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^{13}C NMR COUPLING CONSTANTS IN DELOCALIZED ORGANO-ALKALI METAL COMPOUNDS. MODELS OF POLYMERIZATION SYSTEMS

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Summary

2,5-Diphenyl-2,5-dipotassiohexane, 2-lithio-4,4-dimethyl-2-phenylpentane, and 1-lithio-2,5,5-trimethylhexene-2 have been prepared, all labelled with ^{13}C in the position adjacent to the alkali metal atom. The ^{13}C NMR spectra of these compounds have been measured and the ^{13}C—^{13}C coupling constants found for the charged atom. The first two compounds have coupling constants consistent with an sp^2 hybridized C_α, with relatively little effect of the charge on the coupling constant. The third compound, when dissolved in either THF or benzene, gave much smaller coupling constants, which are more difficult to interpret.

There has been some discussion on the hybridization of the carbon atom (C_α) bonded to the alkali metal in systems open to charge delocalization such as benzyl- and allyl-alkali metal compounds [1—12]. These systems are of interest in polymerization studies as they are involved in certain stereospecific polymerizations. Charge delocalization most likely will be extensive in the benzylic compounds with all alkali metals, especially in solvating solvents such as THF, and has been shown to be considerable in hydrocarbon solvents even with lithium as the metal. Opinions differ whether allyllithium compounds are substantially delocalized ionic compounds or covalent in either type of solvent [2,3,10—13].

Extensive charge delocalization in an ionically bonded alkali metal compound could be expected to result in sp^2 hybridization of the valence electrons on C_α. Covalent bonding (or even non-delocalized ionic bonding) would leave the normal sp^3 structure. An indication of the type of hybridization can be obtained from ^{13}C NMR coupling constants [14]. ^{13}C—^{1}H coupling constants also have been used [7,8] in this manner for a study of some benzylic compounds. However, the fractional change with hybridization changes is larger for ^{13}C—^{13}C coupling constants, and although other factors are of importance [15,16], a

TABLE 1

$J(^{13}C—^{13}C)$ RANGES FOUND FOR DIFFERENTLY HYBRIDIZED C ATOMS [14]

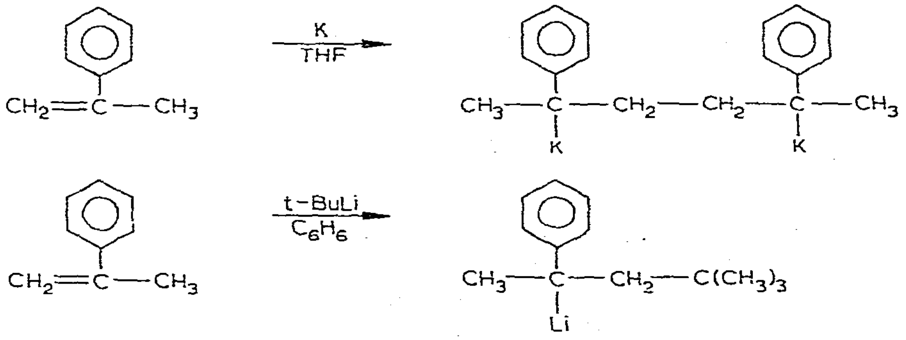
Bond type	J values (Hz)
sp^3—sp^3	34—40
sp^3—sp^2	40—60
sp^2—sp^2	65—80

reasonably non-overlapping sequence of changes with hybridization can be described (Table 1).

In order to determine whether such coupling constants would be of value in the study of simple organometallic compounds related to polymerization systems, α-methylstyrene and isoprene suitably labelled with ^{13}C were prepared and some appropriate benzyl and allyl organometal compounds prepared from them (for structures see Table 3). The α-methylstyrene was labelled in the α position, and from it 2,5-diphenyl-2,5-dipotassiohexane (I) labelled in the 2 and 5 position was prepared as an example of a fully delocalized system. Also prepared from the α-methylstyrene was 2-lithio-4,4-dimethyl-2-phenylpentane (II). The NMR spectra of these two compounds were measured in THF solution only, because of their limited solubility in hydrocarbons. Isoprene was labelled at C(1) and from it was prepared 1-lithio-2,5,5-trimethylhexene-2 (III) with the C(1) labelled. The coupling constant of this compound was found in both THF and benzene solution.

Experimental

Isoprene-$^{13}C_1$ was prepared from ^{13}C formaldehyde (Merck, Sharpe and Dohme) by a two stage synthesis. HCHO (2 g, 45% ^{13}C) was allowed to react with propanal to give methacrolein by the Mannich synthesis (yield 69%). The methacrolein was then converted to isoprene by the Wittig reaction with triphenylphosphinemethylene. The isoprene was converted directly to the sulphone for purification purposes and regenerated by heating (overall yield, 13%).



$$CH_2{=}CH—C(CH_3){=}CH_2 \xrightarrow[C_6H_6]{t\text{-}BuLi} (CH_3)_3C—CH_2—CH{=}C(CH_3)—CH_2Li$$

α-Methylstyrene-$^{13}C_1$ was prepared by a two-stage synthesis from $^{13}C_\alpha$ benzoic acid (Merck, Sharpe and Dohme). The benzoic acid (4 g, 45% $^{13}C_\alpha$) was converted to α,α-dimethylbenzyl alcohol by treatment with methylmagnesium bromide in diethyl ether. The alcohol was dehydrated by treatment with acetic anhydride (overall yield, 56%).

