Photoisomerisation of Ion Pairs of Diphenylallyl Carbanions

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The normal *trans,trans* conformation of the ion pairs of the 1,3-diphenylallyl and 1,3-diphenylbutenyl carbanions is converted into *cis,trans* by photolysis with white light. The kinetics of the reverse dark reaction have been studied; the rate of this process is much greater for the tight than for the loose ion pair.

PREVIOUS results from this laboratory [1,2] have shown that the visible absorption spectra of the alkali-metal salts of 1,3-diphenyl-propene and -butene can be interpreted in terms of the presence of tight (contact) and loose (solvent-separated) ion pairs. The absorption spectrum of the loose ion pair is indistinguishable from that of the free anion. However, in the tight ion pairs the perturbation of the molecular orbital energy levels by ion association is marked. The ground state is stabilised to a greater extent than is the excited state, and the absorption maxima of the tight pairs are shifted to the blue to an extent which increases with decreasing cation radius.

The existence of two types of ion pair has been confirmed by n.m.r. spectroscopy [3] which has, in addition, showed [4,5] that these ions adopt the *trans,trans* conformation. Substitution of the allylic 2-position by an alkyl group causes the absorption maxima to suffer a hypsochromic shift of some 30 nm relative to those of the parent ion. N.m.r. spectroscopy reveals [6] that these substituted ions adopt the *cis,trans* conformation, as anticipated from simple steric considerations.

One anomaly of some interest was the observation [7] that the reduction of 2-methyl- or 2-t-butyl-1,3-diphenyl-propane under certain rather specific conditions led initially, on incomplete reduction, to the formation of the *trans,trans* ion pairs, metastable with respect to the *cis,trans* conformers. Kinetic control (rather than thermodynamic) was concluded to be the cause of this behaviour. The subsequent observation of variability of the spectra of samples of the lithium salt of 1,3-

diphenylpropane which had been exposed to light suggested that the question of conformation was at once more complex and interesting than had hitherto been supposed.

EXPERIMENTAL

Tetrahydrofuran (THF) and diethyl ether were dried under high vacuum by stirring over Na–K alloy in the presence of a little benzophenone. Methylamine, obtained as a cylinder of compressed gas, was transferred to a flask on the vacuum line and dried by dissolving in it a small volume of Na–K alloy. The hydrocarbons 1,3-diphenylbut-1-ene, 1,3-diphenylpropene, and 2-methyl-1,3-diphenyl-propene were prepared as described previously; [1,2] reduction of their solutions in THF, Et_2O, or methylamine with alkali-metals led to the generation of the corresponding diphenylallyl ion pairs, respectively designated DPB^-M^+, DPP^-M^+, and $MDPP^-M^+$. Methylamine solutions of $(DPP^-)_2M^{2+}$ where M = Ca, Sr, or Ba were prepared by reduction using the appropriate alkaline-earth metal. The corresponding solutions in THF were prepared indirectly, by evaporating the methylamine solution to dryness under high vacuum. The residue was dissolved in THF and again evaporated to dryness, this cycle being repeated twice to ensure that no significant quantity of methylamine remained.

The reactors used for the reductions were fitted with side-arms bearing glass or quartz cells (0.1 or 1 cm pathlength). In order to record the absorption spectrum, the cell was placed in an unsilvered Dewar vessel partially filled with alcohol, and located in the cell compartment of a Perkin-Elmer 137 spectrometer. A suitable quantity of solution was transferred to the side-arm and was diluted by distilling *all* the remaining solvent from the reactor into the side-arm.

[1] J. W. Burley and R. N. Young, *J. Chem. Soc. (B)*, 1971, 1018.
[2] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.
[3] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.
[4] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.
[5] G. J. Heiszwolf and H. Kloosterziel, *Rec. trav. Chim.*, 1967, **86**, 1345.
[6] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1843.
[7] G. C. Greenacre and R. N. Young, *J.C.S. Perkin II*, 1975, 1661.

