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Rotational Barriers of Allyl Anions in Solution

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Abstract: Barriers to rotation about the carbon-carbon bonds of allylalkali metal compounds in THF have been measured by NMR exchange rates of the terminal allyl protons: $\Delta G^{\ddagger}$, kcal/mol (coalescence temperature, °C), = 10.7 ± 0.2 (−51) for allyllithium, 16.7 ± 0.2 (68) for allylpotassium, and 18.0 ± 0.3 (68) for allylcesium. The barrier for allylcesium is a new experimental lower limit to the rotational barrier of a free allyl anion in solution. Barriers to rotation about carbon-carbon bonds of 2-methylallylpotassium, (*Z*)-1-methylallylpotassium, and (*Z*)- and (*E*)-1-isopropylallylpotassium also have been measured. The (*Z*)-1-alkyl groups have little effect on C_2–C_3, but the (*E*)-1-isopropyl group decreases the C_2–C_3 barrier by 2.7 kcal/mol. Both (*Z*)- and (*E*)-1-alkyl groups increase markedly the barrier of C_1–C_2. Mechanisms of bond rotation are discussed in terms of the role played by the cation.

The allyl anion is particularly important because it is the simplest delocalized carbanion. Experimental data concerning the structure and bonding of the allyl anion would contribute to our understanding of the delocalized π bonding in many organometallic compounds and ion pairs. In particular, a measurement of the electronic barrier to rotation about the carbon-carbon bond would provide a direct measure of the π resonance energy, if the influence of the cation could be factored out. No results have yet been presented which can confidently be taken as an estimate of the rotational barrier of the simple allyl anion in solution.

The temperature-dependent NMR spectrum of allyllithium in THF (tetrahydrofuran) and diethyl ether solutions, reported in 1968 by West, Purmort, and McKinley,[2] established the delocalized structure of the anion. Similar NMR behavior has been reported for 1-methylallyllithium[3] (2-buten-1-yllithium[4]). The allyllithium barrier ($\Delta G^{\ddagger}{}_{-50}$ = 10.7 kcal/mol), however, cannot be taken to represent the rotational barrier of the allyl anion because of the important role played by the lithium counterion. The barrier to rotation about the C_2–C_3 bond of 1-phenylallyl anion varies from 15.7 kcal/mol with Li^+ counterion in ether to greater than 20 kcal/mol with K^+ counterion in THF.[5] There is a similarly high barrier of 18.9 kcal/mol to rotation about the C_2–C_3 bond of 1-phenyl-3-methylallylpotassium in liquid ammonia.[6] Such cation dependence is also evident in pentadienyl and benzyl anions. Exchange of the terminal methylene protons of pentadienyllithium in THF occurs with a coalescence temperature of 30 °C,[7] from which we can calculate an approximate barrier of 15 kcal/mol. In contrast, the slow-exchange NMR spectrum of pentadienylpotassium remains sharp up to 50 °C, and qualitatively the exchange barrier increases as the radius of the alkali counterion increases, Li < Na < K < Rb ≃ Cs.[8] Increased barriers upon substitution of K^+ for Li^+ have been reported for phenyl rotation in the benzylic 2-phenyl-4,4-dimethylpent-2-yl anion[9] and in related compounds.[10] Complete NMR line-shape analysis of spectra of the (1-naphthyl)methyl anion has shown that the barrier to rotation about the naphthyl-CH_2^- bond increases in the same order: Li^+ (12.9 kcal/mol), Na^+ (14.8 kcal/mol), K^+ (17.8 kcal/mol).[11] The class of 1,3-diphenylallyl anions contradicts this general trend, showing either no cation dependence[12,13] or even partially inverted order.[14d] These ions, however, are more extensively delocalized than the other examples, and there is good evidence that the lithium compounds exist as solvent-separated ion pairs in THF, whereas the sodium and higher analogues are contact ion pairs.[14]

Theoretical calculations likewise indicate that the rotational barrier for the allyl anion should be larger than the 10.7 kcal/mol observed for allyllithium. A recent estimate of the resonance stabilization of the allyl anion, based on the electron affinity of the allyl radical, gave 14.5 kcal/mol as a lower limit.[15] Two independent ab initio molecular orbital calculations using minimal basis sets gave rotational barriers of 25[16] and 29 kcal/mol.[13a] Empirical molecular orbital calculations are less in agreement: CNDO/2 calculations gave 44 kcal/mol[17] while MINDO/3 gave 11 kcal/mol.[13a] Hoffmann[18] has argued that the rotational barrier for the allyl anion should be larger than for the radical or cation, and experimental evidence for 1-*tert*-butylallylpotassium[19] and 1,3-diphenylallyllithium[20] suggests lower barriers for the corresponding radicals. Since recent work indicates a lower limit of 17 kcal/mol for the allyl radical[21] and 18.0 kcal/mol has been measured for 1,1,3,3-tetramethylallyl cation,[22,23] this argument further supports a higher allyl anion barrier.

