NEOPENTYLALLYLSODIUM

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Summary

Neopentylallylsodium (NpANa) has been prepared by the reaction of neopentylallyllithium with an equivalent amount of sodium 2,2-dimethyl-1-butoxide in hydrocarbon solvent. NpANa is stable in diethyl ether and THF solvents for extended periods of time, and proton NMR and UV data are reported for NpANa in THF at various temperatures. A more substantial degree of ionic delocalization is indicated for NpANa as compared to NpALi and apparently is greater for the *cis* isomer than the *trans* isomer of NpANa. UV absorption maxima for NpANa and NpALi are explained in terms of *cis/trans* ratios rather than in terms of ion pairing.

The nature of allyl-Group IA metal derivatives continues to be of interest primarily due to the intermediacy of these species in diene polymerizations [1] and also because of their various bonding habits [2]. Freedman and coworkers [3] and more recently Young and his group [4] have examined allyl-Group IA metals with substituents on the allyl group capable of delocalization of the carbanion charge, for example phenylallyllithium and related compounds. Such compounds are usually soluble only in electron-donating solvents such as ethers, and apparently exist as delocalized ion pairs. The degree of solvent separation varies with the nature of the solvent, the cation and substituents on the allyl group. Solvent separated and contact ion pairs may be readily distinguished by different maxima in the UV-visible absorption spectra and to a lesser extent by comparison of PMR data for various compounds with different alkali metal counter-ions [4].

The alkyl derivatives of allylmetals, such as crotyllithium, are less well characterized. With the exception of a brief report on allylsodium [5] only information on the lithium derivatives may be found in the literature. Our knowledge in this area may be summarized as follows [6-11]. (1) Allyllithium derivatives with alkyl substituents such as neopentylallyllithium [6] (I-III, R^2 = neo-

pentyl; $R^1 = R^3 = R^4 = H$) are sometimes soluble in hydrocarbon solvents in which they exist as aggregated species [6b]. *Cis* and *trans* forms of these compounds (I and II) may be recognized in the PMR spectra and it appears that these isomers are not in dynamic equilibrium [6,11]. No conclusive evidence has been found for the secondary form III except in cases where the primary form is precluded (e.g., with $R^1 = R^2 = Me$) [10]. (2) The PMR, UV, and IR data available

$$\begin{array}{ccc} \text{(I)} & \text{(II)} & \text{(III)} \end{array}$$
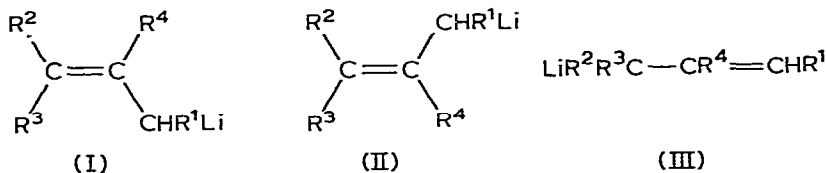
indicate that allyllithium species such as I-III are largely localized in hydrocarbon solvents, that is, that they are not to be regarded as classical ionic species. However, the spectral data suggest that some delocalization of charge from the C(1) (α) to the C(3) (γ) position has occurred as compared to nonmetallic allyl species [6,10,11]. The extent of this delocalization and an exact description of the bonding in unsolvated allyllithiums have remained unresolved*. (3) The addition of strong Lewis bases such as THF causes substantial delocalization of charge from the C(1) to the C(3) position as evidenced by downfield and upfield shifts in the C(1) and C(3) protons respectively and concomitant red shifts in the UV and IR spectra (C=C stretch region). (4) By analogy with phenylallyllithium we may postulate that alkyl-substituted allyllithiums are largely in the contact ion pair from in THF, but no direct spectral proof has been presented on this point to this date.

