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RADICAL IONS IN PHOTOCHEMISTRY 10. THE PHOTOSENSITIZED (ELECTRON-TRANSFER) ISOMERIZATION OF 1,2-DIPHENYLCYCLOPROPANES.[1]

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The photoisomerization of the 1,2-diphenylcyclopropanes in polar solvent sensitized by 1-cyano- and 1,4-dicyanonaphthalene proceeds via an electron-transfer mechanism. An analysis of photo-CIDNP results provide details regarding the intermediates.

The photochemical trans—cis-isomerization of 1,2-diphenylcyclopropanes (trans (1), cis (2)), is particularly interesting because of the unusual electronic excited states and/or intermediate(s) which must be involved.[2-6] Substituted naphthalenes have been used as photosensitizers for this reaction and a mechanism involving an exciplex or an electron-transfer process (favoured when electron withdrawing substituted naphthalenes were used) has been suggested.[4,5] We report here, results of a photophysical and photo-CIDNP study of this isomerization, using 1-cyanonaphthalene and 1,4-dicyanonaphthalene as photosensitizers, which supports a mechanism involving formation of a radical ion pair and subsequently the 1,3-biradical triplet as shown in the Figure.

Irradiation of a benzene or acetonitrile solution of 1 and naphthalene (3), 1-cyanonaphthalene (4), or 1,4-dicyanonaphthalene (5) leads to isomerization of 1 to 2. Other products are also formed in some cases and these have not yet been identified. The photostationary state (2/1), attained upon irradiation, depends upon both the solvent and the sensitizer; for example, 1.01[6] and 1.10 for 3 and 4 or 5 in benzene, and 0.37 and 0.43 for 4 and 5 in acetonitrile, respectively.

Fluorescence from the naphthalene (3) singlet is quenched by trans-1,2-diphenylcyclopropane (1) and weak exciplex emission (λ_{max} ca. 430 nm) is observed in benzene solution. The fluorescence from (4) and (5) is also quenched by 1; however, in these cases no exciplex emission is observed even in this non-polar solvent. The quenching rate constants of the fluorescence of 4 and 5 by 1 approach the diffusion limit (acetonitrile solution).[7] These results are consistent with the established concepts of the effect of solvent polarity on the relative stability of exciplexes and radical ions, and the free energy change for the electron-transfer process as estimated using the Weller equation.[8] The rapid quenching of the fluorescence of 4 and 5 by 1, and the absence of emission from an exciplex involving these components, is consistent with the large negative free energy change for the electron-transfer process (see Table).

Table The calculated (Weller equation) free energy change (ΔG) associated with the geminate radical ion pair from the encounter complexes.[8]

Donor	Acceptor	Donor $E^{ox}_{1/2}$, V[9]	Acceptor $E^{red}_{1/2}$, V[9]	Acceptor $\Delta E_{0,0}$, kcal mol^{-1}	ΔG kcal mol^{-1}
1	3	1.17	- 2.89[10]	92.0[12]	0.3
	4		- 2.33[11]	89.4[11]	- 10.0
	5		- 1.67[11]	86.4[11]	- 22.2
2	3	1.41	- 2.89	92.0	5.9
	4		- 2.33	89.4	- 4.5
	5		- 1.67	86.4	- 16.7

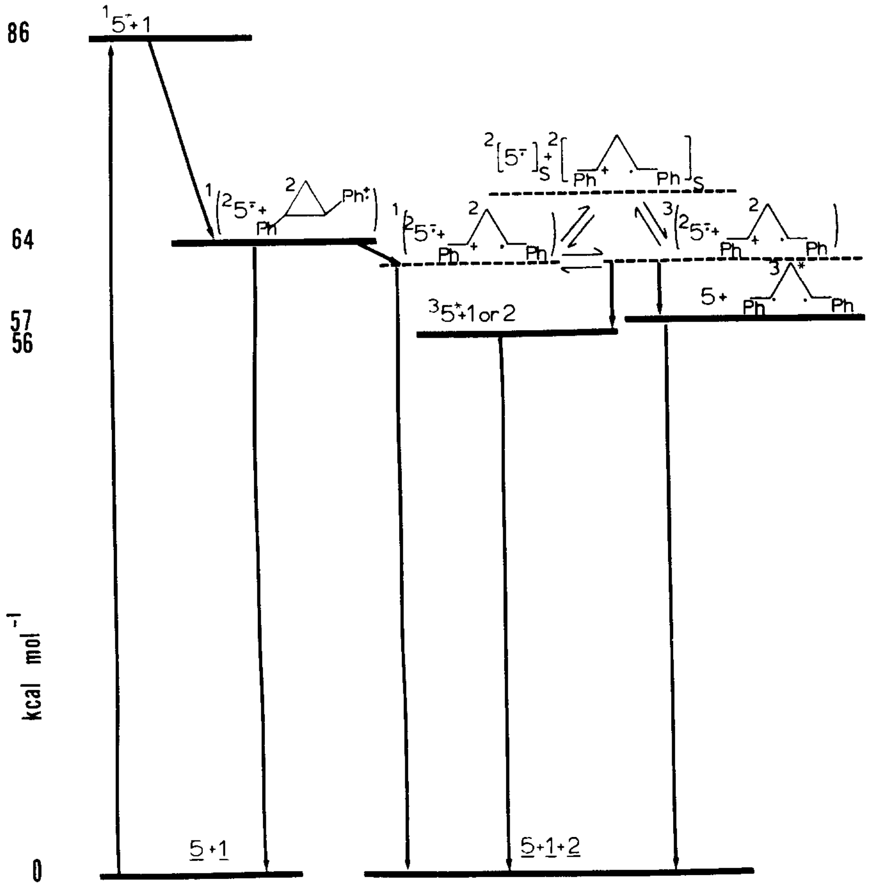
Photochemically induced dynamic nuclear polarization (CIDNP) has been used to gain insight into the mechanism of the isomerization. Irradiation of a degassed acetonitrile-d_3 solution of 1 and 5 in the ^{1}H nmr spectrometer gives a multiplet effect (AE) of the methine protons of 2, while the signal intensity for 1 remains almost unchanged. There is no observed polarization of the signal corresponding to the phenyl protons of 2; and unfortunately, it is impossible to detect any change in the signal due to the methylene protons of 2 since they are well hidden under the strong signal due to the methylene protons of 1. The irradiation also causes extensive broadening of the signal due to the protons of 1,4-dicyanonaphthalene which is probably the result of electron exchange between 5 and the radical anion of 5.[13]

