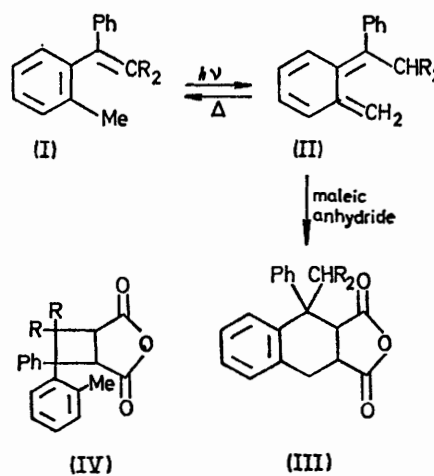


Diels-Alder Trapping of a Photochemically Generated *o*-Xylylene Intermediate from 1-Phenyl-1-*o*-tolylethylene

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Summary On irradiation, 1-phenyl-1-*o*-tolylethylene undergoes an intramolecular γ -hydrogen abstraction reaction; the resulting intermediate was trapped as the adduct with maleic anhydride.



THE exchange of deuterium between the vinylic and benzylic positions of 1,1-dideuterio-2-phenyl-2-*o*-tolylethylene (I; R=D) has recently been reported.¹ A mechanism involving reversible formation of an *o*-xylylene intermediate (II, R = D) by intramolecular γ -hydrogen transfer was postulated.¹ However, an intermolecular mechanism was not excluded by the results presented. The photochemistry of 1-phenyl-1-*o*-tolylethylene (I; R=H) in the presence of maleic anhydride has now been investigated with the intention of trapping the suggested intermediate (II; R=H) as the Diels-Alder adduct.

Irradiation† of a cyclohexane solution containing 1-phenyl-1-*o*-tolylethylene (I, R=H) and maleic anhydride yielded a 1:1 adduct, *m/e* 292, m.p. 192°. The n.m.r. spectrum was consistent with the tetralin structure (III, R = H), the product of a Diels-Alder reaction between the postulated intermediate and maleic anhydride. The alternative cyclobutane structure (IV, R = H), the product of 2 + 2 photocycloaddition, was excluded on the basis of the n.m.r. spectrum of a deuteriated adduct. The product from (I, R = H) displayed a three-proton methyl singlet at δ 1.94, whereas the corresponding signal for the adduct from (I, R = D) integrated for only a single proton. The deuteriated and non-deuteriated adducts both displayed

identical four-proton resonances in the δ 4.2—2.2 region. Thus vinylic hydrogen in the olefin (I) appears in the methyl group of the adduct (III).

The isolation of the adduct (III) provides convincing evidence for the formation of the *o*-xylylene intermediate (II) from excited 1-phenyl-1-*o*-tolylethylene (I), is in accord with the intramolecular mechanism proposed¹ for deuterium scrambling in (I), and also lends further weight to the analogies that have been suggested between the photochemistry of benzophenones and 1,1-diphenylethylenes.

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† Medium pressure mercury vapour lamp with Vycor filter.

¹ F. Scully and H. Morrison, *J.C.S. Chem. Comm.*, 1973, 529, and refs. therein.