In this paper we present spectral data on the new compound neopentylallylsodium (NpANa) which sheds new light on the bonding of alkyl-substituted allylmetal compounds. In subsequent papers we will describe neopentylallylpotassium and will also describe some interesting and somewhat surprising chemical reactions of these species.

Experimental section

Solvents. n-Pentane (Phillips Pure Grade) was purified by prolonged stirring over sulfuric acid followed by distillation, bulb-to-bulb distillation from sodium mirrors, and finally distillation from sodium—potassium alloy. Tetrahydrofuran (MCB) and THF-d_8 (Merck, Sharpe and Dohme of Canada) were

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* Morton has suggested that primary allyllithium forms (I and II) are localized (σ-bonded) whereas secondary forms (III) are ionic delocalized [10d]. Bywater prefers to consider the difference between the structures in hydrocarbon and ether solvents to be one of degree rather than kind [11c], both being delocalized to some extent. Another possibility is intriguing, namely, that allyllithium species are fluxional [12]. In this view, the lithium atom could oscillate rapidly between two potential minima located near the α and the γ positions without concomitant *cis—trans* isomerization [6c]. The relative lifetime of the metal atom at the α and γ positions would vary from one compound to another and would depend on substituents at these two positions, i.e. on the depth of the potential minimum at that position. The aggregated nature of these species in hydrocarbon solvents [6b] would seem to facilitate exchange processes of this type.

distilled repeatedly from sodium mirrors until a fresh metal surface remained. Diglyme and diethyl ether were purified similarly.

Prepration of sodium 2,2-dimethyl-1-butoxide. 2,2-Dimethyl-1-butanol (Chemical Samples) was distilled on a vacuum line prior to use. Twenty ml of the alcohol (0.2 mol), 50 ml of dried n-pentane, and 0.3 mol of sodium were refluxed on the vacuum line for approximately one week. (The sodium had been cut into pieces and placed in the apparatus in a helium filled dry box). The pentane and other volatiles were removed by distillation on the vacuum line and the white solid which remained was pumped dry overnight. Pentane was redistilled onto the solid and the resulting solution filtered through a medium frit. The resulting clear solution of the alkoxide, which was 2.62 M, was divided into break-seal ampoules using standard vacuum line methods.

Preparation of neopentylallylsodium. The compound was prepared using a modification of the method developed by Lochmann et al. [13]. Although the procedure followed varied somewhat from one preparation to another, we will describe in detail the use of the apparatus shown in Fig. 1. After insertion of a glass enclosed magnetic stirring bar through opening a, this opening was selaed and the entire apparatus pumped to "sticking vacuum". Stopcock d was closed and the contents of bulb b (7.6 mmol of sublimed t-butyllithium in 4.5 ml pentane) were transferred to reservoir c. Ampoule b was carefully washed clean with refluxed pentane and sealed off. Butadiene (6.9 mmol, Phillips Pure Grade, redistilled from sodium mirror) was transferred into the reservoir c while cooling c with liquid nitrogen. The contents of c were allowed to stir at room temperature for about 1 and 0.5 h. To this solution of neopentylallyllithium (NpALi) [6b] the contents of ampoule f were added (3.0 ml of 2.62 M alkoxide in pentane). A bright yellow precipitate immediately formed which was collected on the medium frit h. The pentane filtrate in bulb g was redistilled repeatedly back through the frit to wash the precipitate. Bulb g was sealed off and the entire apparatus pumped to dryness overnight. The following morning approximately 15 ml of dried diethyl ether was distilled into the reservoir. Portions of
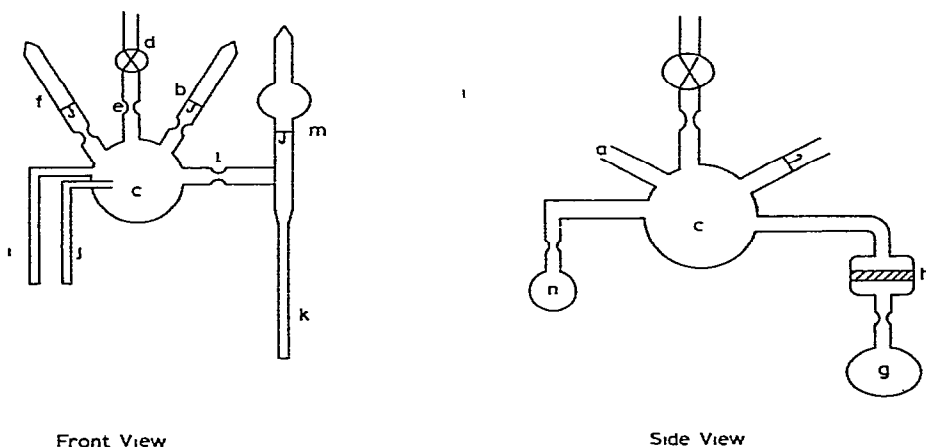

