Ion-pairing of Substituted 1,3-Diphenylallyl Carbanions with Alkali-metal Cations

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The visible absorption spectra of ether solutions of the alkali-metal salts of several substituted 1,3-diphenylpropenes are shown to correspond to the presence of tight and loose ion pairs. The enthalpy and entropy changes for the interconversion of these ion pairs have been measured for 22 combinations of anion, cation, and solvent.

PREVIOUS results from this laboratory [1] have shown that the dependence of the visible absorption spectra of ether solutions of the alkali-metal salts of 1,3-diphenyl-propene and -butene upon temperature, cation, and solvent can be interpreted in terms of the presence of up to three types of ion pairs viz. the loose (solvent-separated) and two tight (contact) ion pairs differing in their degree of solvation. These conclusions have been confirmed by n.m.r. spectroscopy [2] which has in addition revealed that these anions adopt the *trans,trans*-conformation. Preliminary studies have shown [3] that substitution of the

[1] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.

[2] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.

[3] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1843.

2-position of the 1,3-diphenylallyl carbanion by an alkyl group alters the preferred conformation to *cis,trans*. The objective of the present work was to investigate the influence of substitution upon the thermodynamics of the ion pairing.

EXPERIMENTAL

2-Methyl-1,3-diphenylpropene (MDPP) was synthesised by condensing two moles of benzylmagnesium chloride with one mole of methyl acetate and dehydrating the product by distillation from potassium hydrogen sulphate. Purification of the crude material by liquid chromatography on an alumina column and using n-hexane as eluant yielded a mixture of *cis*- and *trans*-isomers. Preparative scale g.l.c. with nitrogen as carrier gas on a Carbowax column set to rise from 150 to 200° afforded pure samples of each isomer. Except in a few cases discussed below, identical behaviour was observed for the *cis*- and *trans*-compounds. In the interests of economy, the sample of mixed isomers was employed wherever it was certain that the validity of the results would not be in doubt.

2-t-Butyl-1,3-diphenyl- (BDPP) and 1,2,3-triphenyl-propene (TPP) were prepared by procedures analogous to that used for MDPP but starting respectively from methyl pivalate and methyl benzoate.

2-Methyl-1,3-di-*p*-tolylpropene (MDTP) was prepared by dehydration of the condensation product of 1,3-di-*p*-tolylacetone with methylmagnesium iodide.

The procedures used for the purification of the solvents and the method of spectral analysis have been described previously.[1,3] The spectra were obtained using quartz cells (0.1 mm pathlength) and an alcohol-filled unsilvered Dewar vessel as thermostat. Cooling was achieved by passing liquid N_2 through a coil of narrow-bore copper tubing immersed in the alcohol. As before, it was assumed that the extinction coefficients were independent of temperature. Whilst this is probably not rigorously correct, the range of temperature of interest in any given system was generally relatively small. Furthermore, it was noted that the increase of absorbance with decreasing temperature in systems which either persisted as tight ion pairs, or which were already exclusively present as loose ion pairs was precisely that anticipated from the calculated solvent contraction.

RESULTS AND DISCUSSION

The reduction of the hydrocarbons commenced as soon as their solutions were brought into contact with alkali-metal, although in some cases several hours were required for completion. As with 1,3-diphenylpropene,[4] the immediate products of reduction were the dimer-di-anions which very rapidly abstracted an allylic proton from unreduced hydrocarbon, resulting in the ultimate conversion of about half of the starting hydrocarbon to the allylic carbanion and half to the dihydro-dimer. The generation of the 1,2,3-triphenylallyl carbanion could not be achieved by this route since the radical anion of TPP is stable towards dimerisation, as is to be expected of a stilbene. In consequence, the triphenyl-allyl carbanion had to be prepared by the abstraction of

[4] J. W. Burley, R. Ife, and R. N. Young, *Chem. Comm.*, 1970, 1256.

an allylic proton from TPP by a suitable base such as n-butyl-lithium or 'living' poly-α-methylstyrene dissolved in the appropriate solvent. The identities of the anions were verified by derivatisation with CO_2 or D_2O as described earlier.[1]

The visible absorption spectra of ether solutions of the alkali metal salts of MDPP, MDTP, and BDPP exhibited

