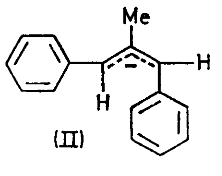
Nuclear Magnetic Resonance Spectroscopy of Diphenylallyl Carbanions. Part II.[1] Conformational Studies

By **J. W. Burley** and **R. N. Young,*** Department of Chemistry, The University, Sheffield S3 7HF

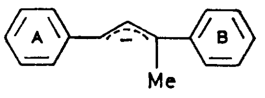
A study of the ^{1}H n.m.r. spectra of three diphenylallyl carbanions in the range 30 to −60 °C has revealed the occurence of rotational processes. The 1,3-diphenylallyl and 1-methyl-1,3-diphenylallyl carbanions exhibit hindered rotation of the phenyl groups, whilst the 2-methyl-1,3-diphenylallyl carbanion additionally shows hindered rotation about the C–C bonds of the allyl system.

ALTHOUGH the use of n.m.r. spectroscopy to study hindered rotations and inversions of neutral organic molecules is common, conformational studies of carbanions are much less frequent. To our knowledge, the only examples of such work are investigations of the phenylallyl[2] and 1-methyl-3-phenylallyl[3] anions. In the former system it was possible to observe hindered rotation of both the allylic methylene and the phenyl group. The present study has demonstrated the occurrence of similar phenomena in three diphenylallyl carbanions, 1,3-diphenylallyl (I), 2-methyl-1,3-diphenylallyl (II), and 1-methyl-1,3-diphenylallyl (III).

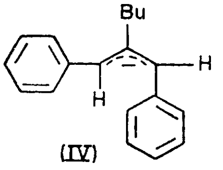
(I)



(II)



(III)



(IV)

EXPERIMENTAL

1,3-Diphenylpropene[4] and 1,3-diphenylbut-1-ene[5] were prepared and purified as previously described. 2-Methyl-1,3-diphenylpropene was synthesised by the dehydration of 1,1-dibenzylethanol and was purified by g.l.c.

Tetrahydrofuran (THF) was purified by distillation under high vacuum from sodium–potassium alloy, to which a little benzophenone had been added to act as an indicator.

Solutions of the alkali-metal salts of the hydrocarbons were prepared in sealed Pyrex vessels with quartz cells (1·0 mm pathlength), or conventional n.m.r. tubes, integral with the apparatus. Sodium, potassium, or rubidium was introduced into the reaction vessel by distillation. The lithium salts were prepared using n-butyl-lithium. In order to minimise the decomposition of butyl-lithium caused by reaction with THF, these solutions were prepared immediately prior to use. Approximately 0·5 cm^3 of a stock solution of 2·4M-butyl-lithium in hexane was introduced into the reaction vessel from an ampoule *via* a breakseal; the hexane was removed under high vacuum, and THF was distilled onto the residue. The final concentrations of the carbanion solutions were approximately 10^{-3}M for studies of the visible absorption spectra and 1M for the n.m.r. spectra. Tetramethylsilane was used as internal reference in the latter.

Visible spectra were recorded using a Perkin-Elmer 137 u.v. spectrophotometer. N.m.r. spectra were obtained using a Varian HA-100 MHz instrument fitted with a variable temperature attachment. The spectra were recorded in the range 30 to −60 °C.

RESULTS AND DISCUSSION

The n.m.r. spectrum of the lithium salt of 2-methyl-1,3-diphenylpropene (II) is presented in Figure 1. This spectrum differs strikingly from that of the lithium salts of (I) and (III) recorded under the same conditions,[1] in that there are no signals due to the 1- or 3-protons of the allyl skeleton. The remainder of the spectrum is, however, essentially similar to that of (I) and (III) since the *ortho*- and *meta*-proton signals occur together at τ 3·37 and the *para*-proton signals are distinctly to higher field at τ 4·07. The spectrum of the potassium salt of (II) in THF (at 30 °C) occurs downfield of that of the lithium salt and differs from it in that a resonance due to the 1- and 3-allyl protons is evident at *ca.* τ 5·3 (Table).