In this paper we report direct experimental evidence for a new lower limit to the rotational barrier of the allyl anion in solution and for the effects of 1-alkyl groups on barriers to rotation in allylpotassium.

Experimental Section

Air- and moisture-sensitive compounds were prepared, handled, and stored in argon in a drybox (Vacuum Atmospheres Corp.) or in benchtop glassware. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl. Hydrocarbon solvents and THF-d_8 (99% D, Merck Sharp and Dohme) were stored over sodium wire. ¹H

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NMR spectra at 60, 100, and 220 MHz were recorded on Varian Associates A-60A, HA-100, and HR-220 spectrometers, the latter equipped for pulsed Fourier transform mode by Transform Technology. Chemical shifts were determined relative to internal Me_4Si, or relative to solvent peaks of known chemical shift. Probe temperatures were determined before and after every spectrum using methanol or ethylene glycol.[25] ^{13}C NMR spectra were recorded on a Varian Associates XL-100 or a JEOL FX-60 spectrometer.

Static and dynamic NMR spectra were simulated on an IBM System/360-75 computer using the programs DNMR2 and DNMR3.[26] Each experimental spectrum was visually matched with simulated spectra (vertically scaled to match peak heights) on a light table. The value of T_2 was determined for each allyllithium and -potassium spectrum from the width of the nonexchanging outer lines in the H_x signal. For other compounds, T_2 was estimated from line widths in the slow-exchange-limit spectra, and checked by treating it as a variable in some of the simulations. The error limits quoted in Table II for $\Delta G^{\ddagger}{}_T$ are based on $T \pm 2$ °C and on the error in k determined by the closest calculated spectra which were clearly distinguishable from the best fit to the experimental spectrum.

Allyllithium. The white powder precipitated from pentane by the reaction of *n*-butyllithium (22 mL of 2.0 M in hexane, Ventron) with tetraallyltin[27] (5.66 g, 20 mmol, Ventron) contained up to 20% *n*-butyllithium. Allyllithium was prepared free of *n*-butyllithium by a variation of this procedure in which the reaction was carried to completion in ether, solvent was removed under vacuum, the resulting oil was triturated with pentane, and allyllithium was filtered off.[28]

The 1:1 complex of allyllithium with tetramethylethylenediamine (TMEDA) was prepared by metalation of propene with *sec*-butyllithium-TMEDA.[29] A serum-stoppered, thick-walled glass tube was charged with *sec*-butyllithium (5.0 mL of 2.0 M in hexane, Ventron), TMEDA (1.14 g, 9.8 mmol, Aldrich, distilled from CaH_2 and stored under nitrogen), propene (0.63 g, Linde), and pentane (5.0 mL). The tube was cooled in liquid nitrogen, sealed with a flame, allowed to warm to room temperature on a shaker for 30 min, and shaken for 10 min in a hot-water bath at 50 °C. The tube was opened in the drybox and the product was filtered and washed with pentane.

Allylpotassium. A. From Trimethylsilylmethylpotassium (TMSK) and Propene.[30] Potassium sand was prepared by melting a freshly cut piece of potassium (0.33 g, 8.4 g-atoms) under mineral oil in a serum-stoppered glass tube vented to an argon line and agitating with a vortex mixer. After cooling, the mineral oil was replaced by 5 mL of pentane, and bis(trimethylsilylmethyl)mercury[31] (1.30 g, 3.5 mmol) was added. After 15 min the finely divided black solid was washed with pentane, and propene (2.0 mL, 1.3 g, 30 mmol, Linde) was condensed into the tube cooled by dry ice. The tube was sealed, agitated at room temperature overnight, and opened in the drybox. The solids were filtered, washed with pentane, dried, and extracted with 1 mL of THF-d_8. The solution was filtered into an NMR tube, which was stoppered, removed from the drybox, and sealed. Satisfactory variations on this procedure included (1) bubbling propene through the suspension of TMSK in pentane overnight or (2) drying the solid TMSK, dissolving it in THF at −78 °C, condensing propene into the solution, and keeping the mixture at −20 °C for 5 h.

B. From Allyllithium and Potassium Menthoxide.[32] In the drybox, a solution of potassium menthoxide[33] (4.19 g, 21.5 mmol) in 20 mL of diethyl ether was filtered into a 50-mL flask containing a magnetic stirring bar. As a solution of allyllithium (1.00 g, 20.8 mmol) in 20 mL of ether was filtered into this with stirring, the solution turned orange and allylpotassium precipitated as a yellow powder (0.67 g, 40% yield). Analysis of a hydrolyzed sample by atomic absorption spectroscopy gave a ratio Li/K = 0.002 by weight.