Compounds I, II, and III were prepared from these labelled products as before [9,10] by the reactions illustrated above. The ^{13}C NMR spectra recorded at ambient temperature were measured on a Varian CFT 20 spectrophotometer, those at low temperature on a Varian XL 100 instrument.

Results

Previous measurements [10] of the ^{13}C NMR spectrum of 1-lithio-2,5,5-trimethylhexene-2 in C_6D_6 solution have left in doubt the assignment of the C(1) and CH_3 atoms. In the presently measured spectra with labelled compounds this uncertainty was removed and the shifts are recorded in Table 2. Some small differences in the position of the peaks occur from those recorded earlier (ca. 0.3 ppm); this could be due either to the heavier ^{13}C substitution, or a concentration effect.

The coupling constants measured are recorded in Table 3. The coupling constants for isoprene and α-methylstyrene conform with the ranges in Table 1. Unfortunately, $J_{1,7}$ in α-methylstyrene could not be determined because of the proximity of $\delta(C(7))$ to the enriched $\delta(C(1))$. Compound I has been shown to be a highly delocalized carbanionic species [9,10]. Estimates of charge distribution in THF, from ^{13}C shifts indicate about 0.6 electronic charge on ring carbons [10]. Rotation of the phenyl rings cannot be observed at temperatures up to 75°C [9]. These observations, together with magnetic equivalence of the CH_2 protons, strongly suggest sp^2 hybridization for C(7). The ^{13}C coupling constants are in agreement with this conclusion. $J_{7,9}$ has increased somewhat over the corresponding value for α-methylstyrene, but the value is well within the range expected for sp^3—sp^2 bonding, as is $J_{7,8}$. $J_{1,7}$ also agrees with sp^2—sp^2 bonding. The results for compound II are very similar. In this case ring rotation can be observed on the NMR time scale at 50°C in THF, but the activation energy is rather high (~14 kcal/mol [17]). $J_{7,9}$ has again increased even over that in the potassium compound, but $J_{1,7}$ is slightly lower and $J_{7,8}$ is essentially unchanged. Predominant sp^2 bonding of C(7) is again indicated. In these examples, the effect of charge on C(7) on the coupling constant appears to be sufficiently small that the coupling constant still appears diagnostic.

TABLE 2

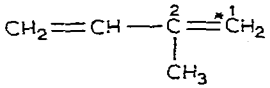
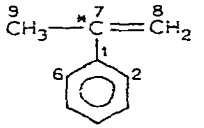
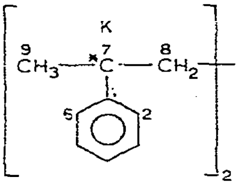
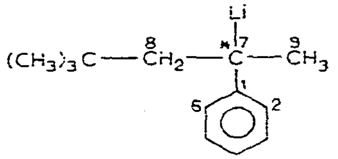
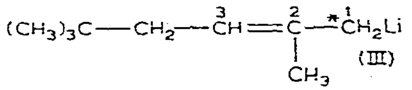
^{13}C NMR SHIFTS OF 1-LITHIO-2,5,5-TRIMETHYLHEXENE-2 [a]

Carbon	δ *cis*	δ *trans*
C(1)	24.21	27.77
CH_3	28.17	21.04

[a] Chemical shifts are in ppm downfield from TMS, using the central line of C_6D_6 (δ 128.0 ppm) as reference. Concentration ca. 10%.

TABLE 3

^{13}C COUPLING CONSTANTS (concentration 10%)

Compound		Solvent	Temperature	Constant	$J_{(C,C)}$ (Hz)
Isoprene  $CH_2{=}CH{-}\overset{2}{C}(CH_3){=}\overset{*1}{C}H_2$		C_6D_6	RT	$J_{1,2}$	70.9
α-Methylstyrene 		C_6D_6	RT	$J_{7,8}$	72.4
				$J_{7,9}$	41.8
	(I)	THF	RT	$J_{1,7}$	73.4
				$J_{7,8}$	49.4
				$J_{7,9}$	47.7
	(II)	THF	−20°C	$J_{1,7}$	71.7
				$J_{7,8}$	50.1
				$J_{7,9}$	51.2
 $(CH_3)_3C{-}CH_2{-}\overset{3}{C}H{=}\overset{2}{C}(CH_3){-}\overset{*1}{C}H_2Li$	(III)	C_6D_6	RT	$J_{1,2}cis$	36.3
			RT	$J_{1,2}trans$	35.1
		THF	−20°C	$J_{1,2}cis$	46.5
			−80°C	$J_{1,2}cis$	46.3

