Organic Anions. Part 6.[1] Thermal and Photochemical Interconversion of (E,E)- and (E,Z)-Diphenylallyl Anions

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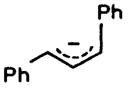
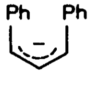
Whereas the position of the $E,E/E,Z$ equilibrium for 1,3-diphenylallyl-lithium in tetrahydrofuran is highly photosensitive, the corresponding equilibrium in liquid ammonia appears to be unaffected by light. N.m.r. measurements for the sodium salt in this solvent between −20 and +20 °C yield a ΔH value for the E,E to E,Z conversion of *ca.* 6.9 ± 1.0 kJ mol^{-1}.

N.M.R. studies of 1,3-diphenylallyl anion using liquid ammonia as solvent were first reported by Heiszwolf and Kloosterziel [2] and similar results were obtained for tetrahydrofuran solutions by Freedman *et al.*[3] and later by Burley and Young.[4] These seemed to indicate that only the E,E-conformer (1) was present. When we investigated the protonation of this anion and its derivatives (in liquid ammonia) we were, therefore, surprised to find that substantial amounts of the *cis*-olefins were obtained [5] (4—5% for the parent system and up to 11% for some ring-substituted derivatives). This could only be explained if the solutions contained corresponding amounts ($\geqslant$4%) of the E,Z-conformer (2). [The Z,Z-conformer (3) can probably be discounted on steric grounds.] We consequently re-examined the ^{1}H n.m.r. spectra and were able to find additional resonances which we attributed to this conformer.[6] The integrals corresponded to *ca.* 7% E,Z- and 93% E,E-conformer at −30 °C (15 : 85 t-butyl methyl ether–ammonia). While our results were in process of publication a more detailed, independent study by Boche and Schneider appeared.[7] They reported that the resonances for the E,Z-conformer could also be detected in THF and at −30 °C the mixture was composed of 5.6% of the E,Z- and 94.4% of the E,E-conformer. In view of the experimental difficulties and the difference in solvent we regard these results as being in satisfactory agreement with our own. They also studied the temperature dependence of the equilibrium from which an enthalpy change for $E,E \longrightarrow E,Z$ of 9.1 ± 1.7 kJ mol^{-1} (THF) may be derived.† We also examined the electronic absorption spectra [6] in liquid ammonia and observed, not only the expected adsorption at 550 nm for the E,E-conformer, but also a weak shoulder at 525 nm whose intensity increased with temperature and which we tentatively assigned to the E,Z-form. Subsequent findings have tended to confirm this conclusion. It has been shown that the E,Z-conformer does, indeed, absorb at *ca.* 30 nm shorter wavelength than the E,E-conformer [8,9] and it has been pointed out that the enthalpy change estimated from our absorption spectra [9] (6—9 kJ mol^{-1} ‡) is in reasonable agreement with the value for the $E,E \longrightarrow E,Z$ change (9.1 ± 1.7 kJ mol^{-1}) determined from Boche and Schneider's n.m.r. spectra.


(1)


(2)


(3)

Despite this wealth of confirmatory evidence Parkes and Young have recently questioned the validity of our conclusions [9] and reaffirmed their view [4] that 'these ions normally adopt the *trans,trans*-conformation'. They have shown that in THF light can convert the E,E- into the E,Z-form and report that in the n.m.r. spectrum 'several duplicate experiments failed to show any signals other than those of the *trans,trans*-conformer' except in one experiment in which the tube had been irradiated with white light. They furthermore suggested that the build up of the shoulder in the electronic absorption spectrum at 525 nm (liquid ammonia), which we observed, was a photochemical rather than thermal effect. Our experiments were performed starting at a low temperature and allowing the apparatus to warm to room temperature and so the build up of E,Z-conformer could (they argue) be the result of stray light. Since they mainly used ether solvents and we only used liquid ammonia we decided to reinvestigate the situation and have found that the photosensitivity of these compounds is markedly solvent sensitive.

Firstly, as may be seen from the Figure, when liquid ammonia is used as the solvent, there are no difficulties in observing the ^{1}H n.m.r. signals for the benzylic protons of both the E,E-, δ 4.71 (d), and E,Z-conformers, δ 5.23 and 4.28 (2 d). We found no significant difference in the relative intensities of these signals whether or not the sample had been exposed to light or (provided a short time was allowed for equilibria to be established) whether the sample had previously been heated or cooled. Over a range of temperatures we found the following percentages of E,Z-isomer: −20 °C, 6.7%; −10 °C, 8.5%; 0 °C, 9.1%; +10 °C, 9.9%; +20 °C, 10.6%, leading to a value for ΔH of 6.9 ± 1.0 kJ mol^{-1}.