This was particularly important when mixtures of THF and Et_2O were employed since incomplete distillation would result in the preferential transfer of the more volatile component to the cell. A copper coil was immersed in the Dewar and by continuously pumping through it cold alcohol from a Townson and Mercer 'Minus Seventy' thermostatted bath, it was possible to limit the drift of temperature of the cell to *ca.* 1 °C over 30 min. Kinetic data were obtained by setting the spectrometer to operate at constant wavelength, the change in absorbance being monitored using a time-drive motor.

Flash photolysis studies were conducted using conventional apparatus based on the discharge of a capacitor bank through a zenon lamp.

RESULTS AND DISCUSSION

The visible absorption spectrum of DPP^-Li^+ in THF at temperatures below −20 °C consists of a strong band at 565 nm with shoulders at *ca.* 535 and 460 nm (Figure 1). At higher temperatures there is a considerable tail
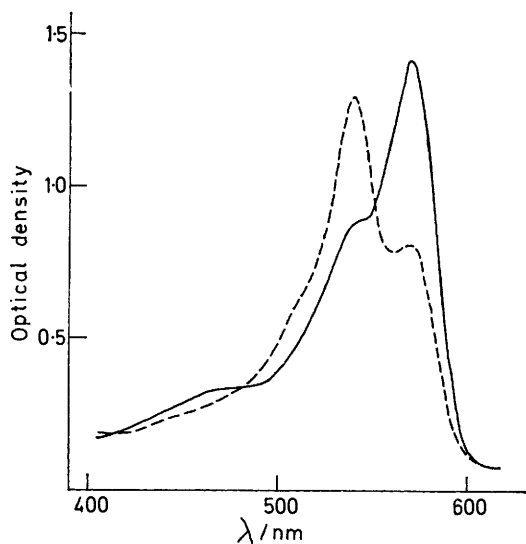

FIGURE 1 Absorption spectrum of DPP^-Li^+ in THF at −45 °C: before photolysis, ——; after photolysis, − − − −

to shorter wavelength from the 565 nm band. Previous studies have shown [2] that at low temperatures the salt is exclusively present as the loose ion pair but at higher temperatures a small fraction exists as the tight pair. [1]H N.m.r. spectroscopy has provided unequivocal evidence [3-5] that both ion pairs adopt the *trans,trans* conformation. In contrast, $MDPP^-Li^+$ has been shown by n.m.r. to have the *cis,trans* conformation, [6] the concommitant loss of coplanarity being reflected in the visible absorption spectrum by a shift of *ca.* 30 nm to the blue of the absorption maxima of both tight and loose pairs.

When a solution of DPP^-Li^+ in THF was cooled to −45 °C under the weak illumination of an overhead fluorescent light, the spectrum exhibited a *peak* at 533 nm in place of the shoulder observed following similar cooling in the dark. When the same solution was cooled to −45 °C under the strong illumination provided by a 50 W quartz–iodine lamp located *ca.* 10 cm away

