Ion Pairing in Alkali-metal Salts of 1,3-Diphenylbut-1-ene

By J. W. BURLEY and R. N. YOUNG*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary Alkali-metal salts of 1,3-diphenylbut-1-ene are shown to exist in ether solvents as contact and solvent separated ion pairs.

SPECTROSCOPIC evidence has been presented recently for the occurrence of two different kinds of ion pairs.[1] The fundamental importance of such information prompts us to report our preliminary results for the alkali-metal salts of 1,3-diphenylbut-1-ene (I). The allylic anion (II) was prepared by direct reaction between the alkali metals and ether solutions of chromatographically pure 1,3-diphenylbut-1-ene. Treatment of the anion with CH_3OH, D_2O, or CO_2 produced mixtures of (III) and (IV) ($R \equiv H$, D, CO_2H, respectively) which were identified by n.m.r. and mass spectrometry, confirming that formula (II) correctly represents the anion.

The Effect of Counter-ion: In tetrahydrofuran (THF) at +20° the visible spectrum of (II) consists of two absorption maxima. The first of these is centred at 565 nm. for the salts of all of the alkali metals, but the intensity progressively decreases with increasing atomic weight (Figure 1) until with caesium the band is barely perceptible. In contrast, the intensity of the second band increases with increasing atomic weight and in addition undergoes a marked bathochromic shift from 530 to 543 nm. in going down the group from lithium to caesium (Table 1).

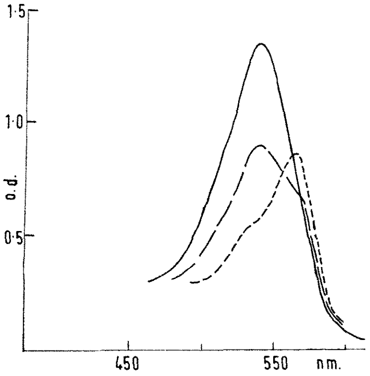


FIGURE 1. *The visible spectrum of* (II) *in THF at* +20° Cs$^+$ ——; Rb$^+$ — —; Li$^+$ -----.

Spectrum of (II) *in THF at* +20°

M$^+$	λ_{max} (±2) nm.	
Li$^+$	530[a]	565
Na$^+$	535	566
K$^+$	538	566
Rb$^+$	541	565
Cs$^+$	543	—

[a] Shoulder only.

The effect of solvent: Figure 2 shows the effect of a change of solvent upon the spectrum of (II) with Na$^+$ as counterion at +20°. In α-methyltetrahydrofuran (α-MeTHF), a weak solvating agent, absorption is only observed at 520 nm. whereas in dimethoxyethane (DME)—a strong solvating agent—there is only absorption at 563 nm. In tetrahydrofuran, a solvent of intermediate solvating power, absorption occurs at 535 and at 565 nm.

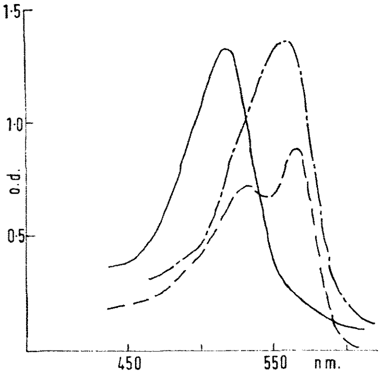


FIGURE 2. *The visible spectrum of* (II) *at* +20°; M = Na. α-MeTHF ——; THF — —; DME — - — - —.

The effect of temperature: Figure 3 shows the spectrum of (II) with K$^+$ as counterion in THF solution. At 20° the absorption at 538 nm. is stronger than that at 565 nm. As the temperature is lowered, the relative intensities change, until at −40° they are completely inverted. This change, which is perfectly reversible, was shown by other combinations of ethers and alkali metals.

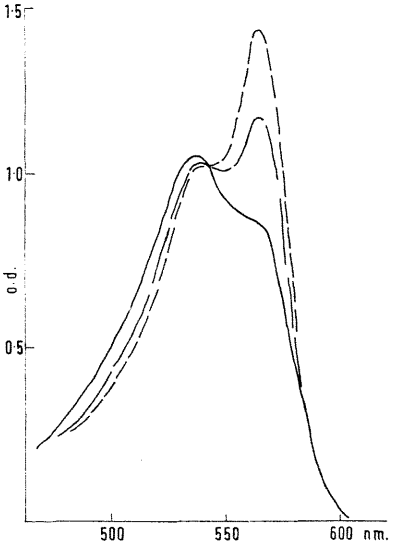
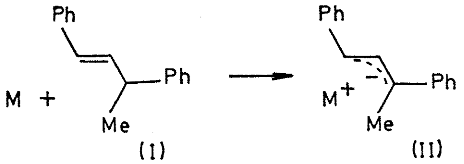


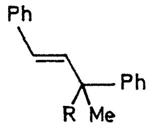
FIGURE 3. *The visible spectrum of* (II) *in THF*; M = K +20·5° ——; −12·5° — —; −40° -----.

Conductivity measurements on 10^{-4}M-solutions of these salts gave results consistent with the occurrence of about 1% of dissociation to free ions.

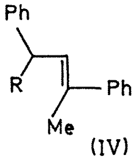
These results can be rationalised if it is assumed that (II) is present in solution as both contact and solvent-separated ion pairs. In the latter, the cation is separated from the anion by a layer of solvent molecules and the absorption spectrum is independent of the nature of the cation *i.e.* this species absorbs at 565 nm. However, in the contact ion pair, the cation is sufficiently close to the anion to perturb the molecular energy levels. As predicted by Carter *et al.*,[2] the perturbation will be greatest for the smallest ion and will cause a blue-shift. Accordingly the band in the range 530—543 nm. corresponds to the contact ion pair. Lowering the temperature increases the fraction of ion pairs present in the solvent-separated form, as expected for the exothermic solvation process. As was observed, the formation of solvent-separated ion pairs is favoured in solvents that can strongly solvate the cation. Finally, although Li^+ is the smallest cation of the series, and must therefore give a contact ion pair absorbing at the shortest wavelength, its high polarizing power will also cause it to be the most easily solvated cation. Accordingly the fraction of contact ion pairs present in any given solvent, will be smaller than with any of the other alkali-metal ions.



(I) (II)



(III)



(IV)

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[2] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455.