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THE STEREOCHEMISTRY OF 1-ALKYLALLYLPOTASSIUM COMPOUNDS

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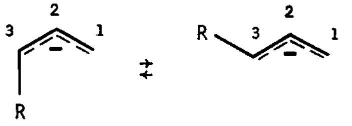
Proton magnetic resonance has been widely applied to study stereochemistry and rotational barriers of allyl Grignard reagents [1], allyl alkali metal compounds [2], and pentadienyl metal compounds [3]. Recently, Fourier transform carbon-13 magnetic resonance has added more detail for allyl and pentadienyl carbanions [4].

We wish to report the carbon-13 chemical shifts of a series of 1-alkylallylpotassium compounds. These carbanions were prepared by direct metalation of the corresponding 2-alkene (I) with trimethylsilylmethylpotassium in cyclohexane [5]. The cyclohexane was removed, the precipitated allylpotassium compounds dissolved in THF, and the carbon-13 spectra examined at 26° (eqn. 1).

$$RCH{=}CH{-}CH_3 \quad + \quad Me_3SiCH_2^-K^+ \xrightarrow[2.\ THF]{1.\ C_6H_{12}}$$

R = H, Me, Et,
= i-Pr, t-Bu
(I)



(IIa) (IIb) [1]

The carbon-13 chemical shifts are summarized in Table 1. Only one stereoisomer is observed for 1-methylallylpotassium (crotylpotassium). These resonances were assigned to the (Z) isomer (IIa). It has been proposed that the (Z) isomer is thermodynamically more stable than the (E) isomer (IIb) for crotyl carbanion based on extended Huckel calculations [6] and on evidence from base-catalyzed isomerization of olefins [7]. Further, proton and carbon-13 measurements have shown that the (Z) isomer dominates for crotyllithium [2i,4a] and for crotylmagnesium chloride [1e]. As the size of the alkyl substituent becomes larger in going to 1-ethyl and then to 1-isopropylallylpotassium, an increasing amount of the (E) stereoisomer is seen. For 1-tert-butylallylpotassium, only the (E) isomer (IIb) is observed.

Proton coupled spectra were used to differentiate the substituted allyl carbon, C3 (a doublet) from the terminal allyl carbon, C1 (a triplet). The terminal carbons were consistently upfield (17 to 41 ppm) from the substituted carbons, indicating that the terminal carbons bear substantially more negative charge [8]. With the assumption that crotylpotassium exists mainly

Table 1. Carbon-13 Chemical Shifts of 1-Alkylallylpotassium Compounds [a]

R	δ_{C1}		δ_{C2}		δ_{C3}		δ_R [b]
	IIa	IIb	IIa	IIb	IIa	IIb	
H	52.80		144.00				
CH_3	45.30	-	139.12	-	62.76	-	CH_3: 14.63
CH_3CH_2	45.77	43.53	137.49	141.06	73.68	75.17	CH_3: 16.05, 14.24 CH_2: 23.23, c
$(CH_3)_2CH$	45.52	44.12	136.78	139.12	80.97	81.61	CH_3: 24.14, 22.92 CH : 32.57, 31.79
$(CH_3)_3C$	-	44.22	-	136.63	-	84.94	CH_3: 34.33 C : 30.04

[a] Chemical shifts (δ) in ppm downfield from tetramethylsilane (internal); 0.5 M potassium salts in THF at 26°. Spectra obtained with JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer using ~1500 average transients. [b] Alkyl carbons not assigned to specific stereoisomers. [c] Obscured by upfield THF resonance.

as the (Z) isomer, chemical shift assignments for the (Z) and (E) isomers of 1-ethylallyl and 1-isopropylallylpotassium are easily made. The terminal carbons of the (Z) stereoisomers are consistently about one ppm downfield from the resonances of the (E) isomers, while the substituted and central allyl carbons of the (Z) isomers are upfield by a similar amount (Table 1).

Figure 1 shows the carbon-13 spectrum for 1-isopropylallylpotassium dissolved in THF. A resonance is observed for each carbon of the (Z) and (E) stereoisomers, showing that rotation about the C2-C3 bond (IIa $\rightleftarrows$ IIb) is slow on the carbon-13 time scale. Similar observations have been made for crotyllithium with both proton and carbon-13 measurements [2i, 4a]. These observations are in contrast with the results for 1-alkylallylmagnesium compounds in which rotation is rapid about the C2-C3 bond on the proton time scale even at -80° [1e]. Attempts to determine the activation barrier for 1-ethylallyl and 1-isopropylallylpotassium failed because no significant broadening had taken place at 50°, where reaction of the carbanion with solvent becomes rapid. However, it may be estimated that the activation barrier is greater than approximately 17 kcal/mol.

Isomer populations were estimated for 1-ethylallyl and 1-isopropylallylpotassium by measuring the area under the well-separated resonances of the C2 carbon and lead to the following distributions at 26°: R = Me (Z)/(E), 100/0; R = Et, 86/14; R = i-Pr, 65/35; R = t-Bu, 0/100 These values differ substantially from those reported for 1-alkylallylmagnesium compounds (R =

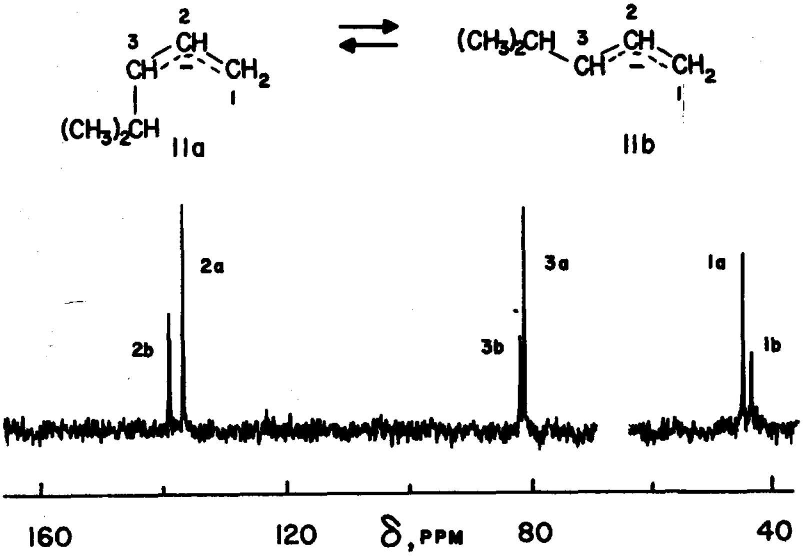


Figure 1. Allyl resonances of isopropylallylpotassium. Solvent and alkyl resonances not shown.

Me, 60/40; R = Et, 45/55; R = i-Pr, 30/70; R = t-Bu, 3/100) [1e], and for crotyllithium (R = Me, 90/10 [4a]; 85/15 [2i]). These differences probably reflect the sensitivity of the equilibria to the solvation state and size of the cation. It has been found previously that carbanions in which the negative charge is delocalized over much larger π-systems than allyl, such as fluorenyl [9, 10] and triphenylmethyl [10], exist as contact ion pairs when the cation is potassium. Therefore it is reasonable to assume that the allylpotassium compounds reported here exist as contact ion pairs in THF at 26°.

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