from the spectroscopic cell, the spectrum (Figure 1) consisted of a maximum at 533 with a shoulder at 565 nm. When this solution was stored in the dark at −45 °C, the band at 533 nm decreased in intensity whilst that at 565 nm increased. Successive spectra passed through isosbestic points at 477 and 547 nm. In due course, the spectrum became indistinguishable from that of a sample cooled to −45 °C in the dark. The kinetics of this relaxation process are discussed below. Comparison of the spectrum of $MDPP^-Li^+$ with that of photolysed DPP^-Li^+ strongly suggests that the latter corresponds to the *cis,trans* conformer of DPP^-Li^+. This conclusion also very satisfactorily accounts for the ready conversion of the photochemical product back into *trans,trans*-DPP^-Li^+ in the dark. The most unambiguous means of vertification would be to determine the [1]H n.m.r. spectrum of the photolysed ion pair. In a single experiment in which the n.m.r. tube and its contents had been irradiated with white light at −50 °C, weak signals were observed at δ 5.25 and 4.30 in addition to the strong signals of *trans,trans*-DPP^-Li^+ which were located as previously described. [3] Comparison with the n.m.r. spectrum [6] of $MDPP^-Li^+$ in which the allylic 1- and 3-protons appear at δ 5.32 and 4.20 would seem to provide the desired evidence. However, several duplicate experiments failed to show any signals other than those of *trans,trans*-DPP^-Li^+. In view of the necessarily rather high concentration of the solution (*ca.* 0.2M) and the tendency of the n.m.r. tube to act as a cylindrical lens, the failure to generate a readily observable concentration of the *cis,trans* conformer is not really surprising. It is therefore particularly interesting to note the results recently reported by Bushby and Ferber. [8] These authors studied solutions of DPP^-M^+ in butyl ether–liquid ammonia (15 : 85 v/v); with M = Li, Na, and K, only the loose ion pairs were present. They concluded that the n.m.r. spectrum of the Na salts, recorded at −30 °C, corresponded to the presence of 7% *cis,trans* and 93% *trans,trans* conformer. Similarly, the visible absorption spectra of their Li, Na, and K salts recorded at −20 and +15 °C, all exhibited, in addition to the absorption band of the *trans,trans* ion pair at 550 nm, a weak shoulder at 525 nm which they ascribed to the *cis,trans* loose ion pair. Since their spectra passed through an isosbestic point, they concluded that the conformers were in rapid equilibrium with each other. Simple considerations show that the logic which led to this last conclusion is unsound, but it is interesting to examine the conclusion nonetheless. Making the plausible assumption that the extinction coefficients of the two conformers are the same at their respective absorption maxima, it is possible to estimate the supposed equilibrium constants from their reported spectra. The application of the van't Hoff formula shows that the enthalpy change for the process *trans,trans*- ⟶ *cis,trans*-DPP^-M^+ ranges from *ca.* 6 to 12 kJ mol⁻¹. The procedure followed by these authors was to cool their samples to −70 °C, allow them to warm, and to record the spectra when the temperature

[8] R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, 1976, 1688.

reached -55, -20, and $15\ ^\circ\mathrm{C}$. Since at no point in their paper is there any suggestion that they were aware of the possibility of photolysis, it is conceivable that the increase in the fraction of the *cis,trans* conformer they observed with increasing temperature might have additionally been a consequence of increasing exposure to light. This would account for the variation of the relative intensities of the absorption bands due to the *cis,trans* and *trans,trans* conformers evident on comparing the spectra of their Li, Na, and K salts. Experiments in our laboratory have shown that in methylamine, a solvent similar to liquid ammonia, the photochemically induced absorption band at 525 nm in a solution of $\mathrm{DPP^- M^+}$ persists much longer in the dark than does the corresponding band in a solution in THF or $\mathrm{Et_2O}$.

The direct synthesis of *cis,trans*-$\mathrm{DPP^- Li^+}$ in THF has been reported by Boche and Schneider; [9] they devised two methods, the reaction of *cis*-1,3-diphenylpropene with lithium cyclohexylisopropylamide at $-45\ ^\circ\mathrm{C}$ and the reaction of 1-bromo-*cis,trans*-2,3-diphenylcyclo-propane with lithium metal at $-60\ ^\circ\mathrm{C}$. By the use of $^1\mathrm{H}$ n.m.r. they were able to determine the equilibrium constant $K = [trans,trans]/[cis,trans]$ over the range -30 to $17\ ^\circ\mathrm{C}$. The precision claimed was rather low, but analysis of the van't Hoff plot suggests that the enthalpy change for the process *cis,trans* $\longrightarrow$ *trans,trans* is *ca.* -9 kJ mol^{-1}, *i.e.* similar to the range we have estimated from the visible spectra in Bushby and Ferber's paper.