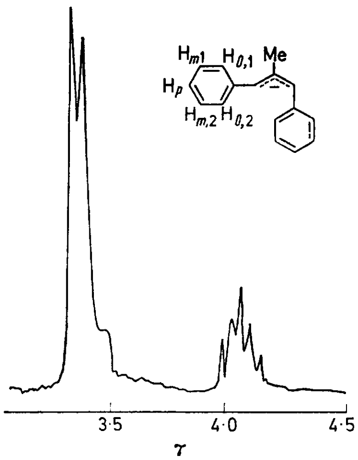


FIGURE 1 The n.m.r. spectrum of the lithium salt of 2-methyl-1,3-diphenylallyl ion in THF at 30 °C (sweep width 1000 Hz)

---

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

[2] V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1968, **90**, 485.

[3] G. J. Heiszwolf, J. A. A. Van Drunen, and H. Kloosterziel, *Rev. Trav. Chim.*, 1969, **88**, 1377.

[4] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*C*), 1971, 3780.

[5] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*B*), 1971, 1018.

Detailed spectroscopic studies[5,6] of the salts of (I) and (III) in THF have shown that the lithium salts are almost entirely in the form of solvent-separated ion pairs, whereas the potassium salts are contact ion pairs. Accordingly, since the cation withdraws electron density from the anion in the contact ion pair, the ^{1}H resonances occur at lower field for the potassium than for the lithium salt. Indeed, as we have reported,[1] this may be used as the basis of a method for the determination of the equilibrium constant for the solvation process. In order to verify that this effect also accounts for the observations on the salts of (II), visible absorption spectra were measured. The results (Table) confirm that the lithium and potassium salts are respectively solvent-separated and contact ion pairs. Significantly, however, the absorption maxima of (II) are *ca.* 30 nm to shorter wavelength than those of (III) and (I), suggesting that the conformations of these anions are different. This suggests that (II) adopts the *cis–trans* conformation in order to minimise steric interactions between the methyl and phenyl groups, rather than the *trans–trans* structure of (I) and (III). In support of this hypothesis, it was observed that the lithium salt of (IV), having the even larger t-butyl substituent, has an absorption maximum at 533 nm under identical conditions. Although no comparable data are available for carbanions, it is well known that the absorption spectra of the *cis*-conformers of neutral aromatic hydrocarbons are typically at shorter wavelength than the *trans*-conformers.[7]

N.m.r. (τ values) and visible spectroscopic data for the alkali-metal salts of 2-methyl-1,3-diphenylallyl ion in THF at 30 °C

Metal	$H_o + H_m$	H_p	$H_a + H_b$	$\lambda_{max.}$/nm ± 2	
Li	3·37	4·07			536
Na	3·16	3·84		500	536
K	3·26	3·94	5·3br	505	
Rb	3·27	3·95	5·3br	507	

The appearance of the resonance of the 1- and 3-protons of the potassium salt of (II) as a broad singlet at τ 5·3 and the complete absence of such a signal in the lithium salt indicate the occurrence of a rapid exchange process at ambient temperature. The influence of temperature upon the resonance of the 1- and 3-protons of the potassium salt was investigated in the range 30 to −60 °C and the results are shown in Figure 2. As the temperature was lowered, the broad singlet at τ 5·3 first collapsed and was then replaced by sharp singlets of equal intensity at τ 4·678 and 5·899. Clearly, these changes correspond to the freezing of the conformational equilibrium A. A consideration of ring current effects leads to the assignment of the signals at τ 4·678 and 5·899 to H_a and H_b respectively. Coincident with the variation in the 1- and 3-allyl proton resonances there were changes in the $H_o + H_m$ signal which were too complex for a simple first-order interpretation. Clearly, a complete analysis would have to take account of the different rotational rates of the two different phenyl groups about the C–Ph bonds as well as of the influence of the hindered rotation about the allyl C–C bonds upon the phenyl proton signals.

