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CHARGE DISTRIBUTION IN SUBSTITUTED ALLYL-ALKALI METAL COMPOUNDS BY ^{13}C NMR

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Summary

The ^{13}C NMR spectrum of 5,5-dimethylhexen-2-ylmetals and 2,5,5-trimethylhexen-2-ylmetals have been measured where the metal (M) is Li, Na, K, Rb, Cs, Hg and $Si(CH_3)_3$. When M = Li, the solvents have been C_6D_6, diethyl ether, tetrahydrofuran, and dimethoxyethane. Substantial changes of the chemical shifts of the α, β and γ carbons occur in the alkali metal compounds as the counter ions vary, and all are changed relative to the parent hydrocarbon. Very small temperature effects are found down to —80°C. If allowance is made for a change in hybridization of the α carbon, the sums of these chemical shift changes from the parent hydrocarbon are similar for all the alkali metals. It is suggested that all these compounds are delocalized ionic compounds, with the charge in the caesium compound favouring slightly the α position over the γ position. But as the counter ion becomes smaller the charge resides more on the α position.

In contrast the behaviour of the Si and Hg compounds is more that expected of covalent compounds.

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^{13}C NMR measurements have been made on a number of organic anion-pairs mostly with the counter-ion lithium [1—6]. Configuration, barriers to internal rotation and some estimate of charge distribution can be made by this technique.

The 5,5-dimethylhexenyl-2 (I, $(CH_3)_3CCH_2CH{=}CHCH_2{-}M$) and 2,5,5-trimethylhexenyl-2 (II, $(CH_3)_3CCH_2CH{=}C(CH_3)CH_2{-}M$) derivatives of the alkali metals have an obvious interest as models of the active centres in the anionic polymerization of butadiene and isoprene. Their lithium derivatives have been studied in benzene by ^{13}C NMR spectroscopy [7]. The present work extends this data to derivatives of the other alkali metals in a number of polar solvents.

Experimental

The allyl-alkali metal compounds were made in all cases by treating the corresponding allylmercury (0.5 g) with either an alkali metal film or finely

TABLE 1

^{13}C CHEMICAL SHIFTS [a] OF I—ALLYLMETAL COMPOUNDS [b]

Solvent	Temperature (°C)	*trans* (%) [c]	^{13}C NMR (δ, ppm)						M
			$(CH_3)_3$	C	CH_2	CH	CH	CH_2	
C_6D_6	20		29.4	31.4	41.3	103.0	140.3	20.0	Li
		77	(29.4)	(31.4)	(48.2)	(103.3)	(144.3)	(20.7)	Li
DEE [c]	—20		29.8	32.8	42.2	87.6	140.0	30.7	Li
		75	(29.4)	(32.4)	(49.6)	(84.4)	(144.1)	— [d]	Li
THF	—20		30.1	32.8	43.2	81.9	142.5	31.0	Li
		35	(29.4)	(32.6)	(50.7)	(79.6)	(146.0)	—	Li
THF	—20		30.1	33.1	43.8	72.3	138.8	35.7	Na
		23	(29.4)	(33.1)	(51.3)	(70.9)	(145.0)	(34.5)	Na
THF	—20		30.3	32.0	44.6	67.5	137.5	45.0	K
THF	—20		30.4	31.7	45.1	67.5	138.2	47.4	Rb
THF	—20		30.5	31.7	45.8	69.0	139.5	51.4	Cs
THF	20		29.7	31.6	41.3	121.0	131.1	39.6	Hg
			(29.5)	(31.6)	(47.9)	(122.6)	(133.4)	(43.7)	Hg
THF	20		29.4	31.5	41.3	126.9	124.7	18.7	$Si(CH_3)_3$
			(29.4)	(31.3)	(48.0)	(128.7)	(126.1)	(23.1)	$Si(CH_3)_3$
THF	20		29.3	31.7	41.1	127.8	125.3	12.8	H
			(29.4)	(31.1)	(47.7)	(128.7)	(127.1)	(17.9)	H

[a] Shifts are recorded in ppm downfield of TMS using the following solvent peaks as standards. C_6D_6, 128.0; DEE, 15.55; THF, 26.10; DME, 58.66. [b] The figures in brackets are for the *trans* form, all others are for the *cis* form. [c] *Trans* (%) form is quoted where both forms are in equilibrium. [d] Not observed, believed obscured by the *cis*-t-butyl group absorption. [c] DEE = diethyl ether, THF = *tetrahydrofuran*.

divided lithium, in the appropriate solvent (5 ml), and then filtering the solution into the NMR tube. All reactions were performed in all glass vacuum apparatuses fitted with breakseals at —20°C for 30 minutes.

