Photochemical and Thermal Cycloadditions of *cis*-Stilbene and Tolan (Diphenylacetylene) to Tetrachloro-*p*-benzoquinone. Photodecarboxylation of an α-Diketone

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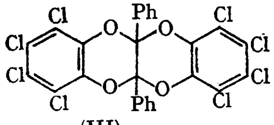
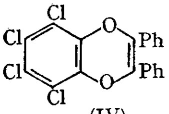
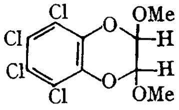
trans-Stilbene adds to tetrachloro-*p*-benzoquinone both thermally and photochemically to give adduct (I)†.[1] *cis*-Stilbene (in excess) adds thermally to the quinone at 128° to yield the corresponding adduct (II); but the corresponding photoreaction (benzene; $\lambda > 400$ nm.; 15°) follows an unusual course. Only a trace of a 1 : 5 mixture of adducts (I) and (II)† was obtained. The main photoproduct, m.p. 134°, was a 1 : 2 adduct (III), presumably formed by thermal addition of quinone to an intermediate adduct (IV). The very rapid thermal addition of *cis*-dimethoxyethylene to the quinone at 15° giving adduct (V), m.p. 164°, provides an analogy for this proposed step. Further, irradiation of tolan and the quinone in benzene at 15° gave the same 1 : 2 adduct (III), and no trace of the expected intermediate (IV).



(III)



(IV)



(V)

Formation of the proposed intermediate (IV) during the reaction with *cis*-stilbene could be rationalised through concerted suprafacial photodehydrogenation of either *cis*-stilbene (much less probable for *trans*-stilbene) and/or of adduct (II) by the quinone. However, control experiments showed that these processes occur with much

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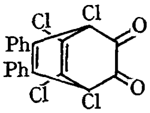
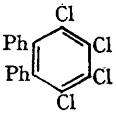
† Compounds (I) and (II) are the same as those in the preceding Communication.

lower quantum yields than that found for the formation of adduct (III) from *cis*-stilbene.

We could not confirm a report that adduct (IV) is formed by the thermal addition of tolan to tetrachloro-*p*-benzoquinone.[2] In our hands, reactions of equimolar mixtures of the components at temperatures over the range 98—150° gave a single 1:1 adduct (VI), m.p. 185° (decomp.), in yields of up to 70%. The main spectroscopic evidence for structure (VI) is as follows. The i.r. spectrum shows two carbonyl stretching frequencies at 1755 and 1735 cm.$^{-1}$, consistent with such groups in the indicated environment (and no hydroxylic absorption): thereby structure (IV) is excluded. The u.v spectrum (hexane) had $\lambda_{\max}$ (ϵ) 265 nm. (9,600), and 439 nm. (480). The n.m.r. spectrum showed only aromatic protons.



(VI)



(VII)

Adduct (VI) cleanly eliminated 2 mol. of carbon monoxide (i.r. spectrum) on irradiation of the crystals or a solution in benzene with visible light, giving a compound, m.p. 173,° which has analytical and spectroscopic data consistent with formulation as the *o*-terphenyl (VII). Such aromatisations are common with monoketones, but have not hitherto been known to occur with α-diketones, or in the solid phase.

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[1] D. Bryce-Smith and A. Gilbert, preceding Communication.

[2] L. Horner and H. Merz, *Annalen*, 1950, **570**, 89.