Front View   Side View

Fig. 1. Apparatus used for the preparation of neopentylallylsodium.

the resulting solution of NpANa were separated into the two ampoules i and j which were then sealed off for Gilman analyses. The double titration indicated an active organometallic concentration of 0.32 M with less than 2% "other base" Some of the remaining solution was poured into the NMR tube k, the system was reconnected to the vacuum line and pumped dry. The NMR cell was sealed off from the remainder of the system at point l and the breakseal m broken to allow a measured amount of THF-d_8 to enter the NMR cell. After solution of the NpANa the NMR tube was sealed off and stored at —196°C until the spectrum of NpANa was recorded. Diethyl ether was distilled into the reservoir c to redissolve the remaining NpANa. The resulting solution was transferred to bulb n and sealed off. The sodium and lithium content of this solution was determined by atomic absorption spectrophotometry after hydrolysis. The atomic absorption results showed that the metal content of the organometallic solution was 97% Na and 3% Li.
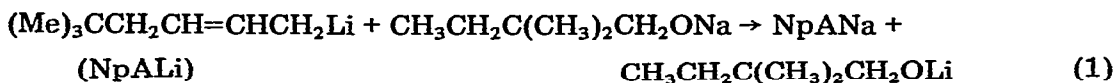
In subsequent experiments a similar apparatus was used to prepare NpANa for UV studies. The NMR cell shown in Fig. 1 was replaced with a quartz cell connected to the apparatus by way of a graded seal. The cell had a nominal path length of 2 mm with a spacer to decrease the path to 0.035 mm when required. Solutions of NpANa were prepared in THF which had been rigorously dried as described above.

Hydrolysis of NpANa solutions was carried out by quenching solutions prepared as described above. The hydrocarbon layer extracted with ether was analyzed as described earlier [6]. Only C_8H_{16} olefins corresponding to structures IV, V, and VI were found.

Spectral measurements. NMR spectra were taken on a JEOL PS-100 with variable temperature probe assessory. Both constant field and constant frequency experiments were conducted, but the majority of the data reported here were taken at constant frequency. Temperatures in the probe were checked periodically with methanol. UV spectra were taken on a Cary Model 14 spectrophotometer using a special Dewar with quartz windows for low temperature measurements. The Dewar was filled with methanol or isopropyl alcohol with appropriate quantities of liquid nitrogen added to adjust the temperature to the required value. Temperature control was estimated to be ±3°C. Reproducibility of UV data was ±2 nm. Reproducibility of chemical shifts was ±0.02 ppm.
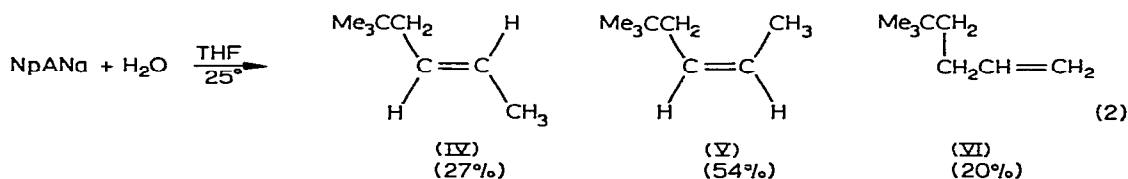
Results and discussion