A repeat of Parkes and Young's determination of the electronic absorption spectra [9] for the lithium salt in THF confirmed that in this solvent the position of the $E,E/E,Z$ equilibrium is quite remarkably light sensitive. It even responds to changes in weak overhead lighting.

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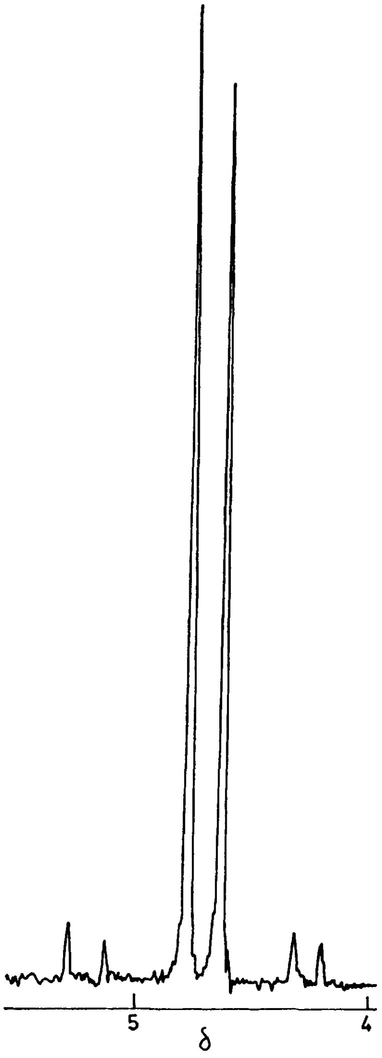
† Professor Kloosterziel, personal communication, has reported that re-examination of his spectra [2] shows resonances for both E,E- and E,Z-conformers.

‡ The estimate of the error here is probably somewhat conservative. The value obtained depends markedly on what assumptions are made.

Furthermore we found that the position of the photostationary state was markedly dependent on the type of lamp employed and could be manipulated by the use of suitable filters. Thus, filter with a 550 nm cut off * gave an apparently complete conversion into the E,Z-form, even the shoulder for the E,E-conformer apparent in the literature spectrum [9] disappearing. In marked contrast to the behaviour in THF, in liquid ammonia no light sensitivity could be detected. Even when a lamp (fluorescent tube, quartz–iodine, or medium pressure mercury u.v.) was placed within 5 cm of the cell immediately before the spectrum was determined there was no significant change. Similarly a repeat measurement of the temperature dependence of the absorption spectra for the lithium, sodium, or potassium salts in liquid ammonia showed that the changes previously reported [6] are quite reproducible and independent of whether an ascending or descending temperature scale is employed. This confirms that the changes we observed are indeed the result of a thermal rather than photochemical phenomenon.



Benzylic region of the 90 Mz ^{1}H n.m.r. spectrum for the sodium salt of 1,3-diphenylallyl anion in liquid ammonia at −25 °C

In conclusion there can be no doubt that both in liquid ammonia and in ether solvents salts of the diphenylallyl anion are an $E,E/E,Z$ mixture. Accurate estimation of the enthalpy difference between the two forms is not easy because of the small changes involved and the limited temperature range accessible. However, the values obtained by n.m.r. spectroscopy, 6.9 ± 1.0 (NH_3) and 9.1 ± 1.7 kJ mol^{-1} (THF),[7] are doubtless in the right region. Similarly there can be little doubt that the changes we reported in the temperature dependence of the visible absorption spectra in liquid ammonia were the result of a thermally induced shift in the $E,E/E,Z$ equilibrium since we have now shown that the solutions are not photosensitive and the changes are as expected both in position [8,9] and in magnitude.[9]

EXPERIMENTAL

The methods employed for the generation and observation of the ions were as described previously and, as in previous work, all Pyrex apparatus was used in the absorption spectroscopy experiments.[6] Some difficulty was experienced in obtaining good integrations of the n.m.r. spectra and the percentage values for the E,E- and E,Z-forms were therefore based on peak height measurements. They were averaged over at least four determinations at each temperature. Checks were made for saturation of the n.m.r. signals but none was detected. Both in n.m.r. and adsorption spectroscopy experiments it was necessary to allow some time [7] for equilibrium to be established, particularly at the lower temperatures.

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* Perspex Amber 300 supplied by Barkston Rubber and Plastics Co., Leeds.

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