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ALLYL ALKALI METAL COMPOUNDS *

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Summary

Physical measurements, primarily high resolution nuclear magnetic resonance, support the contention that the allyl alkali metal compounds are ionic in solution but exist as intimate ion pairs or clusters. The sodium, potassium, rubidium and cesium compounds, when first formed at low temperatures, are in a more freely rotating form.

Introduction

Allylic alkali metal compounds are usually considered to be ionic in nature although reservations are sometimes made for the case of lithium [1—3] where rapidly equilibrating covalent structures have been suggested. Allyllithium itself has been studied by ^{1}H NMR [4] and on the basis of a change from an AX_4 to a AA'BB'X type spectrum at low temperatures in tetrahydrofuran (THF) assigned a delocalized ionic structure. ^{13}C chemical shifts for both allyllithium [3] and potassium [5] have also been determined in THF. More recently a study of rotational barriers in the lithium, potassium and cesium compounds has been reported [6]. A ^{13}C NMR study of the 5,5-dimethylhexen-2-yl and 2,5,5-trimethylhexen-2-yl compounds of a wide range of alkali metals in ether solvents was interpreted in terms of a delocalized ionic model involving increased charge equalization at α and γ positions as the size of the alkali metal increased [7]. With rubidium and cesium, however, small deviations from the main trend of chemical shifts were observed which must be attributed to other effects. The allyl anion itself is symmetrical so that end-to-end charge redistribution cannot play a role and so smaller effects for example produced by the field of the counter-ion might be more visible. For this purpose the series from allyllithium to allylcesium has been examined in THF.

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Experimental

All measurements and preparations of the alkali metal compounds were made in small glass vacuum apparatuses fitted with break-seals. The Na to Cs compounds were prepared by contacting diallylmercury in THF solution with an excess of a film of the appropriate metal in the following manner. A 100 ml flask was used having three side-arms. One provided with a break-seal contained diallylmercury, the second a 12 mm NMR tube and the third a distillation tube for the alkali metal. After evacuation, for example, 1 g ampoules of rubidium or cesium were distilled to cover a large part of the flask surface. THF (4 ml) was distilled into the flask which was then sealed-off and cooled to —20°C. The diallylmercury (~0.3 g) was then added and the flask was agitated at this temperature for about 30 min. The product was either filtered or decanted into the NMR tube which was then sealed-off and stored at —78°C until required. The lithium compound was prepared similarly using lithium oil emulsion that had been washed free of its oil.

The NMR measurements were made on a Varian XL 100 instrument with a Nicolet FT system and multinuclear probe, the UV spectra on a Cary 14 and the conductances measured with a Wayne Kerr B221 bridge.

The carbon-13 and deuterium labelled compounds were also prepared from the correspondingly labelled mercury compound. These were prepared with either ^{13}C or ^{2}H in one of the terminal positions starting from the appropriately labelled paraformaldehyde (Merck, Sharpe, and Dohme). The deuterated compound was used as received, but the ^{13}C compound (90% ^{13}C) was diluted with two times its weight of normal paraformaldehyde.

First vinylmagnesium bromide was prepared at 40°C by slowly adding 25 g vinyl bromide (dried over P_2O_5) dissolved in 75 ml THF to 6 g of Mg turnings in 50 ml THF, under N_2. This solution was rapidly cooled with strong mechanical stirring to —10°C to form a slurry of crystals, and 6 g of paraformaldehyde sublimed in slowly to maintain this temperature. After the addition, the solution was allowed to come to room temperature and the excess Grignard reagent destroyed with aqueous ammonium chloride. The reaction mixture was extracted four times with diethyl ether, the extract dried with sodium sulphate, and fractionally distilled to remove all the ether and some THF. The yield of allyl alcohol in the residual solution was 7.3 g by gas chromatography.