The mercury compounds were prepared as before [7,8] from the corresponding lithium compounds prepared from t-butyllithium and either isoprene or butadiene [7]. The spectra were measured on a Varian XL 100 NMR spectrometer. The solutions in ether solvents were prepared and measured at —20°C to avoid reaction with the solvent. The solution concentrations were nominally 0.5 *M*, but solubility may have limited the concentration to below this value in some cases.

The silicon compounds were prepared as described elsewhere [8,9].

Results

The allyl compounds may exist in two forms *cis* (*Z*) and *trans* (*E*). It was found in most cases only the *Z* form could be observed. The Li compound of I in all solvents, and the Na compound in THF gave easily measurable equilibrium amounts of the *E* isomer, as did the lithium compound of II in benzene and diethyl ether. It is possible that small absorbances in the appropriate positions in the K and Rb compounds of I were due to the *E* form, but they are not recorded here because of the uncertainty. The chemical shifts downfield from TMS are recorded in Tables 1 and 2. Also included in these tables are the shifts recorded for the corresponding mercury compounds, the trimethylsilyl derivatives and the parent hydrocarbons as comparison covalent compounds. As formed, the mercury compound was a mixture of *cis* and *trans* isomers. Doubling of some of the absorbances in the diallylmercury compounds spectra was attributed to the *cis* and *trans* forms appearing in molecules containing *c*—*c*, *c*—*t* or *t*—*t* units.

The spectra of the solutions of the allyl-alkali metals were also measured at lower temperatures, down to —80°C. Some general broadening of the peaks was observed, but often the compounds precipitated from solution. Changes in chemical shift with temperature were very small in the ppm (or less) range in ether solvents. The largest shift measured was II—Li in cyclopentane solution where the chemical shift of the γ carbon moved 2 ppm downfield in the temperature range +20 to —80°C.

Discussion

The ^{13}C chemical shifts of the β and γ carbons of both the Hg and Si compounds show only minor differences from the parent hydrocarbon; the behaviour is that expected of a σ-bonded organometal compound. This is supported by the appearance of ^{13}C—^{199}Hg coupling, and also of ^{199}Hg—C—^{1}H coupling in the proton spectra. ^{119}Sn—C—^{1}H coupling is also observed in the ^{1}H NMR spectrum of the dimethyltin compound of II.

The C_α absorption of the mercury compound is downfield about 27 ppm from the parent hydrocarbon. This effect is very similar to the large downfield shift of the carbon in dimethylmercury and diethylmercury. The corresponding downfield shift for the silicon compound is surprisingly large at nearly 6 ppm, consid-

TABLE 2

^{13}C CHEMICAL SHIFTS [a] OF Π—ALLYLMETAL COMPOUNDS [b]

Solvent	Temperature (°C)	*trans* (%) [c]	^{13}C NMR (δ, ppm)							M
			$(CH_3)_3$	C	CH_2	CH	C	(CH_3)	CH_2	
C_6D_6	20		29.6	32.0	43.4	100.4	148.4	28.2	24.2	Li
		65	(29.6)	(32.0)	(42.9)	(100.1)	(150.6)	(21.0)	(27.8)	Li
DEE	–20		29.8	33.0	43.6	87.6	149.2	27.2	33.3	Li
		25	(29.5)	(33.4)	(45.0)	(81.8)	(150.9)	(20.6)	(36.7)	Li
THF	–20		30.2	32.4	45.0	83.9	149.3	26.8	31.8	Li
DME [e]	–20		30.3	32.7	44.8	82.8	148.1	28.0	33.3	Li
THF	–20		30.1	32.8	44.9	79.2	146.1	27.0	36.7	Na
THF	–20		30.3	31.9	45.9	71.9	143.2	26.1	45.8	K
THF	–20		30.5	31.6	46.6	69.0	143.1	25.8	49.0	Rb
THF	–20		30.6	31.6	47.2	70.8	143.4	26.1	53.7	Cs
THF	20		29.7	32.4	42.7	117.6	137.1	27.4	45.1	Hg
			(29.5)	(32.6)	(42.7)	(118.4)	(137.3)	(19.5)	(52.8)	Hg
THF	20		29.4	31.6	43.0	119.5	134.2	26.6	23.4	$Si(CH_3)_3$
			(29.6)	(32.2)	(42.8)	(120.1)	(133.9)	(18.9)	(30.6)	$Si(CH_3)_3$
C_6D_6	20		29.6	31.8	42.6	122.3	132.4	26.3	18.0	H [d]
			(29.6)	(31.8)	(42.6)	(122.3)	(132.4)	(18.0)	(26.3)	H [d]

