

relatively large activity in PIES, and this is ascribed to the distribution of the orbital spreading out without nodes in the molecular plane.⁵ The enhancement of band 8 suggests that this band is related to the orbital having the $\sigma(C_{Ac}-H)$ character.

An interesting point worth mentioning can be seen in the reactivities of the $\pi(C\equiv C)$ orbitals of the mono- and disilylacetylenes toward the electrophilic attack by the metastable helium atom. In the UPS the band arising from the ionization of the $\pi(C\equiv C)$ orbitals appears at 9.63 eV for bis(trimethylsilyl)acetylene and 10.18 eV for (trimethylsilyl)acetylene, respectively (Table II). Thus substitution of a trimethylsilyl group for the acetylenic hydrogen on the monosilylacetylene decreases the IP by 0.6 eV (Tables I and II). In the context of Koopmans' theorem,¹ this difference reflects that the $\pi(C\equiv C)$ orbitals is destabilized by the inductive and/or hyperconjugative effect of the second trimethylsilyl group. Thus, on the basis of this consideration only, a conclusion could be drawn reasonably that the orbital would be more reactive toward the electrophile compared to that of the monosilylacetylene. However, as is seen in Figure 2 and Table 2, this expectation turned out not to be the case in the PIES. Instead, the $\pi(C\equiv C)$ of the disilyl derivative is found to be less reactive toward the metastable atom. This observation leads us to conclude that the steric effects of

the two trimethylsilyl groups, which shield the orbital from the impact of the metastable atom, overcome the electronic activation.

Although the Penning ionization process is the gas-phase electron-transfer reaction, it is of considerable interest to compare the observed PIES activities of the $\pi(C\equiv C)$ orbitals in these silylacetylenes with chemical reactivities toward electrophilic attack in solution. From the arguments previously advanced, it is expected that the reactivity of the $\pi(C\equiv C)$ bonds toward electrophilic reagents should be retarded by steric shielding as the number of the silyl groups increases. This expectation is found to apply well in the case of the 1,3-dipolar cycloaddition of diazoalkanes to the acetylene derivatives in which bis(trimethylsilyl)acetylene has been found to be much less reactive than (trimethylsilyl)acetylene.¹⁷ Thus, Penning ionization electron spectroscopy has its important application in the study of organosilicon compounds, since it provides useful information on the stereochemical environment of a particular molecular orbital which will take part into chemical reactions.

Registry No. (Trimethylsilyl)acetylene, 1066-54-2; bis(trimethylsilyl)acetylene, 14630-40-1.

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Cis-Trans Isomerization of Alkyl-Substituted Allylic Ion Pairs.

1. Isomerization of (Neopentylallyl)lithium, -sodium, and -potassium in Tetrahydrofuran

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(Neopentylallyl)lithium, -sodium, and -potassium have been prepared by established methods under conditions where the trans configuration is, as far as possible, produced. Their isomerization rates to the thermodynamically more stable cis form have been measured as a function of temperature. Fairly large differences in rates were observed in the order Li > Na > K. Both preexponential factors and activation energies increased in the reversed order. Isomerization barriers parallel those for terminal methylene group rotation. The implications of these observations are discussed.

Rotation about the $\alpha\beta$ and $\beta\gamma$ bonds in alkyl-substituted allyl ion pairs ($R-CH_2-CX_{\beta}-CH_2\alpha^-M^+$; I) is of interest on theoretical grounds and for the interpretation of reaction mechanisms. $\alpha\beta$ -Rotational barriers are relatively easily obtained from coalescence temperatures of the proton NMR signals of the α -methylene group and are available for a number of allylic derivatives of the alkyl metals.¹ Generally, CH_2 rotation of the lithium derivatives is observable at considerably lower temperatures than with those of potassium, and in both compounds when the temperature is raised, it is the trans isomer whose methylene group begins to rotate first. A little qualitative information is available on the ease of rotation around the $\beta-\gamma$ bond (cis-trans isomerization). The earliest indications that allylic lithium compounds are quite labile in