The solute concentration employed in the n.m.r. tube is typically several orders of magnitude greater than that employed in absorption spectroscopy and the likelihood of significant photolysis by stray light is negligible. Direct comparison of the n.m.r. results of the two groups is only possible at one temperature, *viz.* $-30\ ^\circ\mathrm{C}$: Bushby and Ferber determined K as 13 whilst Boche and Schneider found K to be 17 ± 2.

The absorption spectrum of $\mathrm{DPB^- Li^+}$ in THF at $-30\ ^\circ\mathrm{C}$ consists of a band at 565 nm having a shoulder at 530 nm and corresponds to the presence of only the *trans,trans* loose ion pair. Photolysis of this solution reduced the absorbance at 565 nm; the absorption band was broadened and the maximum moved to 560 nm. These changes were rapidly reversed on storing in the
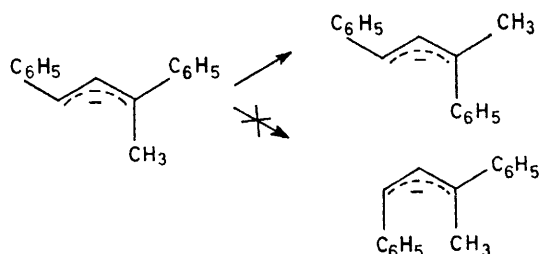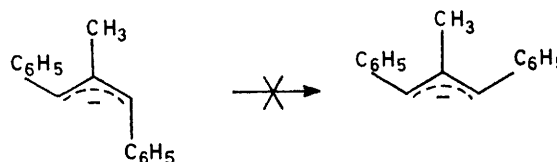

Scheme 1

dark. Although qualitatively similar to the behaviour of $\mathrm{DPP^- Li^+}$, the extent of change was very much smaller. Such a finding is entirely predictable on steric grounds

since only one of the phenyl groups can become *cis* (Scheme 1). Irradiating $\mathrm{MDPP^- Li^+}$ in THF with white light caused no detectable alteration of the visible absorption spectrum in the temperature range 25 to $-60\ ^\circ\mathrm{C}$. The failure to generate the *trans,trans* isomer photolytically is in no way remarkable in view of the very unfavourable steric interaction between the methyl and phenyl groups which would result (Scheme 2).

Scheme 2

The absorption spectrum of $\mathrm{DPP^- Na^+}$ in THF at $-30\ ^\circ\mathrm{C}$ consists of two bands at 534 and 565 nm, due respectively to the tight and loose ion pairs. Irradiating with white light considerably altered the spectrum (Figure 2). The band at 565 nm was greatly reduced in
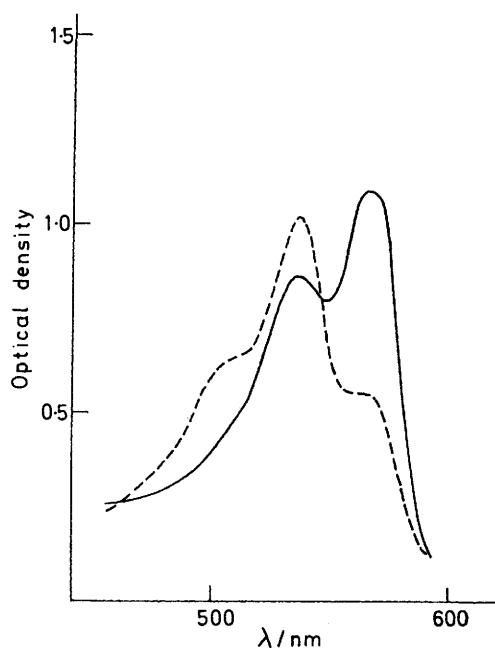