This THF solution of allyl alcohol was refluxed with 22 g of anhydrous $ZnCl_2$ and 13 ml conc. HCl for 1 hour. The mixture was then distilled until all the allyl chloride was recovered with most of the THF, following the distillation by gas chromatography. The rather wet solution was dried with sodium bicarbonate, sodium sulphate and finally calcium hydride. It was again distilled to recover a THF solution of allyl chloride (yield 5 g; 7 g before drying). This solution was used to prepare allylmagnesium chloride at room temperature from 3 g of Mg turnings. The Grignard solution was decanted from residual Mg, still under N_2, cooled to 0°C and a solution of 5 g $HgCl_2$ in 25 ml THF added slowly. Water was finally added to the solution, and the mixture extracted with petroleum ether. The extract was concentrated and the diallylmercury distilled under a full vacuum in a mini-distillation apparatus at 80°C (yield 4.5 g).

The ^{13}C NMR of the intermediate products showed that partial scrambling of the ^{13}C between the two end positions occurred in the preparation of allyl chloride, and this appeared complete in the allylmercury compound.

Results

The ^{13}C spectra of freshly prepared THF solutions of all the allyl alkali metal compounds showed only 2 lines in the ratio of 1 to 2. The end positions are identical as has been shown before for the Li compound in ^{13}C and ^{1}H spectra [3,4]. When first prepared, and always kept below —20°C, the allyl moiety is in a freely rotating metastable state with sodium, potassium, rubidium and cesium as counter-ions. This is evident from proton coupled ^{13}C and proton resonance spectroscopy. The magnetic resonance parameters for the freely rotating allyl species are listed in Table 1.

When these solutions were allowed to rise above the —20°C of their preparation, their proton spectra changed to the AA′BB′X type. This change was irreversible; on re-cooling, the AA′BB′X spectrum is always retained. During this changeover there did not appear to be any exchange, on the NMR time scale, between the species giving the two types of spectra. These results are illustrated in Fig. 1 for the low field proton in allylpotassium. The ^{23}Na resonance of an allylsodium solution in THF before and after warming briefly to +10°C showed a small difference in chemical shift (from 3.2 to 4.3 ppm upfield of saturated aqueous sodium chloride) but the linewidth at half height increased markedly from 440 to 810 Hz. Carbon-13 chemical shifts for the allyl species with hindered rotation (the stable form) are shown in Table 2 together with some C—C coupling constants obtained from ^{13}C enriched compounds. The data for the intermediates are also shown. ^{1}H NMR data of the compounds are given in Table 3.

The stable forms of allylsodium to -cesium showed evidence of rotation at higher temperatures. Allylsodium, after it had stabilized, showed a coalescence temperature (complete coalescence of the α-proton multiplet) at +5°C. The spectra taken between —40°C and +10°C were fitted to theoretical spectra [8], the exchange process being found to be consistent with separate rotations about the two C—C bonds. A concerted mechanism was ruled out. The activa-

TABLE 1

NUCLEAR MAGNETIC RESONANCE PARAMETERS FOR THE METASTABLE ROTATING ALLYL SPECIES FORMED INITIALLY

Cation	Na	K	Rb	Cs
$\delta(C_\alpha)$ [a]	49.3	52.7	61.3	63.3
$\delta(C_\beta)$	144.5	143.6	145.3	144.7
$J(C_\alpha—H)$ [b]	148.4	148.4	145.4	147
$J(C_\alpha—H)$ (long range)		7.0		6.5
$J(C_\beta—H)$	131.8	130.5	136.7	137
$\delta(H_\alpha)$ [c]	2.34	2.14	2.45	2.11
$\delta(H_\beta)$	6.38	6.23	6.07	5.85
$J(H_\alpha—H_\beta)$	11.1	11.4	11.4	11.6

[a] ^{13}C chemical shifts are in ppm to low field of TMS assuming δ(THF) = 26.2 ppm. [b] Coupling constants are in Hz. [c] ^{1}H chemical shifts are in ppm to low field of TMS assuming δ(THF) = 3.58 ppm.