solution were made by Seyferth and Jula.² Transmetalation of *trans*-crotyltrimethyltin with *n*-butyllithium in ether/hexane at room temperature produced a 60/40 mixture of *trans*- and *cis*-crotyltrimethylsilane on quenching with trimethylchlorosilane. Identical results were obtained starting from *cis*-crotyltrimethyltin. Lithium compounds again appear to have lower rotation barriers although no quantitative data are available for the derivatives of the other alkali metals. Ia ($R = \text{neopentyl}$, $X = CH_3$, $M = Li$) undergoes *trans* to *cis* isomerization at $-40^\circ C$ in tetrahydrofuran (THF) with a half-life of ~ 40 min.³ In heptane the *trans* form is more stable, but a similar lifetime is observable at $0^\circ C$ for the *cis* to *trans* isomerization.⁴ Thompson and Ford¹ have indicated that

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Table I. ^1H Chemical Shifts (δ) and J_{HH} Values (Hz) for Neopentylallyl Salts in Tetrahydrofuran ($\sim 10^\circ\text{C}$)^{a,d}

cation/proton	(CH ₃) ₃	δ	γ	β	α	$J_{\alpha\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
Li	0.86	1.80	3.16	6.14	1.09	10.7	9.8	6.4
	(0.75)	(1.76)	(3.34)	(6.02)	(1.34)	(11.2)	(13.2)	(6.8)
Na	0.88	1.88	2.74	6.32	1.48	10.8	9.0	6.1
	(0.71 ₅)	(1.73)	(3.42)	(6.20)			(13.2)	(6.7)
K	0.91 ₅	<i>b</i>	2.52	6.13	<i>b</i>	10.0 ^c	8.6	6.0
	(0.72 ₅)	(1.81)	(2.96)	(6.00)	<i>b</i>	(11.4)	(12.8)	(6.6)

^a Reference Me₃Si, directly for K, via δ_{THF} 1.73 for Na and Li. ^b ~ 1.73 ppm, obscured by solvent. ^c Average of δ 14.0 and 8.0. ^d Upper values, cis isomer; values in parentheses, trans isomer. The lithium compound was also studied in diethyl ether. No trace of the coalescence of the γ -signal at $\sim -30^\circ\text{C}$ reported in ref 10 was observed. Trans \rightarrow cis isomerization (half-life ≈ 25 min at -30°C) is a possible explanation for apparent coalescence at this temperature if the sample is not pre-equilibrated.

metalation of *trans*-2-butene in THF at room temperature for 30 min yields only *cis*-crotylpotassium (Ib, R = CH₃, X = H, M = K⁺). On this basis the half-life time of the trans potassium compound was estimated to be considerably less than 30 min under these conditions. At -30°C in THF however allylic potassium compounds are configurationally stable over extended time periods.⁵ No coalescence of the cis and trans isopropyl proton doublets of (1-isopropylallyl)potassium (Ic, R = isopropyl, X = H, M = K⁺) was observed at 68°C in THF so that the isomerization rate is less than 3 s^{-1} at that temperature.¹

Qualitatively it is clear that, as emphasized by Schlosser,^{6,7} the potassium compounds have greater configurational stability than those of lithium although quantitative studies are lacking. Even less information is available on allylic sodium compounds. Indications of trans to cis isomerization proceeding at a measurable rate in THF at -40°C ⁸ for a compound where R is a polybutadiene chain appear to be the only data recorded. In addition, both solvent and nature of the alkyl group may have some effect on isomerization rates besides the cation effects. In heptane, for example, removal of a branching point in R further from the allyl moiety in an isoprenyllithium compound was found to lead to much more rapid isomerization rates.⁴

In order to begin a more systematic and quantitative study of isomerization rates of allylic alkali-metal compounds, (neopentylallyl)lithium, -sodium, and -potassium have been prepared in THF with a fraction of trans configuration as high as possible. Their isomerization rates to the cis form have been subsequently followed over a range of temperatures.