Preparation and hydrolysis of NpANa. As described in the Experimental Section NpANa was prepared by a modification of the method of Lochmann et al. [13]. This method utilizes the fact that alkyllithiums (in our case neopentylallyllithium) as well as lithium and sodium 2,2-dimethyl-1-butoxide are soluble in hydrocarbon solvents, whereas the desired product NpANa is insoluble (eqn. 1). The method is simple enough to utilize in a dry box where NpANa may

$(Me)_3CCH_2CH=CHCH_2Li + CH_3CH_2C(CH_3)_2CH_2ONa \rightarrow NpANa +$

$\quad$ (NpALi) $\qquad\qquad\qquad\qquad\qquad CH_3CH_2C(CH_3)_2CH_2OLi \qquad\qquad$ (1)

be removed from the reaction mixture by filtration as slightly yellow colored crystals. In this phase of our work, however, we have prepared NpANa using vacuum-tight glassware such as that shown in Fig. 1. In this way we were assured of minimum contamination of samples which were to be used for NMR and UV studies.

It should be noted that NpANa is not soluble in hydrocarbon solvents as far as we can determine; however, it is quite soluble in THF, diethyl ether, and other coordinating solvents. Surprisingly, it is more stable in THF than in diethyl ether and also more stable in THF than is NpALi. Both observations may be rationalized by the assumption that NpANa is more delocalized in THF than in ether or than NpALi in THF, an assumption which tends to be substantiated by the NMR data discussed below. More complete delocalization would reduce the charge density at the C(1) carbon atom thereby reducing the nucleophilicity of the organometallic. Be that as it may, NpANa is more stable than expected in THF and we have obtained good quality NMR spectra for the compound at room temperature with little apparent loss over periods of several hours. At elevated temperatures decomposition is observed, the products of which we have not characterized.

NpANa is hydrolyzed to give the expected olefinic products IV-VI as shown in reaction 2. The relative percentages of the three products were observ-

$$NpANa + H_2O \xrightarrow[25°]{THF}$$

Me$_3$CCH$_2$ H
　　　　＼　／
　　　　C＝C
　　　／　　＼
　　H　　　CH$_3$

Me$_3$CCH$_2$ CH$_3$
　　　　＼　／
　　　　C＝C
　　　／　　＼
　　H　　　H

Me$_3$CCH$_2$
　　|
CH$_2$CH＝CH$_2$

(2)

(IV)　　　　　(V)　　　　　(VI)
(27%)　　　　(54%)　　　　(20%)

ed to vary somewhat depending on the proton donor used, but the variations are not of interest in this paper. More details will be presented later, but for the present we will point out two features of the results shown above as compared to similar reactions of NpALi. Firstly, we note that the *trans/cis* ratio of the internal olefin isomers IV/V is 0.50 as compared to values of 3.3, 3.2, and 1.3 for hydrolysis of NpALi in pentane, diethyl ether and THF respectively [6]. Thus, the *cis* olefin product becomes predominant as the apparent "ionic" character of the allylmetal compound increases. Secondly, the percentage of the terminal olefin VI increases from 2% for NpALi in pentane, to 11% in ether, to 14% in THF, to 20% for the sodium compound in THF. On the surface, this too would appear to be related to the degree of ionic delocalization of the organometallic. However, as we shall show later the percentage of this type of terminal olefin product is not determined entirely by the charge distribution of the organometallic but is also determined by the nature of the metal ion, the proton donor, and by steric factors. Perhaps the most striking evidence in this regard is the observation by several workers that Grignard reagents such as crotylmagnesium chloride give very high yields of this product, most often near 90% [14].