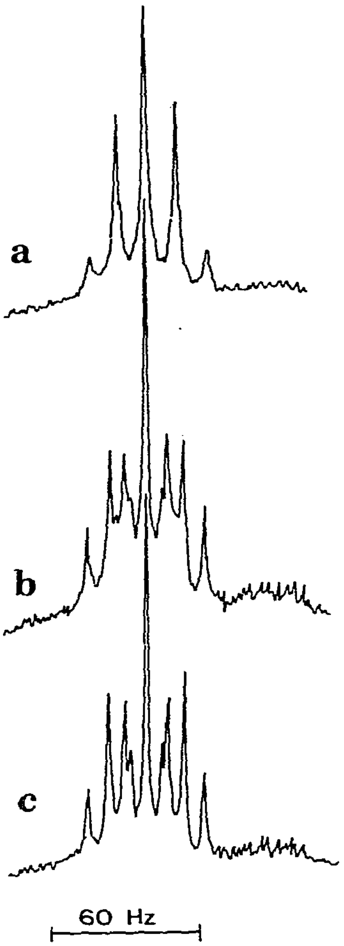

Fig. 1. The proton resonance spectrum at —20°C of the low field proton in allyl potassium. A, After 30 minutes; B, After 60 minutes; C, After 75 minutes.

TABLE 2

^{13}C CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR METAL ALLYL COMPOUNDS IN THF (STABLE FORM)

M	Li	Na	K	Rb	Cs	Hg	Cl	OH
δ_α	50.8	48.7	52.5	54.5	58.7	44.8	45.4	63.3
δ_β	146.0	145.1	143.8	143.9	143.8	140.0	134.9	139.4
δ_γ [a]						108.9	117.9	113.0
$J_{\alpha-\beta}$	—		—		—	42.2	45.3	45.2
	55.9		59.8		61.1			
$J_{\beta-\gamma}$	—		—		—	69.4	69.6	—

[a] Terminal positions equivalent in the alkali metal compounds.

TABLE 3

^{1}H RESONANCE PARAMETERS FOR THE STABLE FORM OF METAL ALLYL COMPOUNDS IN THF

Cation	Li [a]	Na	K	Rb	Cs
$\delta_{\alpha'}$	1.78 (1.79)	1.75	1.94	2.01	2.18
δ_{α}	2.24 (2.23)	2.53	2.32	2.26	2.04
δ_{β}	6.38 (6.22)	6.46	6.28	6.14	5.84
$J_{\alpha-\alpha'}$	1.6 (1.6)	2.6	2.6	2.4	2.6
$J_{\alpha-\beta}$	15.2 (14.6)	14.5	14.7	14.7	14.7
$J_{\alpha'-\beta}$	8.6 (8.3)	8.4	8.2	9.6	8.8
$J_{(C_{\alpha}H)}$ [b]	146 —	148	148	148.5	145
$J_{(C_{\beta}H)}$	133 —	132	131.8	131	132

[a] Figures from ref. 4, or (6) except for $J_{(CH)}$ values measured in the present investigation. [b] Mean values. For Rb individual α,α′ values of 154, 143 measured.

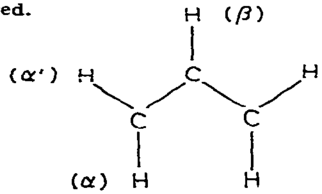

TABLE 4

UV MAXIMA AND EQUIVALENT CONDUCTANCES FOR ALLYL METAL COMPOUNDS IN THF AT 0°C. CONDUCTANCE MEASURED AT 10^{-3} *M*

M =	Li	K	Cs
λ_{max} (nm)	318	346	344
Λ (cm^2 Ω^{-1} M^{-1})	0.037	0.104	0.099

TABLE 5

^{13}C CHEMICAL SHIFT DIFFERENCE (*d*) OF THE CH$_2$ CARBON FOR ALLYL-d_2 METAL COMPOUNDS

M =	Li	Na	K
d (ppm)	0.56	0.44	<0.25
d/Δ	0.004	0.003	<0.002

tion energy determined was 11.5 kcal mol^{-1}. Similar experiments were carried out with allylpotassium, allylrubidium and allylcesium. With allylpotassium there was a coalescence temperature of slightly above 65°C, the activation energy being evaluated as 14.3 kcal mol^{-1}. The free energy of activation at 68°C was found to be 17.1 kcal mol^{-1}, in good agreement with that quoted earlier [6]. Allylrubidium at 70°C had the same lifetime as allylpotassium at 50°C. Theoretical spectra were not calculated for the rates of rotation of the hindered form of allylcesium since the small chemical shift difference between the non-equivalent protons would yield results of more limited accuracy.