Experimental Section

The preparation of (neopentylallyl)lithium by direct addition of near stoichiometric amounts of *tert*-butyllithium in benzene to butadiene has been adequately described.⁹ Hydrolysis followed by gas chromatographic analysis showed that it was $\sim 90\%$ the required compound, the rest being mostly dimer with a little trimer; the trans/cis ratio is approximately 3/1. The hydrocarbon solvent was removed in vacuo and replaced at low temperature with THF added slowly from the vapor phase in order to retain as far as possible a preponderantly trans configuration.

(Neopentylallyl)sodium was prepared from the lithium compound by treatment with sodium 2,2-dimethyl-1-butoxide in benzene as described by Glaze and co-workers.¹⁰ Careful repeated washing of the precipitated sodium compound reduced the lithium content to ~ 1 mol % (flame atomic absorption spectrometry).

From the isomerization rates of the two compounds, it can be calculated that this residual lithium content would contribute, in the worst possible case, 5% to the rate of isomerization of the sodium compound. The precipitate was transferred to THF at low temperatures. Some loss of trans configuration was produced in the manipulations (% trans 45–50). (Neopentylallyl)potassium was prepared from *trans*-5,5'-dimethyl hexene-2 and ((trimethylsilyl)methyl)potassium by a modification of the procedure of Thompson and Ford.¹ The ((trimethylsilyl)methyl)potassium was prepared by the reaction of a fivefold excess of potassium in the form of a mirror with bis((trimethylsilyl)methyl)mercury (Tridom Chemical) in cyclohexane. Immersion of the vessel in an ultrasonic bath for 10–15 min was found to be helpful in promoting reaction followed by stirring for at least 12 h. A final heating to 80°C for 5–10 min helped to coagulate smaller particles and hence induce better filtration. After solvent removal, THF and a small excess of alkene were added at -78°C . A slow two-stage filtration through medium grade fritted disks was used below -60°C to remove insoluble material. The metalation process has a half-life of ~ 6 h at -78°C . All three preparations were carried out in greaseless high vacuum systems using break-seal techniques, the products being stored at -78°C in ampoules for further use.

The isomerization of the lithium compound was followed by the decrease in optical density at ~ 340 nm. The trans form has an appreciably higher extinction coefficient than the cis form at this wavelength.⁸ Lithium concentrations were $\sim 10^{-2}$ M for this type of experiment. The isomerization of the sodium and potassium compounds were followed by ^1H NMR spectroscopy in a Varian XL-100 instrument. Concentrations in this case were considerably higher (~ 0.5 M). Integrals of the cis and trans γ signals could be used, but it was found that better accuracy could be obtained from measurements of the two *tert*-butyl signals which are stronger and well resolvable. Probe temperatures were calibrated by using the standard method involving the temperature dependence of the frequency difference between the ^1H signals of methanol.

Results

The ^1H NMR spectra of (neopentylallyl)lithium¹¹ and sodium¹⁰ in THF have been presented earlier by Glaze and co-workers. Table I summarizes the data obtained in the present investigation which includes the parameters of the potassium compound, not previously reported. The chemical shifts of the former compounds are in general agreement with earlier results. Access to a Bruker 400-MHz NMR instrument allowed a better estimate than previously possible of the equilibrium fraction of cis structures in the case of the lithium compound. It was found to increase from 0.54 at 30°C to 0.70 at -30°C ($\Delta H_{\text{tc}}^\circ \approx -1.6$ kcal mol⁻¹; $\Delta S_{\text{tc}}^\circ \approx -5$ cal/K). The cis fraction of the sodium compound, however, only varied between 0.78 and 0.82 at four temperatures between $+10^\circ\text{C}$ to -40°C with no discernible trend. Glaze reported similar values between -7°C and -31°C but a decrease to 0.55 by -77°C .¹⁰ As the equilibration process for this

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Table II. Observed Overall Rate Constants (s⁻¹) for Isomerization of Neopentylallyl Salts in Tetrahydrofuran