Allylcesium. Trimethylsilylmethylcesium was prepared by the reaction of bis(trimethylsilylmethyl)mercury[31] (1.9 g, 5.1 mmol) with cesium (1.35 g, 10.2 mg-atoms) in pentane. Propene was bubbled through the resulting suspension overnight at room temperature. The pentane was removed under vacuum and the solids were extracted with THF to give a red solution, which was filtered and concentrated under vacuum. Addition of a large excess of ether gave a purple precipitate (0.76 g, 44% yield) which was not completely soluble in THF. The precipitate was triturated with THF-d_8 and the filtrate from this mixture was used for NMR studies.

2-Methylallylpotassium. TMSK was prepared by the reaction of bis(trimethylsilylmethyl)mercury[31] (3.79 g, 10.1 mmol) with potassium-sodium alloy (2.64 g, 83% K by weight, 57 mg-atoms K) in pentane, which was then removed under vacuum. The TMSK was cooled in dry ice, 30 mL of THF was added, and isobutylene (3.5 g, 62 mmol, Linde CP grade) was distilled in. The mixture was kept at −78 °C for 41 h with occasional stirring and allowed to warm to room temperature. Addition of a large excess of diethyl ether to the filtrate from this mixture precipitated 2-methylallylpotassium (1.40 g, 74% yield). Atomic absorption spectroscopy gave a ratio Na/K = 0.005 by weight.

(*Z*)-1-Methylallylpotassium. TMSK (20 mmol) was prepared as for 2-methylallylpotassium, the pentane was removed under vacuum, 30 mL of THF was added at −78 °C, and *cis*-2-butene (1.8 g, 32 mmol, Linde CP grade) was distilled in. The mixture was kept at −78 °C overnight and allowed to warm to room temperature. After the solids had settled, the supernatant liquid was transferred to another vessel by syringe and THF was removed under vacuum. The resulting oil was crystallized and recrystallized from THF-ether at −10 °C, and the supernatant liquid was removed by syringe. The crystals were apparently a low-melting THF solvate of (*Z*)-1-methylallylpotassium, since they reverted to an oil or gum upon filtration at room temperature, upon removal of all the THF by washing with ether at −78 °C, or upon evacuation. Atomic absorption spectroscopy gave a ratio Na/K = 0.01 by weight.

In an attempt to capture the NMR spectrum of (*E*)-1-methylallylpotassium, the above procedure was repeated with 2 mmol of TMSK and *trans*-2-butene (Linde CP grade). The reaction mixture was kept at −78 °C for 3 days and quickly warmed to room temperature to dissolve the solid which had formed at −78 °C. After about 30 min at room temperature only (*Z*)-1-methylallylpotassium was detected in the NMR spectrum.

1-Isopropylallylpotassium. *cis*-4-Methyl-2-pentene (0.33 g, 3.9 mmol, Aldrich) was added to TMSK (2 mmol, prepared as for 2-methylallylpotassium) in 4 mL of THF at −78 °C. After 53 h at −78 °C it was centrifuged, the supernatant liquid was transferred to another vessel, and the solvent was removed under vacuum at room temperature overnight to give a red oil.

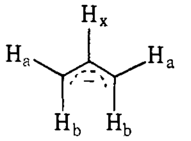
Results

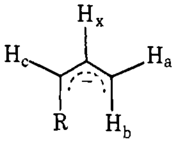
The static NMR parameters determined in this investigation are in Table I. The allyllithium parameters differ slightly from the previous report.[2] Ours are reproducible from sample to sample at 60 or 100 MHz and give significantly better fit to our experimental spectra than the previous parameters do. Line-shape analyses of allyllithium, -potassium, and -cesium used a three-spin ABX approximation to simulate only the signals for H_a and H_b. Temperature dependences of the chemical shift difference $\Delta\nu_{ab}$ were taken into account. The rate constant which most closely simulated each experimental spectrum was multiplied by two to account for symmetry.[34] The most meaningful parameter for comparison between compounds in this study is $\Delta G^{\ddagger}{}_T$, the free energy of activation at the coalescence temperature, reported in Table II. Our value for allyllithium is the same as that reported earlier.[2]

On the supposition that complexation of lithium would raise the exchange barrier for the allyl anion, we prepared the 1:1 complex of allyllithium and tetramethylethylenediamine (TMEDA). However, qualitative examination of its NMR spectrum in THF at −67 and −32 °C showed rates of exchange similar to those observed in the absence of TMEDA. Addition of hexamethylphosphoric triamide (HMPT), 15-crown-5 ether, or [2.1.1]cryptand to THF solutions of allyllithium resulted in rapid decomposition of the complexing agent. Line-shape analysis of a 60-MHz spectrum of allyllithium containing 20 mol % *n*-butyllithium in THF-d_8 gave $\Delta G^{\ddagger}{}_{-56} = 10.4 \pm 0.4$ kcal/mol, not significantly different from the barrier determined for a sample without butyllithium.