The ultraviolet absorption spectra of the allyl compounds in THF were measured, and λ_{max} is recorded in Table 4. λ_{max} for the lithium compound is somewhat smaller than that for the higher alkali metals but within the range calculated for a delocalized structure [9]. Table 4 also reports the electrical conductances of the solutions of allylalkali metals. The dependence of equivalent conductance in no case followed the square root law expected from a dissociation of ion-pairs into free ions. Triple-ion formation was indicated at much lower concentrations than in substituted allylic compounds such as polyisoprenyllithium [10].

Discussion

From Tables 1 to 3 it is evident that as one proceeds along the series sodium to cesium, there is a shift downfield for C_α in both stable and metastable forms. The lithium compound, as is often the case, does not fit in the series. Very strong peripheral solvation would be expected to influence its properties. The chemical shift changes at H_β show the opposite trend with the H_α and H'_α shifts in the stable form moving in opposite directions but with little change in the mean position. There do not appear to be significant variations along the series for the other chemical shifts or coupling constants. All the C_α shifts are well upfield of the terminal sp^2 carbon in propene ($\delta = 115$ ppm) reflecting the large fraction of negative charge residing at the α-positions. C_β shifts vary slightly with alkali metal and in all cases are slightly downfield of the central carbon shift of propene. This situation differs from that observed in π-allyl complexes of transition metals [11,12] in that in the latter case β-carbons also are shielded relative to propene. The general order of C_α shifts is not that expected if an approach to the properties of the free anion is anticipated for large counter-ions. The downfield shifts observed with increasing counter-ion size could be interpreted as being caused by a decreased charge density at the α positions. In order to make an estimate of the C_α shifts with a separated pair, and hence only a small counter-ion effect, allylsodium was prepared and complexed at —60°C with the cryptand "2.2.2" (stability was poor at higher temperatures). The compound was in a freely rotating form at this temperature. The C_α resonance moved downfield only 3.5 ppm on complexing, to approach the position observed in allyl potassium or lithium. It is possible that with large diffuse counter-ions their polarization by the smaller centres of negative charge on the anion effectively reduces anionic charge. There is little difference in C_α shifts between the metastable and stable forms for the sodium and potassium compounds but more marked effects for rubidium and cesium. If some cation solvation is present with the smaller cations (although presumably not as much as with lithium) and absent for larger cations then the shifts might be less sensitive to the overall structure. A simple ion-pair is not indicated even at the low concentrations used for conductance studies so that at concentrations used for NMR measurements aggregation is sure to occur.

The $^1J(CC)$ coupling constants for the alkali metal series fall below the ~70 Hz values normally expected [13] for sp^2—sp^2 bonded carbons as shown by the α—β bonds of the two covalent compounds diallylmercury and allyl chloride. More recent studies have shown [14,15] that coupling constants appreciably below this value are obtained in delocalized systems where the π-bond order is less than unity. The coupling constants observed in the alkali metal series are consistent therefore with delocalized structures although not necessarily proof that these exist. Rapidly equilibrating covalent structures would also give mean values in the range 56—57 Hz as can be seen from the data on allyl chloride or diallylmercury. The $J(\mathrm{CH})$ constants, where measured, tend also to be lower than ~155 Hz expected for sp^2 carbons, especially that for the β-hydrogen. Values of $J(\mathrm{CH})$ between 137 and 157 Hz have been reported [13] for a number of delocalized aromatic anions; evidently other factors than hybridization are important in the determination of $J(\mathrm{CH})$.