PMR spectra of NpANa in THF-d$_8$. Figure 2 is the 100 MHz spectrum of NpANa in THF-d$_8$ at 30, −31, and −47°C. The assignments shown in the figure have been made in analogy with NpALi and are confirmed by the coupling
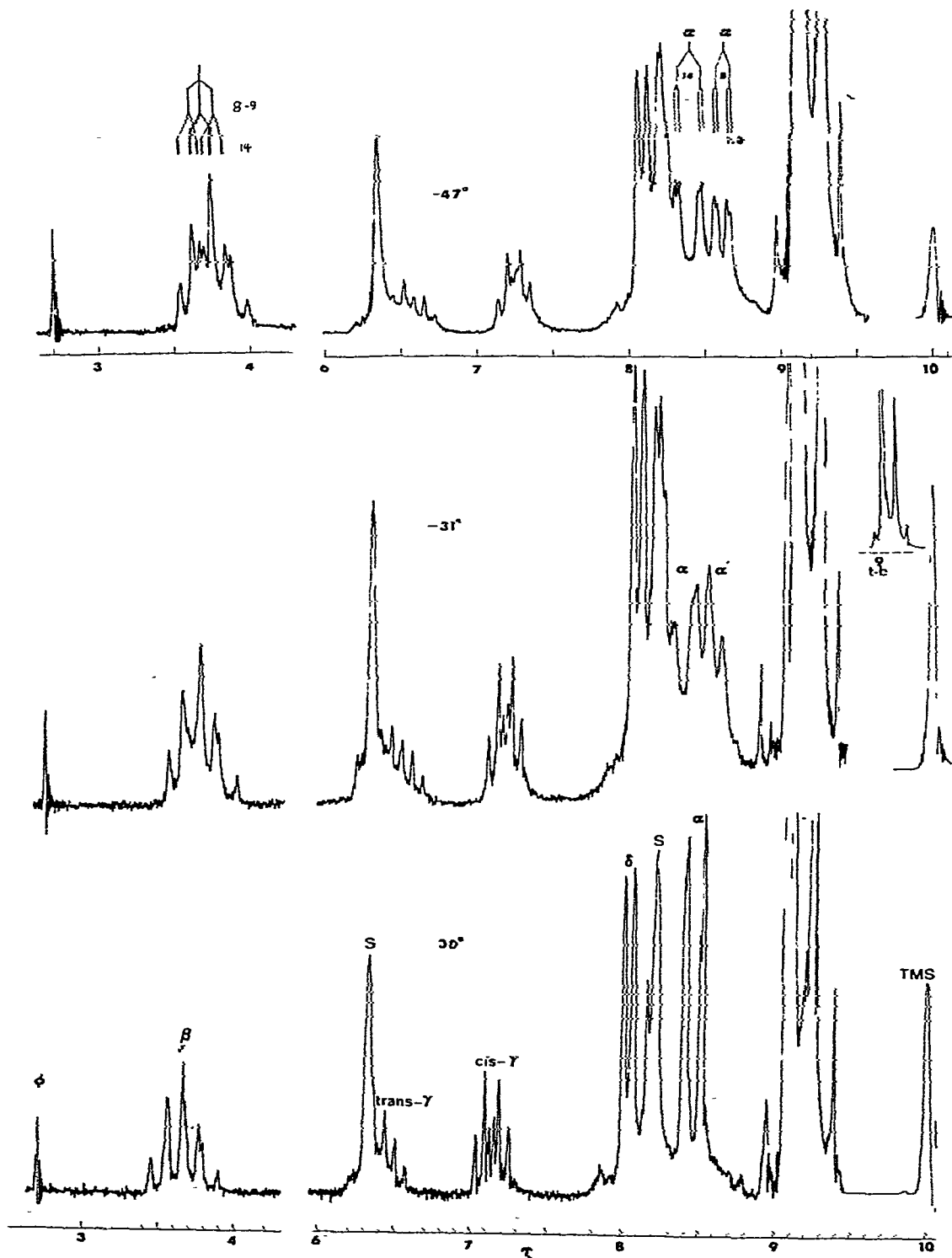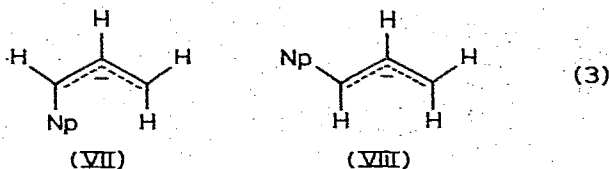
Fig. 2. 100 MHz spectrum of neopentylallylsodium in THF-d_8 at 30, —31 and —47°C.