		-49	-45	-42	-40.4	-37	-35	-29	-29
Li	T, °C								
	10 ⁴ k _{obsd}	1.2	1.97	2.83	3.28	4.82	7.76	12.1	18.1
Na	T, °C	-41.7	-35.5	-25.7	-18.9				
	10 ⁴ k _{obsd}	0.38	0.89	4.27	10.4				
K	T, °C	-5.8	-0.4	+0.3	+3.0	+12.0	+19.0	+25.0	+26.5
	10 ⁴ k _{obsd}	0.165	0.378	0.327	0.48	1.77	5.0	11.2	13.5

compound, as will be seen later, becomes extremely slow below -40 °C, estimates at lower temperatures should be regarded with suspicion. The equilibrium cis fraction of the potassium compound was similarly invariant at 0.79 ± 0.02 over the temperature range +25 to 3 °C. A previous ¹³C NMR study¹² reported no detectable fraction of trans structures at -20 °C (i.e., <10%). Again problems of equilibration arise at this temperature although it is possible that the cis fraction does increase modestly at lower temperatures. (*n*-Butylallyl)potassium, studied over a larger 80 degree temperature range did indeed show this effect which seems to be general for THF solutions of these compounds.

Rotation of the α-methylene group on warming was observable with all three compounds as evidenced by coalescence of α-CH₂ signals and changes in the β-CH region. Exact coalescence temperatures were not determined but can be estimated roughly as -45 °C (Li⁺), -15 °C (Na⁺), and >+40 °C (K⁺) for the cis forms and <-80 °C (Li⁺), -45 °C (Na⁺), and -15 °C (K⁺) for the trans forms. The higher rigidity of cis forms and decrease of mobility of the terminal group as counterion size increases have been noted before for similar compounds.^{1,3,13}

The results on isomerization rates are given in Table II and Figure 1. The observed first-order constant *k*_{obsd} describing approach to equilibrium

$$\text{trans} \xrightleftharpoons[k_{ct}]{k_{tc}} \text{cis} \quad ([\text{cis}]/[\text{trans}])_{\text{eqbm}} = K$$

are related to the forward and back rate constants in the following way: *k*_{tc} = *k*_{obsd} *K*/(*K* + 1); *k*_{ct} = *k*_{obsd}/(*K* + 1); *k*_{obsd} = *k*_{tc} + *k*_{ct}. *k*_{tc} values are plotted; since equilibrium favors the cis structure, then these rate constants are only 20–35% lower than *k*_{obsd}. Large differences in isomerization rates are evident with different counterions, half lives of 10 min for example are attained at temperatures of -30 °C (Li⁺), -16 °C (Na⁺), and +27 °C (K⁺). The activation energy increases noticeably in the same series being 13.7 (Li⁺), 17.2 (Na⁺) and 22.2 (K⁺) in kilocalories per mole. In a parallel fashion the preexponential factor increases, being ~10⁹ (Li⁺), ~10¹¹ (Na⁺), and ~10¹³ (K⁺).

Discussion

Perhaps the most striking feature of the results is the rough parallelism between the trans → cis isomerization rates and the ease of rotation of the terminal methylene group. Both are most facile with lithium and the least so with potassium. This suggests that some general phenomenon promotes both processes although of course, end CH₂ rotation is always more rapid at a set temperature. It has been suggested that delocalization of negative charge from α- to γ-positions increases with counterion size,¹² in which case one would expect an inverse correlation since the αβ bond order would increase and that of the βα bond would decrease in the series. This is obviously not the case, so that no static picture involving bond orders of this or similar type will suffice. Measureable *k*_{tc} values begin to

