Cross-association of n-Butyl-lithium with 1,3-Diphenylbut-1-enyl-lithium

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Summary Spectroscopic evidence is presented for cross-association of n-butyl-lithium and 1,3-diphenylbut-1-enyl-lithium in ether solutions.

THE lithium salt of 1,3-diphenylbut-1-ene ($DPB^- Li^+$) can be prepared in ether solutions by the direct reaction of the chromatographically pure hydrocarbon with lithium metal. Depending upon the solvent, $DPB^- Li^+$ exists as contact or solvent-separated ion pairs.[1] Alternatively, the abstraction of a proton from the hydrocarbon by an equivalent quantity of n-butyl-lithium (BuLi) leads to the formation of the same anion. However, if a large excess of BuLi is employed (approximately 50 fold), pronounced spectral differences are evident in certain solvents.

$DPB^- Li^+$ *with* BuLi *in* 1,4-*dioxan*: The spectrum of $DPB^- Li^+$ in dioxan consists of a single band at 500 nm (Figure 1) corresponding to the contact ion pair. However, when the anion was formed by using a large excess of BuLi, the spectrum showed maxima at 562 and 530 nm but none at 500 nm. On standing, these bands decreased in intensity until they were eventually completely replaced by the normal absorption at 500 nm.

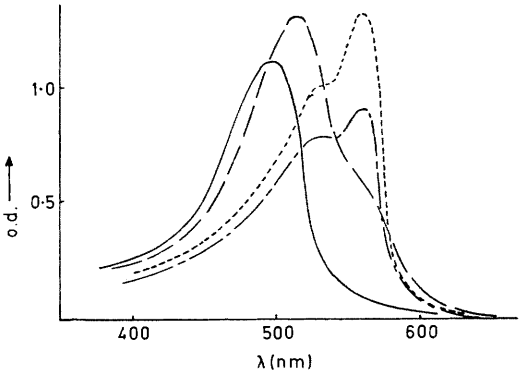

FIGURE 1. *The visible spectrum of* DPB^- *Li*$^+$ *in* 1,4-*dioxan at* 20°. *Prepared from* DPB *and* Li ————. *Prepared from DPB and an excess of* BuLi, *recorded at the times indicated after mixing*: 1 min. -------; 30 min. — - — -; 12 hr. — — —.

$DBP^- Li^+$ *with* BuLi *in* 2,5-*dimethyltetrahydrofuran* (2,5-MeTHF): The presence of an excess of BuLi had no effect upon the spectrum of a 10^{-4} M-solution of $DPB^- Li^+$ in 2,5-MeTHF *viz.* a single absorption maximum at 488 nm corresponding to the contact ion pair. On increasing the concentration to 5×10^{-3} M, the addition of BuLi caused the appearance of a new band at 565 nm; at a concentration of 10^{-2} M this effect was even more pronounced (Figure 2). Simultaneous with the formation of the new band, the absorption maximum of the original band showed a progressive bathochromic shift.

$DPB^- Li^+$ *with* BuLi *in* (Et_2O). The spectrum of $DPB^- Li^+$ in Et_2O—a single absorption at 484 nm due to the contact ion pair—was unaffected by the presence of a large excess of BuLi at ambient temperatures. As the temperature was lowered, two new peaks appeared at 528 and 562 nm, which were not formed on cooling a sample of $DPB^- Li^+$ prepared either by reaction with lithium metal or a stoicheiometric quantity of BuLi (Figure 3).

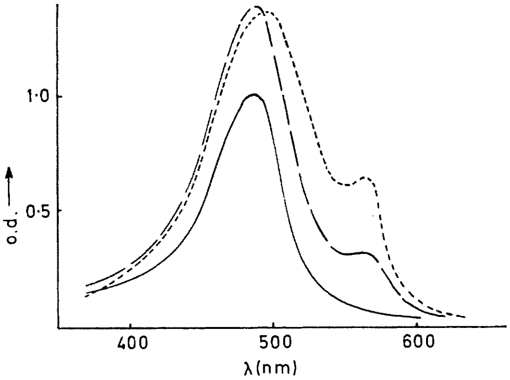

FIGURE 2. *The visible spectrum of* $DPB^- Li^+$ *in* 2,5-MeTHF *at* 20° *as a function of concentration*: 10^{-4} M ——; approx. 5×10^{-3} M — —; approx. 10^{-2} M------.

The concentration-dependence of the spectra described indicates that an association phenomenon is involved. Since other experiments have proved that $DPB^- Li^+$ does not associate with itself in ether solutions,[2] the association must be between BuLi and $DPB^- Li^+$. The disappearance of the bands at long wavelength in dioxan with increasing time is in fact a consequence of the decrease in the concentration of BuLi caused by a decomposition reaction with the solvent.[3] The alternative possibility that the association involves lithium butoxide, which might conceivably be present as an impurity, was ruled out since its addition to the pure ether solutions did not affect the spectra.

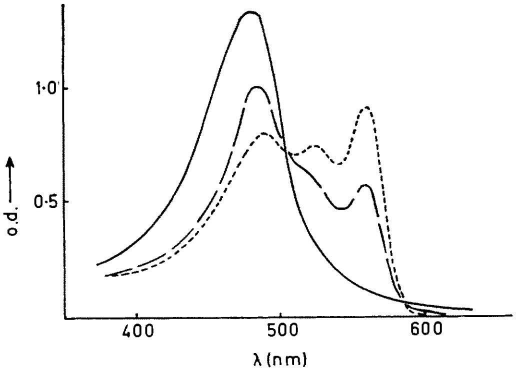

FIGURE 3. *The visible spectrum of* $DPB^- Li^+$ *in* Et_2O *as a function of temperature*: 20° ————; −10° — —; −40° ------.

The cross-associate may be formulated as $(DPB^- Li^+)_n$-$(BuLi)_m$ but we have no evidence, as yet, as to the values of n and m. It has been suggested that the formation of a complex of this type would result in decreased interaction between DPB^- and the lithium cations; the complex would therefore absorb at longer wavelength than the contact ion pair.[4,5] We conclude from our spectral studies that the complex must exist in two forms, one being effectively a solvent separated complex (λ_{max} 562 nm) and the other a "tight" complex (λ_{max} 530 nm). In the case of the simplest possible complex the total equilibrium might be represented as

$$DPB^-\ Li^+ + BuLi \rightleftharpoons DPB^-\ Li^+{\cdot}BuLi \rightleftharpoons DPB^-{\cdot}S{\cdot}Li^+{\cdot}BuLi$$

where $S \equiv$ solvent.

In the case of dioxan and 2,5-MeTHF the shorter-wavelength band is the resultant envelope of two bands—one due to the normal contact ion pair of $DPB^-\ Li^+$, the other due to the "tight" complex ($DPB^-\ Li^+{\cdot}BuLi$). In Et_2O the contact ion pair and the "tight" complex are observed as two distinct bands.

Similar observations have been reported for the solutions of BuLi with fluorenyl-lithium in dioxan but no explanation was put forward.[6] We believe that cross-association may again account for these results.

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