constant values shown in Table 1. For comparison, we have also included in the Table chemical shift and coupling constant data for NpALi in various solvents [6]. Several points relating to those data deserve comment:

(a) The spectra are those of a mixture of the two expected isomers of NpANa VII and VIII. Clearly, the *cis* isomer VII is the predominant form al-

though the variation of the ratio of VII/VIII with temperature (Table 2) indicates that a dynamic equilibrium exists between VII and VIII which is slow on the NMR time scale. The data shown in Table 2 may be used to determine a value for the overall change in enthalpy for the process shown in eqn. 3. The value is 1.9 ± 0.3 kcal/mole. It is significant to note that the ratio VII/VIII has a value of 0.33 for NpALi in toluene and diethyl ether and is temperature independent as far as we can determine [6].

(b) The γ-proton resonance of *cis*-NpANa is remarkably upfield from that of the *trans* form ($\Delta \tau = 0.70$ ppm at 30°C). Both the *trans*-γ and the *cis*-γ chemical shifts are upfield from the corresponding values for the lithium compound but the difference is much greater for the *cis* than for the *trans* species. To the extent that proton chemical shifts reflect charge density distributions we may infer from this observation that the *cis* form is substantially more delocalized than the *trans* form. It is interesting that the apparent stability of the *cis* isomer increases in the same order as the difference in the chemical shifts of the γ proton for VII and VIII. Thus, the *cis* anion appears to gain in stability as its degree of ionic delocalization increases. Further information on charge densities in these anions would be useful and we are presently investigating the carbon-13 NMR spectra of NpALi and NpANa in order to gain more information of this type.

(c) As shown in Fig. 2 the coalescence temperature of the α and β regions of NpANa is above −31°C. Our best estimate of the value of T_c is −20°C. At lower temperatures separate resonances for the α, α' and β protons are observed. The values of the coupling constants shown in Table 1 and in Fig. 3 are in agreement with those reported for allyllithium [16] and for 2-butenyllithium [8].
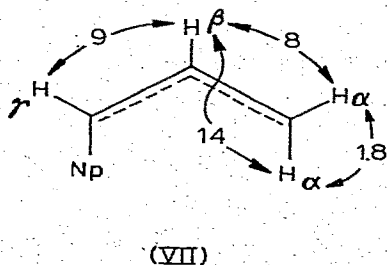

Fig. 3. Values of coupling constants for neopentylallyl-lithium and -sodium.

TABLE 1

PMR PARAMETERS FOR NpANa AND NpALi IN VARIOUS SOLVENTS $[(CH_3)_3CH_2\overset{\delta}{C}H\overset{\gamma}{C}H\overset{\beta}{C}H\overset{\alpha}{C}H_2]^{-}$ M^+