FIGURE 2 Absorption spectrum of $\mathrm{DPP^- Na^+}$ in THF at $-30\ ^\circ\mathrm{C}$: before photolysis, ———; after photolysis, — — — —

intensity, that at 534 nm increased in intensity and the maximum moved to 536 nm and in addition, a new band was formed at *ca.* 510 nm. These changes can again be ascribed to conversion to the *cis,trans* conformation, the tight and loose ion pairs of which respectively absorb at 510 and 536 nm. Similar behaviour is shown by the $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$ ion pairs of $\mathrm{DPP^-}$ in THF, where the predominant species involved are the tight ion pairs of the *trans,trans* and *cis,trans* conformers; the spectral data are summarised in Table 1.

[9] G. Boche and D. R. Schneider, *Tetrahedron Letters*, 1976, 3657.

Kinetic Studies.—A series of experiments was conducted in which samples of DPP⁻M⁺ in THF were photolysed by white light at −30 °C using a quartz–iodine lamp. Following photolysis, the *cis,trans* to *trans,trans* relaxation reaction was monitored spectrophotometrically. Linear first-order plots were obtained and the resulting rate constants are summarised in Table 2. The maximum conversion to the *cis,trans*

TABLE 1

Absorption maxima (nm) of DPP⁻M⁺ in THF at −30 °C

	trans,trans		*cis,trans*	
M	Tight pair	Loose pair	Tight pair	Loose pair
Li		565		536
Na	534	565	*ca.* 510	536
K	537		*ca.* 515	
Rb	540		*ca.* 517	
Cs	545		*ca.* 522	
Na [a]		556		525

[a] Solution in methylamine.

TABLE 2

Rate constants (min⁻¹) for the relaxation *cis,trans-* ⟶ *trans,trans*-DPP⁻M⁺ in THF

Temperature (°C)	Li	Na	K	Rb
−30	0.65	0.085	0.066	
+18	1 300	330		300

conformation attainable under comparable conditions was found to fall with increasing cation radius and in the cases of Rb⁺ and Cs⁺ was too small to permit the determination of meaningful rate constants.

A systematic study of the temperature dependence of the relaxation of THF solutions of *cis,trans*-DPP⁻Li⁺ yielded the results summarised in Table 3. Analysis of

TABLE 3

Temperature dependence of the rate constant for the relaxation *cis,trans-* ⟶ *trans,trans*-DPP⁻Li⁺

In THF

T/°C	18	−30	−33	−40	−43.5	−50
k/min⁻¹	1 300 [a]	0.65	0.34	0.16	0.09	0.03

In 1,2-dimethoxyethane

T/°C	−5.5	−9.5	−13	−16	−20.5
k/min⁻¹	1.13	0.44	0.23	0.16	0.066

[a] Value obtained by flash photolysis.

the results gives an Arrhenius activation energy of *ca.* 79 kJ mol⁻¹. Boche and Schneider reported [9] a very similar value, 74 kJ mol⁻¹; however, their rate constants are about one third of the size of those in the present paper. The cause of this difference is obscure but may be connected with the grossly different concentrations employed in n.m.r. and visible absorption spectroscopy.

The rate constant for the relaxation of *cis,trans*-DPP⁻Na⁺ in THF was found to be unchanged when sodium tetraphenylborate was added to the solution. This salt has been shown [10] to be extensively dissociated in THF. The absence of a common-ion effect shows that the relaxation does not involve any significant participation by the free carbanion. This conclusion was supported by the failure of dilution of a solution of DPP⁻Na⁺ in THF by a factor of ten to alter the rate constant.

The results of flash-photolysis studies of a number of solutions of DPP⁻M⁺ in THF at ambient temperature are summarised in Table 2. Concordant results were obtained by monitoring the changes in absorbance at the wavelengths corresponding to the absorption bands of the *cis,trans* and *trans,trans* conformers. As at lower temperature, the lithium salt has the greatest rate constant; those of the sodium and rubidium salts were very similar to each other. An observation of some interest was that if the solution photolysed was incompletely reduced (*i.e.* if neutral diphenylpropene was present in addition to DPP⁻M⁺) a weak transient species having an absorption maximum at *ca.* 625 nm was detected immediately following the flash. No such intermediate was detectable in solutions which had been completely reduced. It is possible that this transient was the radical-anion of diphenylpropene, formed by capture of an electron ejected from DPP⁻M⁺ by photolysis.