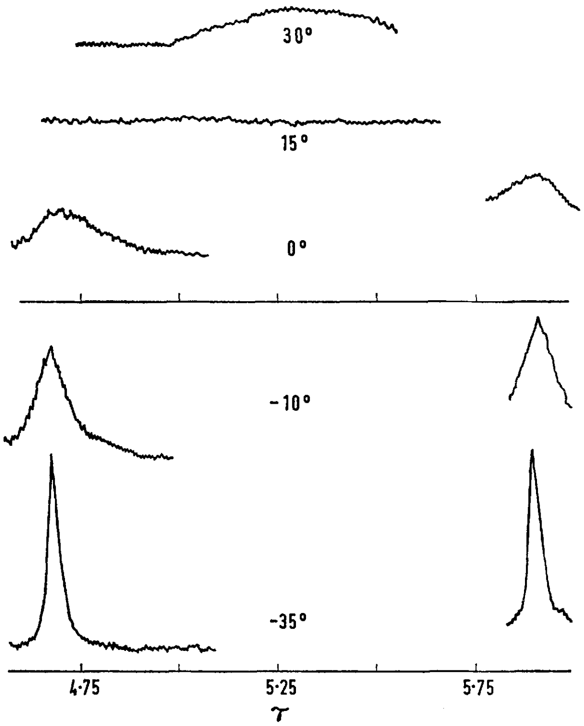
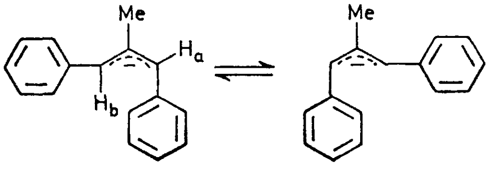


FIGURE 2 The effect of temperature upon the allylic proton signals of the potassium salt of 2-methyl-1,3-diphenylallyl ion in THF (sweep width 250 Hz)



equilibrium A

In suitable instances it is possible to determine the free energy of activation, $\Delta G^‡$, for an exchange process from the coalescence temperature T_c. In the case of the potassium salt, it was not possible to determine an accurate value for T_c since the high-field signal due to H_b was situated too close to the low-field resonance of the solvent. As the temperature was lowered, the solvent resonance broadened sufficiently to distort the base line. However, it was evident that $T_c(K^+)$ is 15 ± 4 °C; $T_c(Li^+)$ was found to be 30 ± 2 °C. These results indicate that $\Delta G^‡(Li^+) > \Delta G^‡(K^+)$. A similar exchange process has been observed for the phenylallyl anion.[2] In contrast to the present anion system, however, they observed that the T_c for methylene rotation was lower for the lithium salt than for the potassium salt. This

---

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

[7] H. H. Jaffe and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962.

apparent anomaly can be rationalised by a consideration of the nature of the ion pairs involved. 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 anion. The lithium salt of (II) is entirely solvent-separated in THF and the maximum possible electron density resides upon the anion. In contrast, the potassium salt is a contact ion pair and some π electron density lies between the cation and anion and the n.m.r. spectrum of the lithium salt is upfield from the potassium salt. Since there is less π electron density on the anion, the barrier to rotation about the allyl system is reduced *i.e.* $T_c(K^+) < T_c(Li^+)$. The results of Sandel *et al.*[2] are in accord with both the lithium and potassium salts of the phenylallyl anion being predominantly contact ion pairs, with the n.m.r. spectrum of the lithium salt being downfield from the potassium salt. The greater electron withdrawing power of the smaller lithium cation results in $T_c(Li^+) < T_c(K^+)$.

The 1,3-*Diphenylallyl Carbanion.*—Since visible absorption spectrometry has shown that only the lithium salt of (I) exists solely as the solvent-separated ion pair in tetrahydrofuran this solution was chosen for detailed study by the n.m.r. technique. The results of measurements in the range 30 to —60 °C are shown in Figure 3. At 30 °C the spectrum can be readily interpreted on a first-order basis.[1,8] Relatively little change is observed in the spectrum between 30 and —15 °C, but below this temperature the $H_o + H_m$ and H_p signals first broaden, then resharpen to show a much more complex splitting pattern at —60 °C. The signal due to the allylic 1- and 3-protons appears as a doublet at τ 5·37 and remains sharp over the entire temperature range, indicating the absence of an allylic conformational exchange of the type observed for anion (II). The spectral changes of Figure 3 must therefore be attributed to hindered rotation of the phenyl groups. Whilst the signal observed for $H_o + H_m$ at 30 °C is apparently simple, it must in reality be a complex signal simplified by coincident H_o and H_m chemical shifts; the complex spectra observed at low temperatures must result from the removal of this coincidence.