Tempe-rature (°C)	Solvent	cis									
		$\tau_{\alpha'}$	τ_α	τ_β	τ_γ	τ_δ	$J_{\alpha\alpha'}$	$J_{\alpha\beta}$	$J_{\alpha'\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
NpANa											
+30	THF		8.48	3.60	7.15	8.05		10		10	6.5
−7	THF		8.49	3.63	7.19	8.09		10		10	6.5
−31	THF	8.58	8.38	3.65	7.21	8.07					
−63	THF	8.58	8.38	3.70	7.23	8.09	1.8	8	14	9	6
−77	THF	8.59	8.38	3.85	7.28	8.1	1.8	8	14	9	6
NpALi											
+30	THF		8.81	3.90	6.65	8.12			9.9	9.7	6.4
−35	THF		9.02	4.01	6.84	8.22			9.6	9.0	6.0
+21	Et$_2$O		8.99	3.92	6.11	8.17			10.0	10.5	6.5
+30	Toluene		9.20	3.39	5.51	8.11			10.0	10.0	6.9

It is significant to note that coalescence of the α and β regions is observed for NpALi in THF at approximately −55°C [6]. Dolinskaya et al. report a T_c value of approximately −75°C for 2-butenyllithium in dimethyl ether [8], and the value for allyllithium is approximately −50°C according to West and coworkers [16]. Our explanation of these NMR data will follow a brief discussion of the UV results.

UV spectrum of NpANa. Using methods similar to those reported earlier [6], we have observed the UV absorption spectrum of NpANa in THF over the range 30 to −70°C. The compound shows a broad band with λ_{max} at 278 nm which remains essentially stationary as the temperature is lowered. The value of ϵ_{max} is 0.1×10^4 l mol^{-1} cm^{-1} at 30°C. Addition of diglyme does not effect the band. These observations are to be compared with our results on NpALi in THF and diglyme where λ_{max} is 297 nm (ϵ_{max} 0.4×10^4) and in diethyl ether where λ_{max} is 310 nm [6]. West has reported that allyllithium has λ_{max} values of 310-320 nm (ϵ_{max} 0.56-0.45×10^4) [16].

Discussion of spectral results. On the basis of the data obtained thus far, we conclude that NpANa is an ionic compound in which the degree of "delocalization" in the anion is substantially greater than in the corresponding lithium derivative. The principal evidence for the conclusion comes from the PMR data;

TABLE 2

EQUILIBRIUM *cis/trans* ISOMER RATIOS FOR NEOPENTYLALLYLSODIUM (THF Solvent)

Temperature (°C)	K = VII/VIII
−7	4.2
−31	3.4
−47	1.9
−63	1.8
−77	1.2
−18 (NpALi)	1.3$_5$

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trans

$\tau_{\alpha'}$	τ_{α}	τ_{β}	τ_{γ}	τ_{δ}	$J_{\alpha\alpha'}$	$J_{\alpha\beta}$	$J_{\alpha'\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
		3.71	6.45	8.19			10		6.5
		3.75	6.51	8.24			10		6.5
		3.77	6.54	8.2			10		6.5
		3.8	6.59	8.3					6.5
		3.9	6.66						
8.71		4.02	6.37	8.15			10.5	13.4	6.5
8.85		4.13	6.48	8.27			10.0	13.8	7.2
8.96		4.03	5.94	8.22			10.1	14.3	6.7
9.23		3.94	5.36	8.07			9.4	14.5	7.0

namely, in the significant upfield shifts of the γ protons and the corresponding downfield shifts of the α protons in NpANa as compared to NpALi. This view of NpALi vis à vis NpANa is supported by the values of the coalescence temperatures T_c below which α—β bond rotation is slow on the NMR time scale. The substantially higher T_c temperature for NpANa as compared to NpALi confirms the conclusion that NpANa has a higher α—β bond order than the lithium derivative at a given temperature.