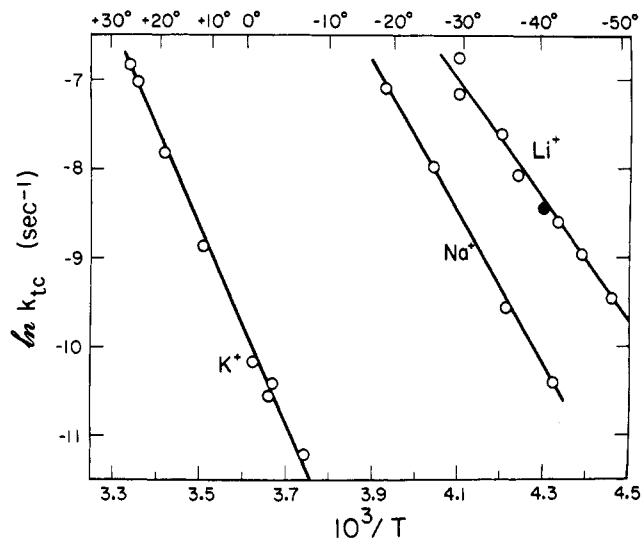


Figure 1. Arrhenius plots of the trans → cis isomerization rate constants of neopentylallyl salts in tetrahydrofuran. *k*_{tc} was calculated from *k*_{obsd} by using average *K*/(*K* + 1) factors of 0.7 (Li), 0.8 (Na), and 0.8 (K). The closed symbol refers to the presence of lithium tetraphenylborate.

be attained in all three cases just above the coalescence temperature for terminal methylene rotation of the trans species; i.e., *k*_{rot} ≈ 10–100 s⁻¹. The isomerization rate constants are, however, many orders of magnitude lower at this point (*k*_{tc} ≈ 2 × 10⁻⁵ s⁻¹). It is, therefore, not surprising that coalescence of the NMR signals attributed to cis and trans isomers has never been observed up to ~80 °C. Despite these very large differences in rate the barrier for both processes decrease in the order K > Na > Li. The present measurements show that not only does the activation energy decrease in the presence of smaller cations but also the preexponential factor falls. In particular, with lithium as the counterion an appreciably negative entropy of activation was measured (~-15 eu). This might suggest that in the transition state, partial removal of the lithium cation and hence its increased solvation are important. Experiments to be reported later, however, in which the *tert*-butyl group is replaced, show an increase of nearly 100 in the preexponential factor. It seems, therefore, that this particular phenomenon is only a characteristic of the model system chosen. Little is known of the magnitude of *A* factors for the related methylene rotation for data are invariably reported as free energies of activation (essentially rate constants at one fixed temperature). Only a preliminary estimate for allyllithium suggests a near normal preexponential factor.¹⁴ Δ*H*[‡] and Δ*S*[‡] (or *A* and *E*) values derived from NMR line-shape analysis around the coalescence temperature are however known to be rather inaccurate.¹⁵

Thompson and Ford¹ have discussed two plausible mechanisms for terminal CH₂ rotation. In both, the alkali-metal cation moves from a near central position over the allyl anion toward a methylene group by either

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maintaining electrostatic bonding or converting to a localized σ C–Li bond. The cation is then able to rotate around the essentially single adjacent $\alpha\beta$ carbon bond with the methylene group finishing on the opposite side of the $C_1C_2C_3$ plane. Methylene rotation while the cation remains near the same position (but presumably somewhat further from the plane) was excluded on grounds of unfavorable energetics. If the same mechanism is valid for cis–trans rotation in 1-substituted allyl anions, cation movement toward the substituted terminal must be much less energetically favored. Certainly although the rates are very different, the trends with cation size suggest quite similar mechanisms. It is possible that both result from higher cation vibrational levels involving oscillation along the anion plane, i.e., roughly above the C_1 – C_3 axis. Evidence for this type of cation vibration has been presented for radical anions of pyracene,¹⁶ acenaphthene,¹⁷ and even naphthalene.¹⁸ Schleyer²¹ has described in a similar manner, the lowest cation vibrational state as a “swinging motion” between C_1 and C_3 . In terms of such mechanisms, steric hindrance by the neopentyl group to movement of a tight but peripherally solvated lithium cation could occur. In any case, the activation energy for the less bulky substituted derivative is largely unchanged. The fundamental reason for increasing barriers for larger counterions is not clear even for CH_2 group rotation. The present study may be of some value in clarification of the problem if the same mechanism is followed in the two cases. The latest *ab initio* molecular orbital calculation of the rotational barrier in the free allyl anion is about 22 kcal mol⁻¹.²¹ This estimate should be appropriate to the real allyl anion in solution for solvation and aggregation are unlikely to be important for the anion in THF. The observed barriers of its alkali-metal derivatives in solution are all lower, tending to this value as cation size increases and interaction with the anion weakens. This would suggest that “lithium–allyl attachment in the rotational transition state”²¹ is particularly effective in that case in lowering the barrier. Solvation and/or aggregation of allylmetal compounds could make calculated barriers quite inaccurate. Aggregation in particular was suggested to be important in lowering the rotational barrier of allyllithium.²¹ If however cis–trans rotation follows the same mechanism, it is unlikely to be important, since the present measurements on substituted allyllithium were carried out at 10⁻² M rather than ~1 M, where ion-pair aggregation is less likely to occur. Yet this has a very low barrier. This conclusion is reinforced by the implication in ref 14 that the CH_2 rotational barrier of allyllithium is much the same in diethyl ether as in tetrahydrofuran despite the much more extensive aggregation in the former solvent. Preliminary experiments on cis–trans isomerization of (1–