The initial formation of freely rotating structures at low temperatures with the sodium to cesium compounds poses unresolved problems. No mention was made of this phenomenon for allylpotassium and -cesium prepared by other methods [6]. Those compounds appear, however, to have been prepared at room temperature so it is not clear if this is a general phenomenon or restricted to anions formed from mercury compounds. It is impossible to remove completely by decanting, or by filtration, all the metallic mercury formed in the reaction. No signal from ^{199}Hg was observed in a solution containing the more freely rotating form of the allyl anion. Separate experiments showed that about 5% of the original diallylmercury would have been detected in this way. From this observation it therefore appears unlikely that the more freely rotating form of the allyl moiety is associated with a bound mercury atom which has not yet precipitated from the solution. It is also possible to reject the hypothesis that the observed equivalence of the $\mathrm{CH_2}$ protons arises via a rapid exchange with traces of diallylmercury, or other mercury compounds since this is not consistent with the observed chemical shifts of the more freely rotating form. The change from rotating to non-rotating structures at a given temperature for allylsodium is accompanied by a broadening of the ^{23}Na resonance linewidth which suggests the structure of the final product has the sodium ion in an environment with a greater electric field gradient. In both cases the linewidths are still much greater than reported for many sodium ion containing solutions [16]; only when caged with the cryptand does it approach a more normal value of 136 Hz.

Any structures proposed for the freely rotating and hindered allyl species must meet the four following criteria. The hindered structure must have a lower potential energy than the freely rotating structure. The environment of the allyl moiety must be more constrained in the hindered species. The electric field gradient at the cation must be greater in the hindered structure. These criteria may be met if we propose that the freely rotating structure is a somewhat separated aggregate of cations and allyl anions produced in the reaction with diallylmercury. This converts to a more compactly bound unit, the hindered form, with greater electrostatic attractions and hence lower energy. Since the charges are closer together in such a form the electric field gradients will be larger. With a more compact form the barrier to rotation about the carbon—carbon bonds of the allyl anion will be greater. As an example, but not necessarily the case, *cis* and *trans* dimer structures have been proposed for allyllithium, with the *cis* structure having greater stability [17]. Under these circumstances there seems little point in attempting to rationalize the increase in free energy barrier to rotation with the heavier alkali metals.

While there appears to be little doubt that the allylalkali metal compounds are basically ionic in character it seemed of interest to examine a recently suggested method for distinguishing between this and the rapidly interconverting covalent alternative [18,19]. Deuteration of one terminal position causes nonequivalence of the two ends. The residence time of the metal will then differ in a rapidly equilibrating structure and two carbon-13 lines will appear. The signal corresponding to the protonated end will be shifted relative to that of the normal compound and be different to that corresponding to the deuterated end. A delocalized system would also be expected to show similar effects [20] but with much smaller shifts. The magnitude of d/Δ where d is the isotopic splitting observed per deuterium atom and Δ the estimated chemical shift difference expected for the α and γ carbons in the "frozen" equilibrium state was suggested to be a good criterion for structural type. Δ for the allyl systems can be estimated in the following way. The γ-shift in a covalent allylic compound must be close to 115 ppm as observed in propene or the covalent structures shown in Table 2. To reproduce the observed C_α shift of allylsodium would require a Δ value of 133 ppm. Slightly different values would be required for the lithium and potassium compounds but this is unimportant. Separate lines from the protonated terminal carbons were observed in a mixture of normal and deuterated material except for allylpotassium where only a broad single line was seen. The signals from the deuterated carbon are difficult to observe because of deuterium splitting. The d/Δ values (Table 5) observed for allyllithium and -sodium are of the same order of magnitude as reported for the delocalized cyclohexenyl and cyclopentenyl cations [20], whereas much larger values (0.03 to 0.18) have been estimated for rapidly equilibrating cations. The d/Δ value expected for a tautomeric system does depend on the K_H/K_D ratio which is unknown in this case. An extremely low value would be required to explain these results on that basis.

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