Combined with the chemical shift data the T_c values also suggest that both NpALi and NpANa exist primarily as contact ion pairs in THF. If, as in many carbanion salts, the lithium compound existed as a solvent separated ion pair and the sodium compound as a contact ion pair, we would expect a higher value of T_c for NpALi as well as higher chemical shift values for the γ protons. In fact, the PMR data suggest that the degree of charge transfer from the metal to the organic portion of the molecule is more complete in NpANa than in NpALi. This is consistent with the view that both are contact ion pairs but that the smaller lithium ion retains a greater fraction of the electronic charge than the sodium atom [4]. We should also note that the data are consistent with the participation of larger fractions of covalent species in the case of the lithium compound (Scheme 1). However, the behavior of allylmetal compounds of Group IA is substantially different from that of allyl-Grignards which are thought to be covalent dynamic (lower line of Scheme 1) [14,15]. Therefore, we tend to support the view of Freedman and others [3,11] that allyllithium and allyl-sodium compounds in ether solvents are to be regarded as ionic species. To what extent covalent species play important roles in α—β or β—γ bond rotation processes or in chemical reaction mechanisms is still not clear.

On the surface it would appear that the UV data contradict the view which we have just presented. Other studies have shown that the absorption maximum of contact ion pairs of allylmetal compounds increases with the atomic number of the alkali metal [17]. Thus, we would expect $\lambda_{max}(Li) < \lambda_{max}(Na)$ in contradiction to our observed results. Although the results could be rationalized by assuming that the lithium and sodium compounds are solvent separated and

SCHEME 1
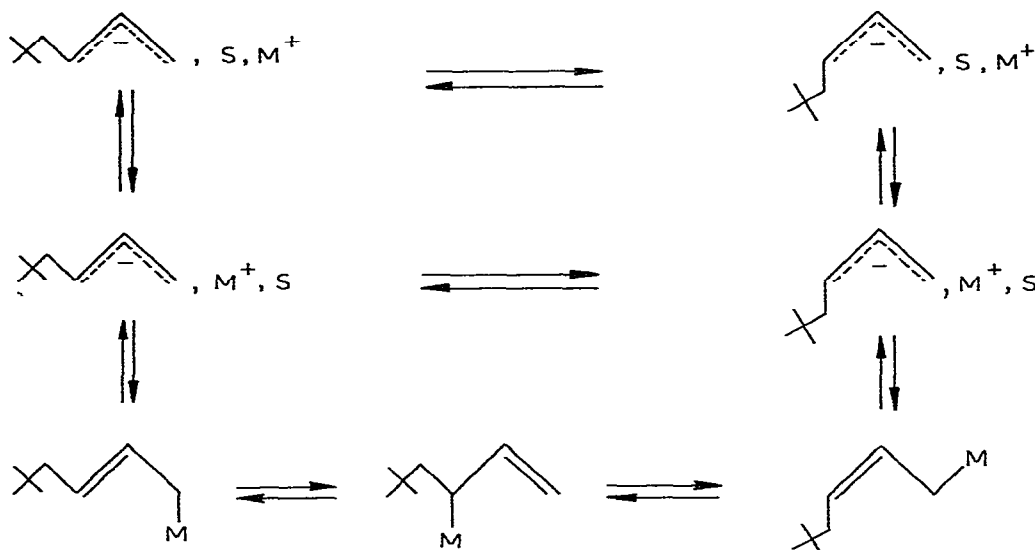
contact ion pairs, respectively, we reject this view as inconsistent with the PMR results given above. Rather, we conclude that the UV spectra of NpANa and NpALi differ primarily because the sodium species contains a much larger fraction of the *cis* isomer which is expected to absorb at lower wavelengths than the *trans* isomer [4,8]. This view is supported by the observation, previously unexplained, that NpALi in diethyl ether (*cis/trans* 0.33) has a λ_{max} value of 310 nm [6].

Thus, we conclude that UV absorption measurements are not suitable for the study of ion pair equilibria in systems such as the one presently being described. The difference in the absorption maxima for the contact and solvent separated ion pair forms is probably too small to utilize and, moreover, the spectra are dominated by changes in the relative abundances of the geometrical isomers whose absorption maxima are substantially different.

Further observations on these compounds will be presented in future publications dealing with neopentylallylpotassium, another new compound in this series which we have recently succeeded in preparing.

Acknowledgements

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