neopentyl–2–methylallyl)lithium in the two solvents confirm that this barrier also is not very different in the two solvents.

It will be noted that although the lithium derivatives were studied at 10⁻² M concentration, the others were studied at much higher concentration in the 0.5–1 M range. End CH_2 group rotations are, of course, always measured in the high concentration range. Ion-pair aggregation can be assumed to be less of a problem with the sodium and potassium compounds although perhaps triple-ion effects should not be completely dismissed. The possibility that ionization is important is not high if indeed rotational barriers are higher in the free anion. Ionic dissociation constants are of the order of 10⁻¹⁰ in THF,^{19,20} so that the free anion would have to be appreciably more labile than the ion pair to produce a measurable effect on rates. This is confirmed by the absence of any effect of lithium tetraphenylborate on the rate of isomerization of (neopentylallyl)lithium.

Contributions from a free anion process could be more likely with the potassium compounds where rates are much lower, and the measured barrier is close to the theoretical value for the anion. A few experiments at ~0 °C were made on (neopentylallyl)potassium by using UV–visible spectroscopic techniques at ~10⁻² M and 3 × 10⁻³ M. Cis and trans forms have appreciably different absorption maxima ($\lambda_{\max}^{\text{cis}} = 314$ nm; $\lambda_{\max}^{\text{trans}} = 344$ nm) which enables good rate measurements to be made. The addition of potassium triphenylcyanoborate was also studied. Two experiments at 10⁻² M gave the same rates with or without ionization suppressant present ($k_{\text{ic}} \approx 2.6 \times 10^{-4}$ s⁻¹), i.e., approximately 10 times faster than observed in NMR experiments. At a concentration of 3 × 10⁻³ M, k_{ic} was measured as 2.3 × 10⁻⁴ s⁻¹ in the presence of salt but 6.5 × 10⁻⁴ s⁻¹ in its absence. Erratic (faster) rates even at the higher concentrations necessary for NMR measurements were, in fact, observed from the first trial metalations of an olefin, 2-heptene. The technique of heating the cyclohexane suspension to 80 °C to coagulate the solid matter produced from the olefin and mercury compound was found to be the key step in obtaining reproducible rate measurements. This may be related to earlier observations of an extremely fine suspension of potassium/mercury amalgam in the final THF solutions. Some catalysis of isomerization by this or other artifacts of the metalation process is therefore also possible if the procedure above is not followed. The increase in measured rate constant on dilution is, however, more likely to be caused by some changes in the form of the ionic species in solution on dilution. The overall isomerization rate differences between the different alkali-metal derivatives are so great, however, that the order K < Na < Li would always remain.

Acknowledgment. We are grateful to Dr. P. Lachance for his preparation of *trans*-5,5-dimethylhexene-2.

Registry No. (Neopentylallyl)lithium, 39056-16-1; (neopentylallyl)sodium, 57741-08-9; (neopentylallyl)potassium, 102493-39-0; sodium 2,2-dimethyl-1-butoxide, 57741-07-8; *trans*-5,5-dimethylhexene-2, 39782-43-9; ((trimethylsilyl)methyl)potassium, 53127-82-5; bis((trimethylsilyl)methyl)mercury, 13294-23-0.

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