The ^{13}C NMR spectrum of allyllithium in THF was determined under a variety of conditions.[34] The chemical shifts of the two types of carbon atoms (C_1 51.7 ± 0.5 ppm, C_2 147.1 ± 0.6 ppm) proved to be remarkably independent of concentration from 0.2 to 2 M, of temperature from −84 to +63 °C, of the presence of TMEDA, and of change in solvent from THF to ether. Both the chemical shifts and the ^{13}C-H coupling constants agree closely with published values.[35]

Table I. ^1H NMR Chemical Shifts (ppm) and Coupling Constants (Hz) in THF-d_8





compd	δ_a	δ_b	δ_c	δ_x	J_{ab}	J_{ax}	J_{bx}	J_{cx}	J_{ac}
allyllithium	1.79	2.23		6.22	1.6	8.3	14.6		
allylpotassium	1.96	2.35		6.29	2.8	8.5	14.8		
allylcesium	2.19	2.09		5.90	2.7	8.5	14.6		
2-methylallylpotassium[a]	1.91	2.37			2.9				
(*Z*)-1-methylallylpotassium[b]	1.86	1.60	2.49	6.14	3.4	8.2	14.5	8.3	1.2
(*Z*)-1-isopropylallylpotassium[c]	*e*	*e*	2.53	5.97	~3.5	~9.1	14.5	~9.1	1.0
(*E*)-1-isopropylallylpotassium[d]	av 1.68		2.96	6.09	*e*	~8.8	~14	13.2	0.0

[a] δ_{CH_3} 1.69 ppm. [b] δ_{CH_3} 1.49; $J_{a\text{-}Me} \sim J_{b\text{-}Me} \sim 0.7$, $J_{c\text{-}Me} = 6.0$, $J_{x\text{-}Me} = 0.7$, $J_{bc} = 0.0$ Hz. [c] δ_{CH_3} 0.96. δ_{Me_2CH} 2.26 ppm; $J_{Me\text{-}CH} = 6.6$, $J_{c\text{-}CH} = 6.0$, $J_{x\text{-}CH} = 0.7$, $J_{bc} = 0.0$ Hz. [d] δ_{CH_3} 0.88, δ_{Me_2CH} 2.26 ppm; $J_{Me\text{-}CH} = 6.5$, $J_{c\text{-}CH} = 5.5$, $J_{x\text{-}CH} = 0.0$ Hz. [e] Could not be determined from available spectra.

Table II. Exchange Barriers of Allyl Anions in THF-d_8

compd	$\Delta G^{\ddagger}{}_T$ (T, °C),[a] kcal/mol
allyllithium[b]	10.7 ± 0.2 (−51)
allylpotassium[b]	16.7 ± 0.2 (68)
allylcesium[b]	18.0 ± 0.3 (68)
2-methylallylpotassium[b]	15.9 ± 0.3 (51)
(*Z*)-1-methylallylpotassium[c]	
(C_1-C_2)	18–22[d]
(C_2-C_3)	17.0 ± 0.3 (68)
(*Z*)-1-isopropylallylpotassium[c]	
(C_1-C_2)	>19.3 (68)
(C_2-C_3)	17.0 ± 0.3 (47)
(*E*)-1-isopropylallylpotassium[c]	
(C_2-C_3)	≲14.0 (28)

[a] Error limits based on the precision in matching calculated with experimental spectrum. [b] Determined at 100 MHz. [c] Determined at 220 MHz. Qualitatively the same results were observed on an independently prepared sample at 100 MHz. [d] Estimated. See text.

The exchange barrier in allylpotassium is 6.0 kcal/mol higher than in allyllithium. Its 60-MHz NMR spectrum is the AA′BB′X type at 13 °C. Similar kinetic behavior was observed with two independent samples, one prepared by metal exchange from allyllithium and the other by a lithium-free route (see Experimental Section). Exchange rates for the former are slightly faster at a given temperature. The sensitivity of the rate to small amounts of lithium was demonstrated by adding 10 mol % allyllithium to allylpotassium. This lowered the coalescence temperature to −9 °C, resulting in $\Delta G^{\ddagger}{}_{-9} = 13.1 \pm 0.5$ kcal/mol. Our ^{13}C NMR chemical shifts (C_1 52.8 ppm, C_2 143.9 ppm) for allylpotassium are practically identical with those reported previously.[36]

Allylcesium has an exchange barrier 1.3 kcal/mol higher than that of allylpotassium. The line-shape analysis was complicated by decreasing solubility of allylcesium in THF with increasing temperature, which caused important variations in $\Delta\nu_{ab}$. These were taken into account by treating $\Delta\nu_{ab}$ as an adjustable parameter in simulation of experimental spectra (Figure 1). The ^{13}C chemical shifts in allylcesium are C_1 59.1 ppm and C_2 144.2 ppm.

