Photoreactions of *o*-Quinones with Olefins: Mechanism of the 1,4-Cycloaddition

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THE photoaddition of *o*-quinones to olefins to yield dihydro-1,4-dioxin and/or α-keto-oxetan derivatives has been much studied.[1] The mechanism of this reaction is, however, still not clear.

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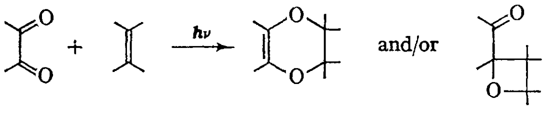

We have recently shown that the photoaddition of phenanthrenequinone to stilbene yields *cis*- and *trans*-1,4-cycloadducts.[2] Since phenanthrenequinone is a photosensitiser for the *cis–trans*-isomerisation of the olefin, we have carried out the reaction at relatively high concentration of either stilbene isomer (10^{-1} M) with a quinone concentration of 10^{-3} M. After the irradiation ($\lambda > 390$ mμ) only 5 ±1% of stilbene had been isomerised in both cases. The product was analysed by use of n.m.r. spectroscopy. The values obtained have been roughly corrected taking into account this slight isomerisation and the fact that the quantum yield for the addition of phenanthrenequinone to *cis*-stilbene exceeds that for *trans*-stilbene by a factor of 2·1 (reaction in benzene), a value which is in good agreement with that found by Bohning and Weiss.[3] The Table gives the ratio of the *cis*-adduct to the total amount of 1,4-cycloadducts in the addition of phenanthrenequinone to *cis*- and *trans*-stilbene, respectively. The fact that stereo-equilibration is approached but not attained can be explained by using a concept similar to that put forward by Bartlett *et al.*,[4] assuming the formation of different biradicals A and B† by the addition of excited phenanthrenequinone to *cis*- and *trans*-stilbene, respectively. Termination of these intermediates to the corresponding adducts is considered to compete with internal rotation. The rotation around the C–C bond is viewed as a reaction proceeding over a small energy barrier. As shown in the Table, the selectivity of the addition is reduced with increasing temperature leading to more stereo-equilibrated product. The data given in the Table allow a calculation of the difference between the activation energies for the internal rotation and termination reactions to be 3·8 kcal./mole for A and 4·8 kcal./mole for B.

TABLE

Product distribution of the reaction of phenanthrenequinone with stilbene in benzene

$$\frac{cis\text{-Adduct}}{cis\text{- + }trans\text{-Adduct}} \times 100$$

Temp. (° C)	Addition to *cis*-stilbene	Addition to *trans*-stilbene
15	72	19
25	69	23
45	65	29
70	60	35

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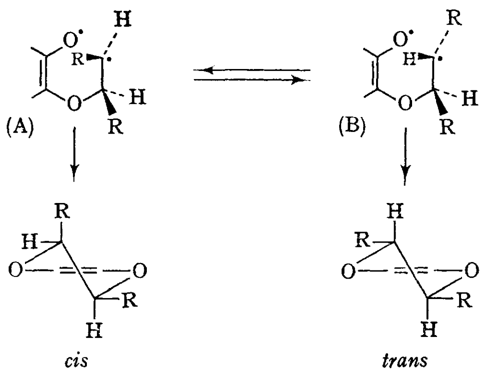

When phenanthrenequinone treated with 1-phenylpropene, one oxetan derivative and both *cis*- and *trans*-dihydro-1,4-dioxins are formed from either geometrical isomer. The ratio of the 1,4-cycloadducts and their temperature dependence are similar to those of the reaction with stilbene. On the other hand, the photoaddition of phenanthrenequinone to but-2-ene, giving among other products (oxetans and phenanthronols) the 1,4-cyclo-adducts in yields of 80%, shows deviation in two points from the above-mentioned examples: (i) The product is very slightly temperature dependent. This means that the differential activation energies are small. (ii) The *trans*-isomer of butene does not react selectively like that of stilbene and phenylpropene. At 25° the ratio of *cis*-dihydrodioxin to the total in the

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† A and B each represent 3 of the 6 possible conformers of the planar radical intermediate.

addition to *trans*-butene is 57%, to *cis*-butene 70%. The postulation of two competitive processes for these reactions (a concerted *cis*-addition and a two-step mechanism with free rotation) is unlikely on the basis of various evidence which will be discussed in a more detailed Paper.

(*Received, October 24th,* 1967; *Com.* 1142.)

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[1] *Cf.* C. H. Krauch, S. Farid, and D. Hess, *Chem. Ber.*, 1966, **99**, 1881; G. Pfundt and G. O. Schenck in "1,4-Cycloaddition Reactions," ed. J. Hamer, Academic Press, New York, 1967.

[2] G. Pfundt and S. Farid, *Tetrahedron*, 1966, **22**, 2237.

[3] J. J. Bohning and K. Weiss, *J. Amer. Chem. Soc.*, 1966, **88**, 2893.

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