At —30 °C the spectrum exhibits a broad *para*-proton signal and a broad triplet at τ 3·38 together with some signals of lower intensity to higher and lower field. When the temperature was lowered to —45 °C, the *para*-proton signal sharpened to a triplet, the broad triplet at τ 3·38 became even broader and two entirely new resonances appeared at τ 3·23 and 3·89. Further lowering of the temperature to —60 °C caused a dramatic increase in resolution which, coupled with the integrated intensities, permitted a simple first-order analysis. A split in the signal of the *para*-proton is induced by the two *meta*-protons which are almost equivalent, giving rise to a triplet at τ 4·13 with $J_{m,p}$ 6·5 Hz. The two doublets at τ 3·23 and 3·89 are attributed to the two *ortho*-protons $H_{o,1}$ and $H_{o,2}$ ($J_{o,m}$ 7·5 Hz). The *meta*-protons $H_{m,1}$ and $H_{m,2}$ are coupled to the *ortho*- and *para*-protons and, since $J_{m,o}$ is very similar to $J_{m,p}$, each *meta*-proton gives rise to a triplet. Overlap of the *meta*-triplets results in the quartet observed at τ 3·46. Whilst it is impossible to give a categorical assignment, it seems likely that the high-field signals are due to $H_{o,2}$ and $H_{m,2}$ since they are further from the influence of the ring current of the other aromatic ring. At the coalescence temperature (*ca.* —30 °C) the $H_{o,1}$ and $H_{o,2}$ signals collapse, but a triplet representing $H_{m,1}$ and $H_{m,2}$ is still evident since the chemical shifts of the latter are more nearly equivalent.

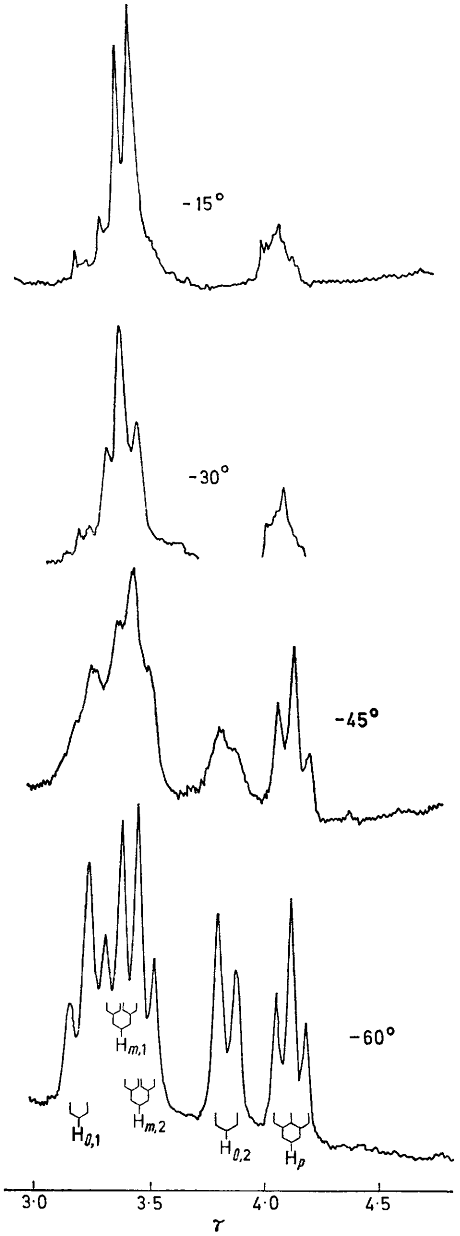


FIGURE 3 The effect of temperature upon the n.m.r. spectrum of the lithium salt of 1,3-diphenylallyl ion in THF (sweep width 500 Hz)

---

[8] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.

Freedman and his co-workers[8] studied the spectrum of the lithium salt of (I) in THF between 40 and −30 °C and consequently observed little change. They did, however, conclude that the barrier to rotation about the allyl system was low, since they obtained *trans–trans*-(I) from both *cis*- and *trans*-1,3-diphenylpropene.

The 1-*Methyl*-1,3-*diphenylallyl Carbanion.*—The n.m.r. spectrum of the lithium salt of (III) in THF at 30 °C indicates that the phenyl groups are non-equivalent, due to the perturbation of the π electron density distribution by the methyl group. We have previously reported full details of this spectrum,[1] which are in accord with the view that the phenyl bearing the higher electron density is the one further from the methyl group. Because of the difference in electron density, it is to be expected that the activation energies for phenyl rotation would also be different. This prediction was vindicated by the observation that although the phenyl signal at higher field became significantly broadened at 0 °C, that at lower field remained sharp until the temperature was brought below −20 °C. Unfortunately, it did not prove to be possible to estimate the values of $\Delta G^{\ddagger}$.

[2/967 *Received*, 1*st May*, 1972]