The spectrum of 2-methylallylpotassium in THF-d_8 at −10 °C was simulated by ignoring the methyl group, assuming $J_{ab'} = 0.0$ Hz, and treating the allylic protons as an AB system, using the parameters in Table I with $T_2 = 0.122$ s (line width = 2.6 Hz). Part of the line width is probably due to unresolved long-range coupling to the methyl group.

The NMR parameters of (*Z*)-1-methylallylpotassium in THF-d_8 in Table I were derived by careful analysis of 100- and 220-MHz spectra, including computer simulation of the static (−19 °C) spectrum by fragments and as a complete seven-spin system. The coupling J_{ac} has precedence in two different (*Z*)-1-phenylallylpotassium compounds.[37] The line-shape analysis of the H_x portion of the spectrum assumed an ABCX spin system with $T_2 = 0.133$ s (line width = 2.4 Hz) to approximate the broadening due to long-range methyl coupling.

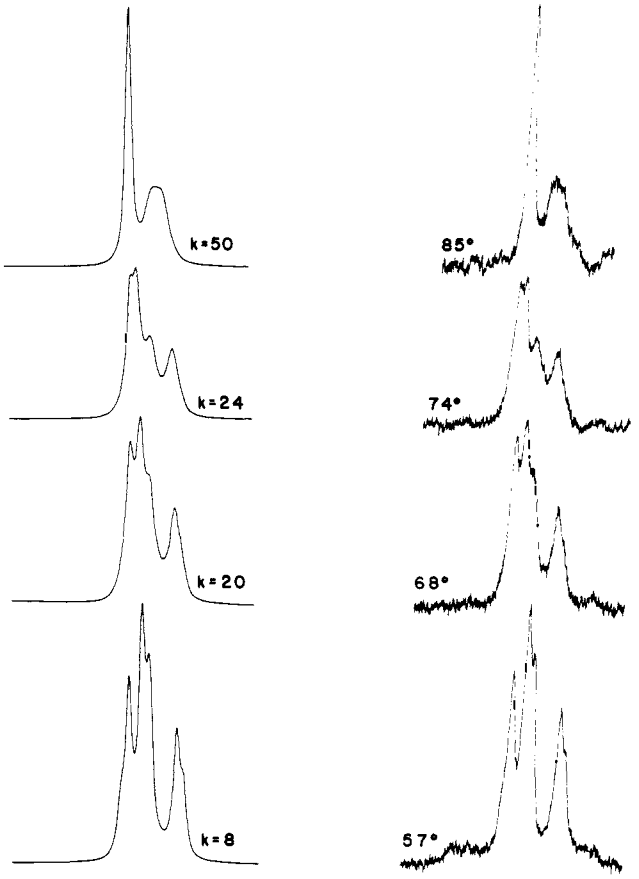


Figure 1. Temperature dependence of 100-MHz ^1H NMR spectrum of allylcesium in THF-d_8: experimental spectra (upfield portion, H_a and H_b) on right, calculated on left.

Although the barrier to exchange at C_1 of 1-methylallylpotassium could not be determined because the equilibrium concentration of the *E* isomer was undetectably low, upper and lower limits were estimated as follows. Since (*Z*)-1-methylallylpotassium is the only isomer present after metalating