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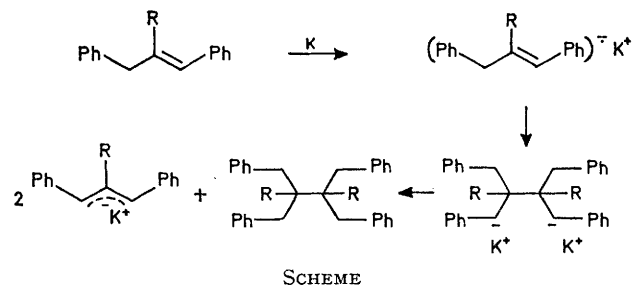
two overlapping bands whose relative intensities were independent of concentration. When the temperature was lowered, the intensity of the absorption band at the longer wavelength increased at the expense of that at
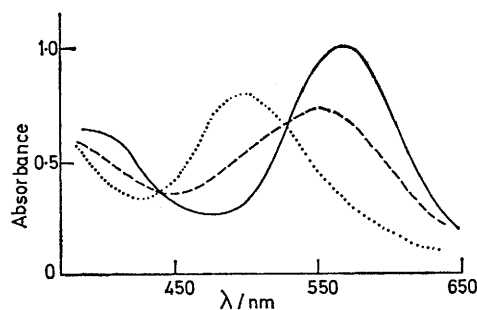
FIGURE 1 The absorption spectrum of 1,2,3-triphenylallyl-lithium in 2,5-dimethyltetrahydrofuran·: · · · −6°, − − − − −30°, —— −70°

the shorter. The position of the former absorption was constant but in contrast, that of the latter underwent a systematic red shift as the cation radius increased, *e.g.* in 2-methyltetrahydrofuran, the wavelengths (nm) for the salts of MDPP were Li+ (472), Na+ (499), K+ (504), and Rb+ (507). These observations are entirely analogous to those reported for the salts of 1,3-diphenylpropene,[1] and are consistent with the presence of tight and loose ion pairs, respectively responsible for the absorptions at short and long wave lengths.[5] The absorption maxima (nm) for the loose ion pairs were MDPP (536), MDTP (538), BDPP (530), and TPP (574). The behaviour of the salts of TPP was essentially similar, but differed in that the loose ion pair exhibited two absorption maxima. In consequence, the spectra of these salts recorded at different temperatures exhibited two isosbestic points (Figure 1). Because of the long wavelength tail in the spectrum of the loose ion pair, the conversion tight →

[5] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1965, **69**, 2466.

loose was accompanied by a particularly striking change in colour from orange to a rich purple.

With most combinations of cation, anion, and solvent, the position of the tight ion pair absorption band remained virtually constant as the temperature was lowered, in accordance with the presence of only one kind of tight ion pair. In conforming with this principle the lithium salts of MDPP, MDTP, and BDPP in 2,5-dimethyltetra-hydrofuran are especially noteworthy since they sharply contrast with the solutions of the lithium salt of 1,3-diphenylpropene in the same solvent, whose spectra have *three* absorption bands corresponding to the presence of three different ion pairs. An exception to this otherwise general rule was found in the lithium salt of MDPP in 3,4-dihydropyran. At ambient temperatures the absorption spectrum consisted of a single maximum located at 472 nm. On cooling the solution, the band progressively shifted to 497 nm, the band width passing through a maximum at intermediate temperatures. Evidently there are two tight ion pairs in this system which are not spectroscopically resolved.

The reduction of a mixture of *cis*- and *trans*-MDPP or -BDPP gave rise to solutions whose spectra neither varied with time nor with the extent of reduction provided that sodium or lithium was employed. However, when solutions of these hydrocarbons were reduced with potassium in tetrahydrofuran or 1,2-dimethoxyethane the spectra recorded immediately upon partial reduction were anomalous. At ambient temperatures, the strongest band was located at 535 nm instead of at 507 nm as predicted, whilst at low temperatures a strong and entirely unexpected band appeared at 565 nm (Figure 2). When the solution was isolated from the potassium (to prevent further reduction) the absorption at 565 nm

dynamic) controlled reduction of one of the isomers of the parent hydrocarbon leads to the formation of the *trans,trans*-carbanion metastable with respect to the
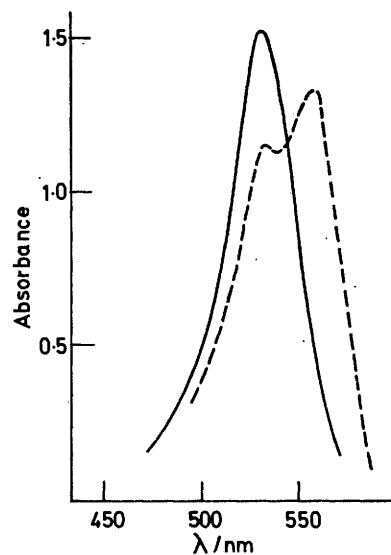

Figure 2 The absorption spectrum of 2-methyl-1,3-diphenyl-allylpotassium in tetrahydrofuran at −40 °. The dotted line was the spectrum recorded immediately following reduction, the continuous line was the spectrum of the same solution recorded 15 min later

cis,trans-isomer. Unfortunately, tests with the meagre quantities available of pure *cis*- and *trans*-hydrocarbons were not entirely conclusive.