The possible roles played by the tight and loose ion pairs was explored by studying solutions of DPP⁻Li⁺ in a series of mixtures of THF with Et₂O. Whereas THF is a strongly solvating solvent, Et₂O is weakly solvating, favouring the formation of tight ion pairs. It was found (Table 4) that increasing the fraction of

TABLE 4

Dependence of the rate constant for *cis,trans-* ⟶ *trans,-trans*-DPP⁻Li⁺ in mixtures of THF and Et₂O at −40 °C

Volume fraction of Et₂O	0	0.30	0.50	0.75	0.90
Approx. mole fraction of tight ion pairs	0.037	0.037	0.043	0.21	0.60
k/min⁻¹	0.16	0.36	0.43	1.34	3.0 [a]

[a] Estimated value only.

tight ion pairs by increasing the volume fraction of Et₂O caused an increase in the relaxation rate constant. In the case of 100% Et₂O the rate was much too fast to measure. The influence of Et₂O upon the rate constant suggests that the tight ion pair is more rapidly converted to the *trans,trans* conformation than is the loose pair. However, when THF was the only solvent, it was found (Table 2) that the rate constants decreased in the sequence Li ≫ Na > K although the fraction of tight pairs increases in this order. It would seem, therefore, that the interionic separation in the tight ion pair may be more important than the fraction present as tight pair.

In order to explore the kinetics of the *cis,trans* ⟶ *trans,trans* relaxation process under conditions where the fraction of tight ion pairs is negligible, a series of experiments was conducted at −10 °C using methylamine as solvent. In this medium, the lithium, sodium, calcium, strontium, and barium salts of DPP⁻ all have very similar absorption spectra, *viz.* an absorption band having its maximum at 555 nm, corresponding to the loose ion pair. Photolysis with white light converted some of the solute into the *cis,trans* conformation, this being reflected by the appearance of a new absorption

[10] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 608.

band at 525 nm accompanied by a decrease in the absorbance at 555 nm. In general, the extent of photolysis was not large and, accordingly, the rate constants for the thermal relaxation reaction are subject to errors possibly as large as $\pm 25\%$. The rate constants (min^{-1}) obtained at -10 °C were as follows for the salts: Li 0.23, Na 0.18, Ca 0.20, Sr 0.25, and Ba 0.26. Within experimental error these rate constants may be regarded as identical to each other.

A study of the post-photolysis relaxation of cis,trans-DPP$^-$Li$^+$ in 1,2-dimethoxyethane yielded the results summarised in Table 3. These correspond to an Arrhenius activation energy of 96 kJ mol^{-1}. Comparison of the rate constants at -10 °C in methylamine and dimethoxyethane shows that the relaxation is somewhat faster in the latter solvent. Although visible absorption spectroscopy indicated the exclusive presence of loose ion pairs in dimethoxyethane solutions, the presence of a minute amount (say 1%) of tight pair cannot be completely ruled out.

Solutions of Ba^{2+} (DPP$^-$)$_2$ and of Sr^{2+} (DPP$^-$)$_2$ in THF were prepared from the corresponding solutions in methylamine as outlined in the Experimental section. Usually, the replacement of a strongly solvating solvent by a weaker one is not a particularly desirable procedure since there is often great difficulty in removing the last traces of the strong solvent. However, the reduction of diphenylpropene by alkaline earth metals in THF is an intolerably slow process. All the results described hitherto in the present paper clearly demonstrate that the rate constants of highly solvated species are much smaller than those of poorly solvated species. Accordingly, it is believed that the kinetic results obtained following the replacement of methylamine by THF are truly meaningful. The rate constants for the thermal relaxation at -30 °C in THF were 0.51 for the strontium and 0.69 min^{-1} for the barium salt.