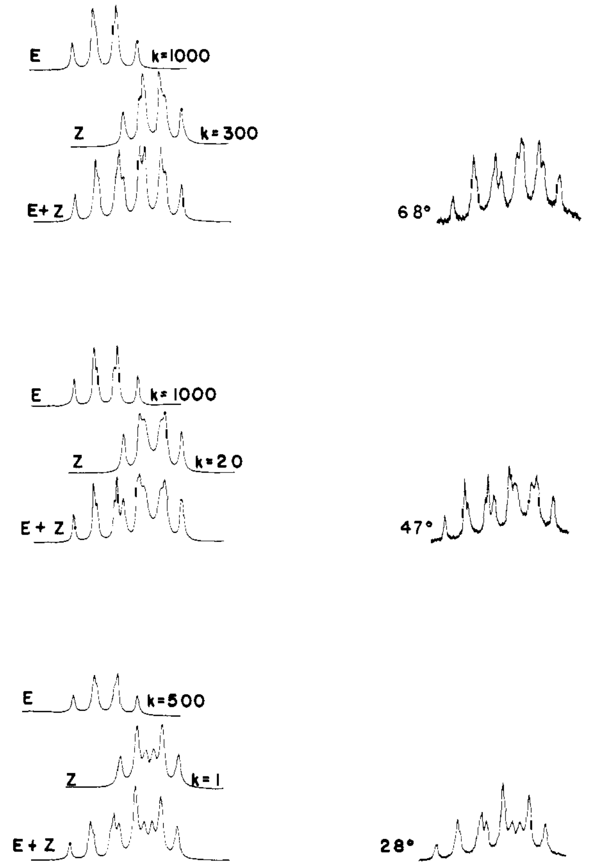


Figure 2. Temperature dependence of 220-MHz ^{1}NMR spectrum of (*Z*)- and (*E*)-1-isopropylallylpotassium (*Z*:*E* = 65:35) in THF-d_8: experimental spectra ($H_x(Z)$, δ 5.97; $H_x(E)$, δ 6.09 ppm) on right, calculated on left, analyzed into contributions from each isomer.

trans-2-butene and allowing it to stay at room temperature for 30 min, the half-life of the *E* isomer is less than that, and $\Delta G^{\ddagger}{}_{25} < 22$ kcal/mol. From Schlosser's[38] trapping of the *E* isomer at -20 °C we can estimate that its half-life is greater than 10 min at that temperature, and $\Delta G^{\ddagger}{}_{-20} > 18$ kcal/mol.

Unlike 1-methylallylpotassium, both (*Z*)- and (*E*)-1-isopropylallylpotassium were observed with *Z*:*E* = 65:35 at 28 °C in THF-d_8, based on integrals of the two sets of isopropyl doublets.[36b,39] The fact that these doublets do not show significant exchange broadening ($k < 3$ s^{-1}) up to 68 °C indicates that $\Delta G^{\ddagger}{}_{68} > 19.3$ kcal/mol for interconversion of the *Z* and *E* isomers. Some of the static NMR parameters (Table I) are uncertain because some signals were unresolved even at 220 MHz, and because we were unable to obtain sufficiently well-resolved spectra below 0 °C to establish the slow-exchange limit for the *E* isomer. The most interesting feature of this molecule is that the barrier to exchange of H_a and H_b in the *E* isomer is 3 kcal/mol *lower* than that in the *Z* isomer. Figure 2 shows the overlapping signals for $H_x(Z)$ and $H_x(E)$ in 220-MHz spectra. The H_x signal for each isomer was simulated separately, assuming ABCX spin systems, and the calculated spectra were added. The signal for $H_x(E)$ is a doublet ($J_{cx} = 13.2$ Hz) of triplets ($J = 11.4$ Hz, average of J_{ax} and J_{bx}), indicating a spectrum close to the fast exchange limit even at 28 °C. In contrast, the signal for $H_x(Z)$ at 28 °C is a doublet ($J_{bx} = 14.5$ Hz) of triplets ($J_{ax} = J_{cx} = 9.1$ Hz), and is close to the slow exchange limit. Upon heating to 68 °C, $H_x(E)$ merely sharpens a bit, while $H_x(Z)$ clearly goes through the same changes seen in (*Z*)-1-methylallylpotassium.[34]

Discussion

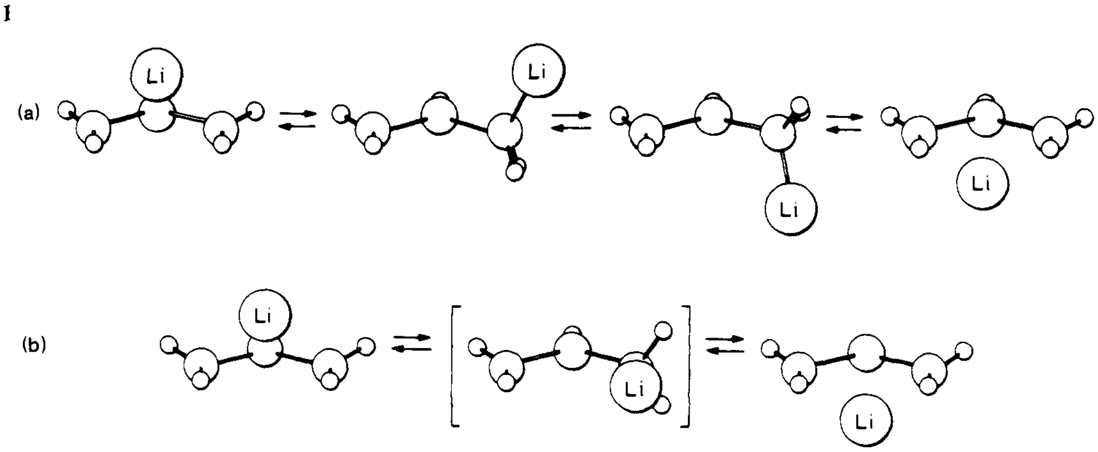
Our value of 18 kcal/mol for the rotational barrier of allylcesium sets a new lower limit for the barrier of the allyl anion in solution.