[a, b, c] See Table 1. [d] The protonated forms are identical. [e] DME = dimethoxyethane.

ering the small shift difference observed between CH_4 and $Si(CH_3)_4$. Specific effects at the α position can be caused therefore in these covalent compounds by replacement of hydrogen by silicon and to a greater extent by mercury. Minor effects only extend to the β and γ positions. The very large α shift in the mercury compound is in fact unusual among the heavy metals [10].

In the alkali metal compounds in contrast, the α, β and γ carbon resonances all show substantial shifts compared with the parent compound. At the β carbon the shift is downfield and is largest with lithium. An upfield movement of the γ resonance is even more marked. The upfield change with lithium increases as the solvating power of the solvent increases. Further upfield shifts occur with sodium and potassium, but there is little further change for Rb and Cs. There is a corresponding downfield movement of the α resonance (Fig. 1). The results in THF can be compared with those on allyllithium [4] and potassium [6]. In both these compounds the α and γ positions are equivalent. Only a small (~1.5 ppm) difference in chemical shift is observed between the two compounds, which suggests little change in structure of two presumably ionic compounds.

In view of these observations a simple ionic model of the derivatives of I and II appears attractive in which the shifting α, γ resonances are caused primarily by transfers of charge between the two positions. In these asymmetrical anions the charge preference will be for the primary C_α, evident in the limiting cases of K, Rb, Cs. The small lithium ion appears to further localize the charge at this position especially in non-solvating solvents. As the effective cation radius is increased (by solvation in the case of Li *) a more equal charge distribution is attained but still retaining some preference for C_α.

In THF the charge redistribution appears to have reached its limit at potassium. Small downfield shifts at the α, β and γ positions occur on moving to the rubidium and cesium compounds. Thus although the major shifts can be accounted for on the above model other small residual effects on chemical shifts of unknown cause can occur in allylic systems.

The picture presented of an essentially ionic structure under all conditions would be expected to cause the hybridization of all three allylic carbons to be sp^2. A study of the $^{13}C_\alpha$—$^{13}C_\beta$ coupling constants of the lithium compound of II [12] shows that neither in benzene (36 Hz) nor in THF (47 Hz) are the constants in the usually found range for sp^2—sp^2 bonding (65—80 Hz). Some perturbations could have been caused by the aggregation certainly present in benzene and perhaps present even in THF at the high concentrations necessary for ^{13}C NMR measurements. Nevertheless these observations must cast some doubt about the applicability of the ionic model at least for lithium. No evidence was found for ^{13}C—^7Li coupling in any solvent, as would be expected for covalent bonding. Coupling of this type is observed for t-butyllithium and s-butyllithium in hydrocarbon solvents but not in the case of n-butyllithium [7,13]. In the latter case rapid exchange processes must eliminate C—Li coupling and probably would do so for the lithium compounds of I and II especially in polar solvents even if it existed. Evidence based on ^{13}C—^7Li coupling is therefore likely to be

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* It is assumed in all cases that only intimate ion pairs are present. Conductivity measurements of THF solutions of polymerizing systems containing these groups give very low ionic dissociation constants. Ref. 11 confirms this with the Li counter ion. The other counter ions are less likely to form solvent-separated ion pairs.