Studies by ^{1}H n.m.r. have shown [6] that the coalescence temperature for the phenyl rotation in THF solutions of the lithium salt of 1,3-diphenylallyl carbanion (30 °C) is higher than that for the potassium salt (15 °C). In contrast, T_c for phenyl rotation in the 1-phenylallyl anion in THF is higher for the potassium salt (-15 °C) than for the lithium salt (-31 °C); the methylene rotation shows a similar cation dependence.[11] The barrier to rotation about a multiple carbon–carbon bond of a carbanion is dependent upon the π bond order which in turn is determined by the total π electron density of the carbanion. The lithium salt of 1,3-diphenylallyl is almost entirely present in THF as the loose ion pair and, in consequence, the maximum possible electron density resides on the anion. In contrast, the corresponding potassium salt is a tight ion pair and some π electron density lies between the cation and the anion. The reduced electron density on the anion is reflected by

a downfield shift of the spectrum of the potassium salt with respect to the lithium salt, and in a reduction of the barrier to rotation.[6] However, when ammonia is employed as solvent, the lithium and potassium salts are both present as loose ion pairs and ^{13}C n.m.r. has shown [12] that phenyl rotation proceeds at identical rates for the two salts. In contrast, the lithium and potassium salts of the 1-phenylallyl carbanion are both predominantly tight ion pairs in THF. The greater ability of the lithium ion to withdraw electron density from the carbanion in a tight ion pair is demonstrated both by the downfield position of the ^{1}H n.m.r. spectrum with respect to that of the potassium salt and by the correspondingly lowered barrier to rotation.

The kinetic results obtained for the cis,trans $\longrightarrow$ trans,trans-DPP$^-$M$^+$ relaxation process mirror the results obtained for the phenyl rotation processes. Thus, the loose ion pairs of DPP$^-$ with the alkali-metal and the alkaline-earth cations all have effectively the same rate constant. In contrast the tight ion pairs have rate constants which are much greater than those of the loose ion pairs. This is particularly evident from the results for DPP$^-$Li$^+$ in THF–Et$_2$O mixtures where the net rate constant is almost linearly proportional to the mole fraction of tight ion pairs. The rate constants in THF for the ion pairs of DPP$^-$ with Li$^+$, Sr^{2+}, and Ba^{2+} are similar and markedly larger than for K$^+$ and Na$^+$ suggesting that interionic separation may also be an important factor, the rate constant being increased by decreasing interionic separation.

Finally, it is interesting to compare the relaxation rate constant in methylamine at -10 °C for DPP$^-$M$^+$ (0.20 min^{-1}) with that for the relaxation of trans-1-phenyl-trans-3-methylallyl ion pairs [13] in liquid ammonia at 0 °C to the trans,cis conformer (1.9 $\times$ 10^{-2} min^{-1}). The smaller rate constant for the latter process is in accord with the reduced delocalisation of charge possible with a single phenyl substituent.

The mechanism of the photolytic reaction is of very considerable interest, not only within the confines of the present paper, but also in as much as the allylic ion represents the three carbon atom analogue of the much-studied two (ethylenic) carbon system stilbene. At the present time we are uncertain whether a singlet or triplet excited state is involved. A further observation under investigation is that whereas the loose ion pair of trans,trans-DPP$^-$M$^+$ is intensely fluorescent at low temperature, that of the cis,trans isomer is at best weakly fluorescent.

[11] V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1968, **90**, 495.

[12] R. J. Bushby and G. J. Ferber, *Tetrahedron Letters*, 1974, 3701.

[13] G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *Rec. trav. Chim.*, 1969, **88**, 1377.