Analogies to all of the available literature on the nature of aggregation of delocalized organoalkali metal compounds in ether solvents, and our observations that the ^{13}C NMR chemical shifts and the rotational barrier of allyllithium are independent of solvent, indicate that the allylalkali metal compounds exist as contact ion pairs or higher aggregates in our NMR experiments. The tendency to form solvent-separated ion pairs decreases with increasing temperature, larger cations, and less delocalized anions.[40] Since the potassium salts of the more highly delocalized fluorenyl,[41-43] diphenylmethyl,[42,43] 1,3-diphenylallyl,[14] and benzyl[43] anions exist exclusively as contact ion pairs in THF at room temperature and above, we assume that allylpotassium and -cesium do also. It is likely that allyllithium is also exclusively a contact ion pair in THF, even at low temperatures. The ^{13}C chemical shifts of allyllithium vary by less than 1 ppm over a temperature range of 147 °C, and the slight downfield shift of both carbons with decreasing temperature is opposite to the direction we might expect for a transformation of contact ion pairs to solvent-separated ion pairs. The UV spectrum of allyllithium in THF and in ether is invariant from -100 to $+25$ °C,[2] which strongly implies only one type of ion pair over the entire temperature range. The observation of a significant proportion of contact ion pairs even with the more delocalized diphenylmethyllithium down to -50 °C[46] makes it unlikely that the single type of ion pair in allyllithium is solvent separated.

Although the aggregation state of allylpotassium has not been studied, allyllithium in THF is predominantly monomeric, with possibly some dimers.[44] We do not believe that the state of aggregation of allyllithium affects its rotational barrier. It is highly aggregated in diethyl ether,[2,28] but the barrier is the same in ether and THF.[2] Qualitatively the barrier in THF is not changed in the presence of TMEDA, which would be expected to suppress aggregation (although TMEDA is stated to be ineffective in converting contact to solvent-separated ion pairs).[40]

The barrier to rotation in allyllithium is abnormally low compared with allylpotassium and allylcesium. Its structure has been calculated at the INDO,[45] CNDO/2,[17] and ab initio SCF levels of approximation.[46,47] The most stable structure is symmetric and delocalized with lithium centered above the plane of the allyl anion and with significant bonding between allyl anion and lithium involving electron donation from the filled nonbonding allyl π_{nb} orbital into the empty Li 2p orbital of proper symmetry. If allyllithium exists as contact ion pairs, what is the fate of the lithium ion as the CH_2 group rotates? We can envision three formally distinct mechanisms: (a) In the σ-π exchange mechanism the lithium shifts from its preferred position centered over the allyl plane to form the C-Li σ-bonded structure in its calculated[46] preferred conformation and exchange occurs by rotation about the carbon-carbon single bond. (b) As the CH_2 group rotates, the lithium cation follows the rotating carbon, remaining associated with the nonbonding electrons as it passes through the plane at the transition state. Mechanisms (a) and (b) are depicted in Scheme I. (c) Lithium stays near the same position above the plane of the anion while the CH_2 group rotates. Mechanism (c) seems least likely since in the transition state the lone pair of electrons would lie in the C-C-C plane, without the stabilization of overlap with either the C-C π bond or the cation orbitals. As we have pictured the transition state in mechanism (b), it is consistent with the iconoclastic contention of Streitwieser[48] that there is *no* covalent bonding between carbon and lithium in methyl-, ethyl-, vinyl-, or ethynyllithium. Schleyer and co-workers[47] carried out careful ab initio calculations of

Scheme I

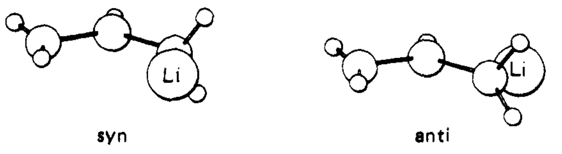


allyllithium with extended basis sets and were unable to find any σ-bonded structure that is a local energy minimum, providing theoretical evidence against mechanism (a). They calculated the rotational barrier through a syn or anti σ-bonded transition structure to be 16 or 18 kcal/mol, respectively (Scheme II). This is significantly lower than the value of 25–29 kcal/mol which has been calculated repeatedly for the allyl anion.[13a,16,20b]

