Nuclear Magnetic Resonance Evidence for Ion Pairing in Alkali-metal Salts of 1,3-Diphenylpropene

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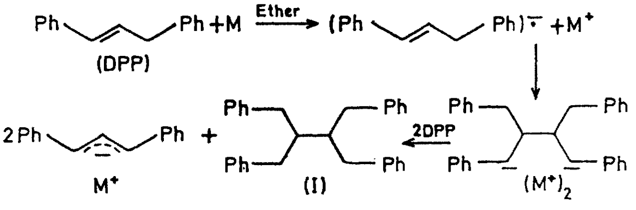
Summary N.m.r. evidence is presented for ion pairing in the alkali-metal salts of 1,3-diphenylpropene in tetrahydrofuran.

THE use of n.m.r. spectroscopy to study ion-pairing phenomena has been very limited.[1] We present our preliminary n.m.r. results for the alkali-metal salts of 1,3-diphenylpropene ($DPP^{-}M^{+}$) in tetrahydrofuran. We believe they represent independent evidence for ion pairing in this system.

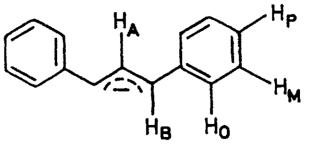
The n.m.r. spectrum of $DPP^{-}Li^{+}$, prepared by the reaction of DPP with n-butyl-lithium (BuLi), has been described previously.[2] We have repeated this synthesis and have extended the investigation to $DPP^{-}M^{+}$, where M=Li, Na, K, and Cs, by treating a 1M-solution of DPP with M under high vacuum. The solutions so obtained were finally sealed into conventional n.m.r. tubes, with Me_4Si as internal reference, and the spectra were recorded on a 100 MHz instrument.

The spectrum of $DPP^{-}Li^{+}$, prepared using BuLi, was in excellent agreement with published data, but the sample prepared using Li metal gave a spectrum containing additional unexpected absorptions at τ 2·9 and 3·1. These peaks were also present in the spectra of solutions of $DPP^{-}M^{+}$, where M=Na, K, and Cs. Since the visible spectra of the solutions were independent of the method of preparation, it was clear that the extraneous resonances were due to the presence of an uncharged hydrocarbon. The addition of CO_2 to the products of the reaction between DPP and Li gave an alkali-soluble carboxylic acid, identified by m.s. and n.m.r. as $DPP{\cdot}CO_2H$ and an ether-soluble hydrocarbon with a molecular weight of 390. The n.m.r. spectrum of the latter had absorptions at τ 2·9 and 3·1 (10H), 7·5 (m, 4H), and 8·0 (m, 1H). The hydrocarbon was therefore considered to be 2,3-dibenzyl-1,4-diphenylbutane (I) and the mechanism of the reaction of DPP with M to be as shown in the Scheme.



SCHEME

The proton chemical shifts and coupling constants for the anion are shown in the Table. It is obvious that the spectrum is dependent upon the cation but an exact interpretation of every chemical shift is impossible due to the differing ability of each cation both to perturb the electron distribution within the anion and also to withdraw charge from it. The shifts of $DPP^{-}Na^{+}$ appear at lowest field and increasing the atomic weight of the cation moves the spectrum to higher field with the exception of $DPP^{-}Li^{+}$ which absorbs at even higher field than $DPP^{-}Cs^{+}$. The effect of temperature on the spectrum of $DPP^{-}M^{+}$ is illustrated by the fact that the spectrum of the Na^{+} salt moves to higher field as the temperature is lowered.



M^{+}	H_A[a]	H_O and H_M	H_P	H_B	J_{AB}[b]
Li	2·78	3·46	4·11	5·37	13
Na	2·58	3·37	3·94	5·23	13
	(2·71)[c]	(3·41)[c]	(4·10)[c]	(5·35)[c]	(13)[c]
K	2·68	3·37	3·95	5·26	13
Cs	2·74	3·34	3·93	5·33	13

[a] τ units.
[b] In Hz.
[c] Measured at −30°, all other data being determined at +30°.

Accepting that the change of chemical shift of a proton—to a first approximation—will be dependent upon the change of electron density at the carbon atom to which it is bound,[3] the shifts may be interpreted in terms of electron density perturbation by the cation. In a contact ion pair some portion of the anion charge will reside between the anion and the cation, the amount being determined by the polarising power of the cation. For a cation with a high charge to radius ratio there will therefore be relatively little charge remaining on the anion and the proton chemical shifts will appear at low field. On this basis, the order of the spectra of Na, K, and Cs indicates that these salts are predominantly contact ion pairs. Since the shifts of $DPP^{-}Li^{+}$ appear at highest field, the highest charge density on DPP^{-} is inferred and we therefore deduce that this salt is predominantly solvent separated. Visible spectroscopic studies of this system confirm these predictions.[4] $DPP^{-}Na^{+}$ and $DPP^{-}K^{+}$ do, however, exist in part as solvent-separated ion pairs and since only one n.m.r. spectrum is obtained for each of these salts, the exchange rate between contact and solvent-separated ion pairs is rapid. The shift to higher field of the spectrum of the Na^{+} salt is explicable on the basis of the conversion of contact into solvent-separated ion pairs.

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[2] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.
[3] T. Schaefer and W. S. Schneider, *Canad. J. Chem.*, 1963, **41**, 966.
[4] Unpublished results from this laboratory.