The polarization observed in the methine protons of 2 is consistent with a major pathway for the isomerization involving the formation of the triplet 1,3-biradical via a triplet exit channel of the caged radical ion pair[13,14] (see Figure).[15] The first step after excitation of 5 is the formation of a singlet geminate radical ion pair. The fluorescence quenching study provides evidence that this step occurs at the diffusion controlled rate which is consistent with the calculated free energy change (- 22.2 kcal mol^{-1}). The initially formed radical cation has the three-membered ring intact since the electron has been taken from a phenyl ring.[16] This radical ion pair can either deactivate, by back electron-transfer, or the radical cation can cleave to give the radical ion pair consisting of the radical anion of 5 and the ring-opened radical cation of 1. The main decay pathway for this radical ion pair involves conversion to the corresponding triplet radical ion pair directly through hyperfine interation and spin orbit coupling. Back electron-transfer then would give mainly the triplet 1,3-biradical and ground state 5. Rapid ring-closure of the 1,3-biradical would then account for the observed polarization of the methine protons of 2.[17]

The triplet 1,3-biradical has been proposed as the phosphorescent state of 1,2-diphenylcyclopropane.[18] An estimate of the energy associated with this state can therefore be obtained from the emission spectra; (ca 57 kcal mol^{-1}), and it is well below the energy of the original geminate radical ion pair (64 kcal mol^{-1}).

Several possible alternative pathways are less likely. Formation of the singlet 1,3-biradical of 1 is energetically unfavourable.[18] Furthermore, simultaneous electron transfer and ring closure of the 1,3-biradical, while energetically favourable, is Franck-Condon forbidden. It follows, therefore, that the only back electron-transfer process, within the caged radical ion pair involving the ring-opened radical cation, which is favoured leads to the triplet 1,3-biradical.

Figure A mechanism (abbreviated) for the photosensitized (electron-transfer) isomerization of 1,2-diphenylcyclopropane (1) by 1,4-dicyanonaphthalene (5).



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References

1. Contribution No. 208 from the Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Canada.
2. G.W. Griffin, J. Covell, R.C. Petterson, R.M. Dodson and G. Klose, *J. Am. Chem. Soc.* *87*, 1410 (1965); E.W. Valyocsik and P. Sigal, *J. Org. Chem.* *36*, 66 (1971).
3. G.S. Hammond, P. Wyatt, C.D. De Boer and N.J. Turro, *J. Am. Chem. Soc.* *86*, 2532 (1964).
4. S.L. Murov, R.S. Cole and G.S. Hammond, *J. Am. Chem. Soc.* *90*, 2957 (1968).
5. S.S. Hixson, J. Boyer and C. Gallucci, *Chem. Commun.*, 540 (1974).
6. G.S. Hammond and R.S. Cole, *J. Am. Chem. Soc.* *87*, 3256 (1965).
7. The quenching rate constants, kq of 4 and 5 by 1 are 1.38×10^{10} and 1.50×10^{10} M^{-1} sec^{-1}, respectively.
8. D. Rehm and A. Weller, *Isr. J. Chem.* *8*, 259 (1970).
9. Redox potentials were measured by cyclic voltammetry reference to $Ag/Ag(NO_3)$ (0.1 M) electrode in acetonitrile.
10. E.S. Pysh and N.C. Yang, *J. Am. Chem. Soc.* *85*, 2124 (1963).
11. D.R. Arnold and A.J. Maroulis, *J. Am. Chem. Soc.* *98*, 5931 (1976).
12. S.L. Murov, "Handbook of Photochemistry", Marcel Dekker, Inc., New York (1973).
13. G.L. Closs and H.S. Czeropski, *J. Am. Chem. Soc.* *99*, 6127 (1977).
14. J. Bargon, *J. Am. Chem. Soc.* *99*, 8351 (1977).
15. The energy of the levels represented by the dash lines are uncertain.
16. This conclusion is based upon an analysis of the photoelectron spectra of 1 and 2 (D.R. Arnold and P.C. Wong, submitted for publication).
17. According to the modified Kaptein rule,[13,14] when Δg ca. 0, $\Gamma_{mij} = u\, \varepsilon\, a_i a_j J_{ij} \sigma_{ij} \gamma = (-)$ (AE) ($u = -$ singlet; $\varepsilon = +$ cage; $a_i = -H_\alpha$; $a_j = +H_\beta$; $J_{\alpha\beta} = +$; $\sigma_{ij} = +$ same radical and $\gamma = -$ triplet exit channel).
18. R.S. Becker, L. Edwards, R. Bost, M. Elam and G. Griffin, *J. Am. Chem. Soc.* *94*, 6584 (1972)

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