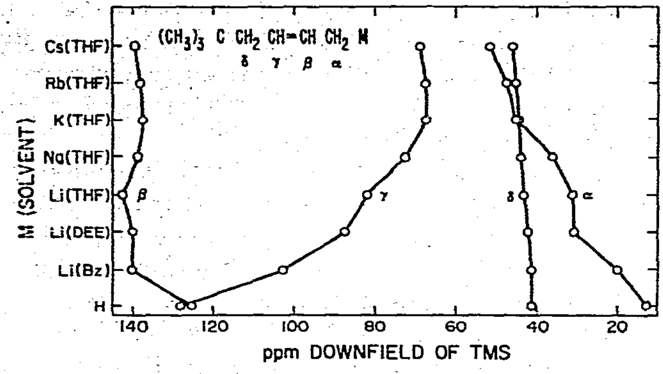

Fig. 1. Change in the chemical shifts of the allyl portion of the I-alkalimetal compound.

inconclusive and in any case, even with t-butyllithium and -butyllithium simple covalent bonding is not indicated.

Models in which the change in the α and γ shifts is due to different proportions of rapidly equilibrating ionic and covalent species can probably be eliminated on the grounds that the shifts are nearly invariant with temperature. In cyclopentane for instance the small temperature effect on the γ peak on the Li compound of II (δ (+20°C) 100.8 ppm, δ(−80°C) 102.7 ppm) would indicate an energy difference of only ca. 170 cal between an ionic and a covalent form *. This would be even smaller for ether solvents and other counter ions. Similar arguments can be applied to a model with the alkali metal exchanging between the α and γ positions. Moreover there was little evidence of any slowing down of such equilibria at low temperatures.

All the alkali metal derivatives of II show a strong absorption band in THF in the near ultraviolet region. For lithium λ_{max} is at 287 nm moving to 318 nm for Na and to 322 nm for the other alkali metals. The absorption band is markedly sharper in the case of lithium and qualitatively at least of higher extinction coefficient. Although some small differences are apparent between lithium and the other alkali metals the absorption is far removed from that expected for an isolated double bond and indicative of considerable charge delocalization.

Some estimation of charge distribution can be obtained from chemical shifts using allyllithium [7] (or potassium) in THF as a model of an ionic compound with one half electron on each terminal position. This requires, to rationalize the differences from propene, that unit electron charge causes an upfield shift of 130 ppm and that a hybridization change sp^3—sp^2 causes a downfield shift of 97 ppm. These two values applied to the chemical shifts of compounds I and II using the protonated compounds as reference would indicate a total charge of between 0.86 and 0.93 electrons on α and γ positions (lowest for Cs/THF and Li/C_6H_6) with the α/γ charge distribution changing towards more equality as the effective counter-ion size increases. Similar figures are obtained if the small downfield shift at the β position in allyl salts is attributed to some positive charge at this position with more than unit negative charge in total at α and γ

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* The energy difference was calculated from equilibrium constants calculated assuming a covalent form would have a γ shift similar to the parent hydrocarbon, and the ionic form a γ shift similar to the caesium compound.

TABLE 3

CALCULATED CHARGES [a] ON ALLYLIC POSITIONS

Counter ion	Solvent	Compounds I				Compounds II			
		α	β	γ	Σ total	α	β	γ	Σ total
		tlc [a]							
Li	C_6H_6	0.79	−0.13	0.22	0.88	0.80	−0.14	0.19	0.85
	DEE	0.69	−0.13	0.35	0.91	0.72	−0.15	0.30	0.87
	THF	0.69	−0.15	0.40	0.94	0.73	−0.15	0.34	0.92
	DME					0.72	−0.14	0.35	0.93
Na	THF	0.65	−0.12	0.49	1.02	0.69	−0.12	0.38	0.95
K	THF	0.59	−0.11	0.53	1.01	0.61	−0.09	0.44	0.96
Rb	THF	0.55	−0.11	0.53	0.97	0.58	−0.09	0.47	0.96
Cs	THF	0.51	−0.12	0.52	0.91	0.54	−0.10	0.45	0.89

[a] Charges tabulated as fractions of 1 electron at that position.

positions. This hypothesis reduces the shift per electron in such systems to 114 ppm/electron. Table 3 shows the calculated charge in compounds I and II on the latter assumption.

A consistent picture can be obtained therefore rationalizing all the allyl-alkali metal compounds presently studied in terms of essentially delocalized ionic structures. Only the $^{13}C_\alpha$—$^{13}C_\beta$ coupling constant data on the II—Li compound is in disagreement [12]. Clearly an investigation of this coupling constant in derivatives of other alkali metals would be of great interest.

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