The results for compound III are significantly different. In THF solution, $J_{1,2}$ is well within the range characteristic of sp^2—sp^3 bonding. Since C(2) must in any case be sp^2 hybridized, this suggests sp^3 hybridization for C(1). In benzene, $J_{1,2}$ has an abnormally low value, a situation which resembles that observed in ^{13}C—^1H coupling in alkyllithium compounds [18,19]. These facts are difficult to reconcile with other evidence on compound III and its higher molecular weight homologue ($R(C_5H_8)_nCH_2CHC(CH_3)CH_2Li$, IV). These in THF show strong optical absorption bands (λ_{max} 287 nm) [20,21] characteristic of π—π^* transitions in delocalized anions. Analogous covalent allylic derivatives of silicon, tin and mercury exhibit absorption at shorter wavelengths, more characteristic of isolated double bonds [22]. Some degree of delocalization in III is also indicated by NMR measurements of the ^{13}C and ^1H chemical shifts at position 3; these are well upfield from the normal olefinic position, particularly in THF. The existence of *cis* and *trans* forms clearly indicates double bond character in C(2)—C(3). But *cis*—*trans* isomerization start slowly at —40°C and must be quite rapid at room temperature [6]. Rotation about the C(1)—C(2) bond becomes slow on the NMR time scale at —60°C. This suggests more double bond character in the bond C(2)—C(3) than C(1)—C(2) but, nevertheless, the behaviour is not normal for a covalent system. Compound III in THF differs from I and II in its freedom of rotation about ultimate and penultimate C—C bonds at room temperature. It assumes a more rigid structure at —80°C [6] but without change in $J_{1,2}$ (Table 3) indicating little change in bond character.

One factor which may perturb the results is the occurrence of association in solution. Compounds III and IV are known to be extensively associated in hydrocarbon solvents [23] and this may persist even in THF, at the concentrations required for NMR measurements. The THF/Li ratio at these concentrations is about 20, which should be adequate to prevent association with benzylic compounds but may not be so for allylic compounds. Kinetic evidence on IV suggests that even at 10^{-4} molar concentration in hydrocarbon solvents even a thousand-fold excess of THF over Li is insufficient to dissociate the aggregates [24], whereas with polystyryllithium a factor of 20 is sufficient [25]. Association of allyllithium in THF under similar conditions has been indicated [2].

References

1 E.J. Lanpher, J. Amer. Chem. Soc., 79 (1957) 5578.
2 P. West, J.I. Purmont and S.V. McKinley, J. Amer. Chem. Soc., 90 (1968) 797.
3 W.H. Glaze, J.E. Hanicak, M.L. Moore and J. Chaudhuri, J. Organometal. Chem., 44 (1972) 39.
4 W.H. Glaze, J.E. Hanicak, M.L. Moore, J. Chaudhuri and D.P. Duncan, J. Organometal. Chem., 51 (1973) 13.
5 W.H. Glaze and D.P. Duncan, J. Organometal. Chem., 99 (1975) 11.
6 F. Schué, D.J. Worsfold and S. Bywater, Macromolecules, 3 (1970) 509.
7 R. Waack, M.A. Doran, E.B. Baker and G.A. Clark, J. Amer. Chem. Soc., 88 (1966) 1272.
8 L.D. McKeever and R. Waack, J. Organometal. Chem., 28 (1971) 145.
9 S. Bywater and D.J. Worsfold, J. Organometal. Chem., 33 (1971) 273.
10 S. Bywater, P. Lachance and D.J. Worsfold, J. Phys. Chem., 79 (1975) 2148.
11 J.P.C.M. van Dongen, H.W.D. van Dijkman and M.J.A. de Bie, Rec. Trav. Chim. Pays Bas, 93 (1974) 29.
12 D. Seyferth and T.F. Julà, J. Organometal. Chem., 66 (1974) 195.
13 J.R. Murdoch and A. Streitweiser, Intra-Sci. Chem. Rept., 7 (1973) 45.
14 J.B. Stothers, ^{13}C NMR spectroscopy, Wiley Interscience, New York, 1972.
15 W.M. Lichtman and D.M. Grant, J. Amer. Chem. Soc., 89 (1967) 6775.
16 G.A. Gray, P.D. Ellis, D.D. Traficante and G.E. Maciel, J. Magn. Res., 1 (1969) 41.
17 S.K. Brownstein and D.J. Worsfold, Can. J. Chem., 50 (1972) 1246.
18 L.D. McKeever and R. Waack, J. Chem. Soc., Chem. Commun., (1969) 750.
19 L.D. McKeever, R. Waack, M. Doran and E.B. Baker, J. Amer. Chem. Soc., 91 (1969) 1057.
20 S. Bywater, A.F. Johnson and D.J. Worsfold, Can. J. Chem., 42 (1964) 1255.
21 A. Garton, R.P. Chaplin and S. Bywater, Eur. Polym. J., 12 (1976) 697.
22 S. Bywater and D.J. Wordsfold, Polymer Preprints No. 2, 15 (1974) 153.
23 S. Bywater and D.J. Wordsfold, Can. J. Chem., 45 (1967) 1821.
24 S. Bywater and D.J. Worsfold, Can. J. Chem., 42 (1964) 2884.
25 S. Bywater and D.J. Worsfold, Can. J. Chem., 40 (1962) 1564.