$. Our results therefore could be ascribed to an increase in association in diethyl ether as compared to THF.