# Stereospecificity in the Thermal- and Photo-additions of *trans*-Stilbene to Tetrachloro-*p*-benzoquinone. Importance of Charge-correlation Factors in Cycloadditions which involve Donor–Acceptor Pairs

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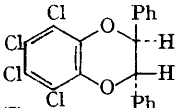
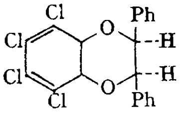
THE Woodward–Hoffmann Rules for concerted cycloadditions require those processes which are thermally allowed to be photochemically forbidden, and *vice versa*.[1] We report now a cycloaddition reaction which is unusual in that it occurs under photochemical conditions with a degree of stereospecificity approaching that found in the thermal process.

Tetrachloro-*p*-benzoquinone reacts with an excess of *trans*-stilbene in the dark at 128° to give the known[2] 1 : 1 adduct (I). The *cis*-adduct (II), m.p. 177°, could not be detected: control experiments with authentic *cis*-adduct (prepared as above, by use of *cis*-stilbene) showed that 1% of it would have been readily found.†


(I)


(II)

Tetrachloro-*p*-benzoquinone (1 mol.) and either *cis*- or *trans*-stilbene (5 mol.) did not react thermally in benzene under nitrogen at a detectable rate at 15°. Irradiation of the *trans*-stilbene system in the main longest-wavelength absorption band of the quinone ($\lambda$ >400 nm.) at 15° gave a product containing 88% of adduct (I) and 12% of adduct (II) (±1%). Although the recovered stilbene contained 9·5% of the *cis*-isomer, it is evident from the results given in the accompanying Communication[3] that *cis*-stilbene was not a significant precursor of the *cis*-adduct (II). The 12% of *cis*-adduct (II) formed during the reaction appears to result from an addition of *trans*-stilbene.

The Woodward–Hoffmann Rules indicate the existence of an allowed pathway for concerted thermal addition of *trans*-stilbene to the quinone; and the observed high stereospecificity accords with this. But it is also necessary to explain why the addition process is greatly accelerated by light, retaining much of its stereospecificity. Thus the corresponding photoadditions of *cis*- and *trans*-but-2-enes to phenanthrenequinone are completely non-stereospecific.[4] Farid observed a definite "memory" effect in the photoaddition of *cis*- and *trans*-stilbene to phenanthrenequinone, although stereoequilibrium was approached as the temperature was increased.[5]

Hence it seems that the photoaddition of *trans*-stilbene to tetrachloro-*p*-benzoquinone is a non-concerted process in which a large measure of steric control results from the marked dipolar character of the first-formed intermediate. The reactants differ more greatly in their electron-affinities than those studied in refs. 4 and 5, and the intermediate can be most simply pictured as a singlet diradical (III),[6] the structure of which contains a substantial contribution from the dipolar

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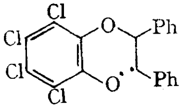
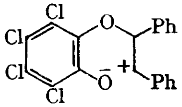
† Stereospecificity in the formation of adduct (II) was >93·5%. Some tetrachloro-*p*-benzoquinone-promoted isomerisation of *cis*- to *trans*-stilbene which occurred during the reaction makes it difficult to give an upper figure. Control experiments showed (a) that no significant amount of *trans*-stilbene was formed in the absence of tetrachloro-*p*-benzoquinone, and (b) that neither of the adducts (I) and (II) dissociates thermally to give *trans*-stilbene at 128°.

canonical form (IV), *i.e.* a polarised diradical, approaching a zwitterion. The corresponding triplet diradical (III) would be subject to similar inductive polarisation, although (IV) could not be written as a canonical form. The increased steric control associated with charge-correlation is visualised to result from an increase in the rate of intramolecular cyclisation of the intermediate in comparison with the rate of internal rotation.



(III)



(IV)

The solutions of the quinone and *trans*-stilbene showed only slight indications of charge-transfer absorption, so the charge-transfer implicit in the proposed mechanism would largely involve donation into a half-occupied bonding orbital in excited quinone.

We suggest that analogous polarised intermediates are likely to be involved in other cycloadditions involving donor-acceptor pairs which are obliged for orbital symmetry reasons to follow a stepwise course. The steric control to be expected from charge-correlation in such systems could render stereospecificity a less certain experimental test of concertedness than is usual.

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[1] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17, and references therein. (L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543, 553, has specified the circumstances under which the Woodward–Hoffmann Rules for concerted cycloadditions should apply to photochemical processes, and has drawn attention to some situations in which the Rules might not apply.)

[2] A. Schonberg and N. Latif, *J. Amer. Chem. Soc.*, 1950, **72**, 4828.

[3] D. Bryce-Smith and A. Gilbert, following Communication.

[4] Y. L. Chow and T. C. Joseph, *Chem. Comm.*, 1968, 604.

[5] S. Farid, *Chem. Comm.*, 1967, 1268: *cf.* S. Farid and K.-H. Scholz, *ibid.*, 1968, 412; S. Farid, D. Hess, G. Pfundt, K.-H. Scholz, and G. Stefan, *ibid.*, 1968, 638.

[6] L. K. Montgomery, K. Schneller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1964, **86**, 622.