Mechanism of Phenanthrenequinone Photocycloaddition to Olefins

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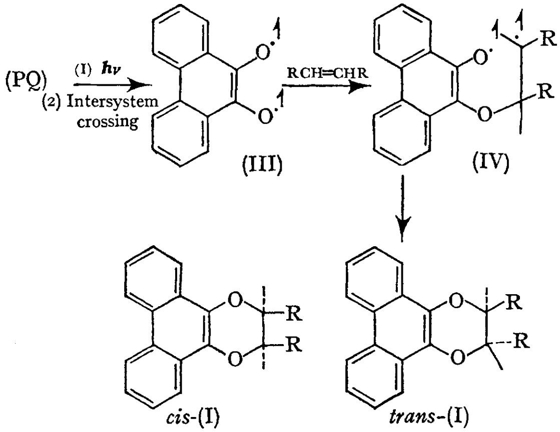
THE photocycloaddition of phenanthrenequinone (PQ) to conjugated olefins has been shown to give non-stereospecific adducts.[1,2] Because of the rapid isomerization of these conjugated olefins through PQ triplet sensitization[1,3] the stereospecificity of the cycloaddition [*e.g.* (III) → (I)] remains uncertain.[2b] To show the mechanism, it is vital to know the stereochemical consequence of the cycloaddition process. As a vertical or non-vertical energy transfer[4] from PQ (E_T = 48·8 kcal./mole)[1] to a simple olefin (E_T = *ca.* 80 kcal./mole)[5] is an unlikely process, investigations on cycloaddition systems have been carried out.

The photocycloadditions of PQ to either *cis*- or *trans*-but-2-ene† were slow and gave an identical mixture of *cis*- and *trans*-(I) in nearly quantitative yield. The n.m.r. integration of the methine protons showed the mixture to have a *cis*:*trans* ratio of 57:43. The assignments of *trans*-(I) (m.p. 162—163°, M^+ 264) and *cis*-(I) (m.p. 89—91°, M^+ 264) follow from the chemical shifts of the methine protons in which the methine proton of *trans*-(I) (240 c./sec. from tetramethylsilane) resonates at higher field[2,6] than that of *cis*-(I) (262 c./sec.). A similar photoaddition to an excess of *trans*-oct-4-ene gave a low yield of a mixture of *cis*- and *trans*-adduct but no *cis*-oct-4-ene in the recovered olefin (v.p.c. analysis). The low yield of this adduct indicates that a photoreduction may occur concurrently since the ketones which undergo photoreduction also add smoothly to olefins.[7] Further, both photoreactions have been shown to occur through the $n \rightarrow \pi^*$ triplet of ketones.[7] 9,10-Dihydroxyphenanthrene (II), the expected photoreduction product of PQ, is readily oxidized by air to PQ.[8] Although an attempt to trap (II) as the acetate in a photoaddition to cyclohexene was not successful, PQ was isolated (*ca.* 15%) even when PQ was shown to be completely consumed at the end of the reaction. The oily adduct (40% total) was a mixture of the *cis*- and *trans*-isomers and showed M^+ 290.



R=Me, Pr, -$[CH_2]_4$-

The points pertinent to the proposed mechanism are as follows. The concurrence of the reduction and the cycloaddition in the photolysis demonstrates that the $n \rightarrow \pi^*$ triplet of PQ (III or its resonance varieties) triggers the reaction in a stepwise manner. The triplet biradical (IV) must possess a fairly long lifetime in order to attain conformational equilibrium before reversing the electron spin and closing the dioxen ring to give the identical mixture of (I). The lack of *trans*-oct-4-ene isomerization proves that neither triplet sensitization of the olefin occurs nor, more specifically, does (IV) revert to (III) and an olefin.

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† The irradiation was performed in a Pyrex apparatus with a 450 watt Hanovia medium-pressure mercury lamp. A solution of PQ (0·5 g.) and excess of an olefin in benzene was bubbled with N_2 and kept at 5—10° while being irradiated for 4—5 hr. The progress of the reaction was followed by t.l.c. and/or u.v. spectroscopy.

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