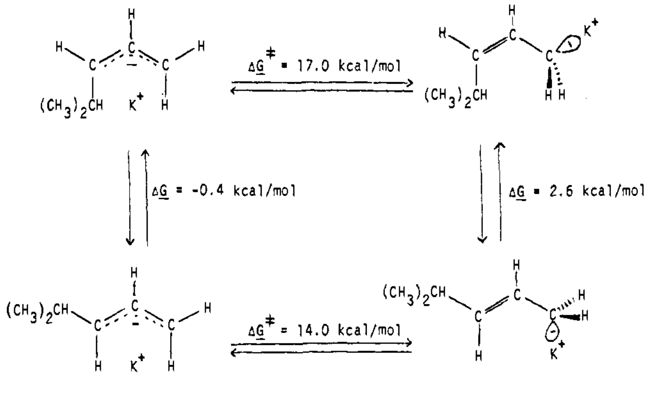
Our results are the first quantitative determination of rotational barriers in alkyl-substituted allylalkali-metal compounds. The anticipated effect of a C_1 alkyl group is to increase electron density at C_3 of the allyl anion, increase C_1–C_2 bond order, and decrease C_2–C_3 bond order. Support for this picture is found clearly in both the ^1H and the ^{13}C chemical shifts of pentadienyllithium in THF[49] and pentadienylpotassium in ammonia,[50] and in ^1H chemical shifts of 1-phenylallylpotassium compounds.[6,37,51] Curiously the addition of a (Z)-methyl group does not have this effect. This is consistent with our finding of a substantially higher C_2–C_3 rotational barrier for (Z)- than for (E)-1-isopropylallylpotassium. Both proton chemical shifts of (E)- and (Z)-1-methylpentadienylpotassium[50] and ^{13}C chemical shifts of 1-methyl-, -ethyl-, -isopropyl-, and -*tert*-butylallylpotassium in THF[36b] indicate that an (E)-1-alkyl group has a stronger charge-repelling effect than a (Z)-1-alkyl group. The chemical shift of the unsubstituted terminal carbon for each of the (Z)-1-alkylallylpotassium isomers is 45.5 ± 0.3 ppm, and that for each of the E isomers is 44.0 ± 0.5 ppm. The *downfield* shift of the Z isomers by 1.5 ppm relative to the E isomers is opposite the steric effect seen in alkenes, which usually moves the alkene carbons in a cis isomer 1.1 ppm upfield relative to the trans isomer.[52] This strongly suggests that the relative ^{13}C chemical shifts are controlled by an electronic through-bond effect rather than a steric or other through-space effect. Lower CH_2 rotational barriers for (E)- than for (Z)-alkyl-substituted allyl compounds have been reported qualitatively for polyisoprenyllithium[53] and 1-neopentylallylpotassium.[54]

Our finding of practically the same CH_2 rotational barrier for allylpotassium, (Z)-1-methylallylpotassium, and (Z)-1-isopropylallylpotassium is consistent with these earlier observations. The source of this phenomenon, though, is not clear. The thermodynamic preference of these compounds for the Z configuration in solution is thoroughly established experimentally,[36b,39] and is supported by CNDO/2[55] and ab initio SCF calculations of the 1-methylallyl anion.[56] This Z preference is usually explained by anionic hyperconjugation of the alkyl group,[18,57] notwithstanding one report of the opposite preference in the gas phase.[16] However, the higher CH_2 barrier in the (Z)-1-isopropyl isomer is not due to lowering of the ground-state energy of Z relative to E because the isomer ratio Z:E = 65:35 accounts for an energy difference of only 0.4 kcal/mol. The difference of 3.0 kcal/mol in activation energies means that the Z transition state is 2.6 kcal/mol *less* stable than the E transition state (Scheme III). If the cation follows the electron lone pair through the syn face of the allyl plane as pictured in mechanism (b) (Scheme I), then steric crowding between the alkyl group and the cation in the transition state for the Z isomer must be significant. But our finding that the magnitude of the barrier is independent of the alkyl group for the Z isomer is difficult to rationalize with this picture. As a more satisfactory explanation, we propose that the CH_2 group in the Z isomer rotates in the opposite direction, carrying the cation through the anti face of the allyl plane, away from the Z alkyl group (Scheme III). On the other hand, the (E)-1-isopropyl substituent on allylpotassium lowers the C_2–C_3 rotational barrier by 3 kcal/mol by pushing electron density toward C_3 and still permits the syn location of the cation in the transition state. This difference of 3 kcal/mol between syn and anti transition state energies is strikingly similar to the 2 kcal/mol calculated by Schleyer and co-workers for the difference between syn and anti transition-state energies for bond rotation in allyllithium[47] (Scheme II).

Scheme II



Scheme III



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References and Notes

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