Analysis of the temperature dependence of the spectra yielded the values of ΔH^0 and ΔS^0 for the conversion of

Changes [a] in enthalpy (ΔH^0/kJ mol^{-1}) and entropy (ΔS^0/J mol^{-1} K^{-1}) for the conversion of tight to loose ion pairs

Metal	Solvent	MDPP		MDTP		BDPP		TPP	
		$-\Delta H^0$	$-\Delta S^0$	$-\Delta H^0$	$-\Delta S^0$	$-\Delta H^0$	$-\Delta S^0$	$-\Delta H^0$	$-\Delta S^0$
Li	MTHF	28	105	38	147	28	93		
Li	Oxepan	35	128	28	109			25	84
Li	THF	28	102	27	109				
Li	DHP	34	145					25	105
Li	*cis*-DMTHF	31	160			33	152	43	175
Na	THF	45	171	38	163	38	132	22	80
Na	MTHF	25	139			24	122	27	130
Na	THP			39	197				
Ba	THF							17	88

[a] These values are generally believed accurate to within ±7%. MTHF = 2-Methyltetrahydrofuran. THF = tetrahydrofuran, DHP = dihydropyran, DMTHF = 2,5-dimethyltetrahydrofuran, THP = tetrahydropyran.

disappeared in the course of a few minutes to be replaced by the normal absorption bands at 507 and 535 nm at ambient temperatures. At −40° the band at 535 nm is the only absorption (Figure 2). The association of this anomalous behaviour with specific reducing conditions, the coincidence of the wavelengths of the absorption bands of the anomalous solution with those of the unsubstituted diphenylallyl carbanion and the reversion of the anomalous spectrum to normal appearance on standing suggest that kinetic (rather than thermo-

tight to loose ion pairs summarised in the Table. The several gaps were occasioned by experimental limitations such as the boiling or freezing of the solvent which prevented the study of an adequate temperature range. Likewise, the extension of the Table to cover the salts of the heavier alkali-metals was impracticable using the present techniques since the extensive overlap of the tight and loose ion pair absorption bands defied accurate deconvolution.

Examination of the Table shows that at any temperature

selected, the ratio of tight to loose ion pairs increases for the salts of the hydrocarbons in the sequence BDPP $\simeq$ TPP < MDPP < MDTP. The ring methyl groups of MDTP must markedly increase the electron density of the carbanion and hence the magnitude of the coulombic attraction for a cation. The substituents of interest in the remaining three anions are attached to C(2) of the allyl skeleton and are therefore not directly in conjugation in the classical Hückel sense. In consequence, the inductive and mesomeric effects seem to be overshadowed by steric effects.

Solutions of the salts of MDPP, MDTP, and BDPP showed no evidence of dissociation in the more weakly solvating solvents. For example, the spectra of the lithium salts in DMTHF recorded using 0.1 mm and 5 cm pathlengths cells were indistinguishable. However, in THF and MTHF, the relative intensity of the long wavelength absorption band was increased on dilution, corresponding to the formation of free carbanion which has the same absorption spectrum as the loose ion pair. This effect was suppressed by the addition of sodium tetraphenylborate *via* the common ion effect. The dissociation constants for the *tight* ion pairs of the sodium salts of MDPP and BDPP in tetrahydrofuran were found to be 2.0×10^{-6} and 3.3×10^{-5} mol dm^{-3} at 25°. The enthalpy for the dissociation of Na$^+$ MDPP$^-$ was determined as -41 kJ mol^{-1}, the same value, within experimental error, as the enthalpy of the conversion of tight to loose ion pairs. Essentially similar behaviour was shown by the sodium salt of 1,3-diphenylpropene in tetrahydrofuran: $K_{\text{diss}} = 2.0 \times 10^{-6}$ mol dm^{-3}, ΔH^0 (tight ion pair $\longrightarrow$ free ions) -27 kJ mol^{-1}, and ΔH^0 (tight $\longrightarrow$ loose ion pair) -27 kJ mol^{-1}. Apparently, the electrostatic work of dissociating the loose ion pairs is almost exactly compensated by the enthalpy of the additional solvation then possible. The entropy of the dissociation of the loose ion pair of MDPP$^-$ Na$^+$ is *ca.* -75 J mol^{-1} K^{-1}. Clearly, the decrease in entropy due to the additional solvation outweighs the increase in entropy arising from the formation of two free ions from one ion pair.

Finally, it is evident from the Table that large enthalpy changes are accompanied by large entropy changes and *vice versa*. A survey of the literature has shown that this pattern of behaviour is not confined to the present allylic systems and a full interpretation is presented as a separate paper.