

Photochemical Entry into the Tetracyclo[4,4,0,0^{3,9},0^{4,8}]decane Ring System

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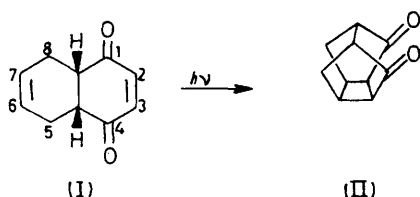
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Summary Irradiation of the duroquinone-*trans,trans*-hexa-2,4-diene *exo* Diels-Alder adduct (III) gives high yields of products (IV) and (V) formed *via* initial hydrogen abstraction; in contrast, irradiation of the corres-

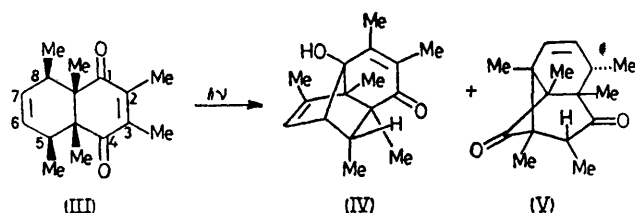
ponding *endo* Diels-Alder adduct (VI), in which hydrogen abstraction is sterically impeded, affords quantitatively the cage compound (VIII), a derivative of the tetracyclo[4,4,0,0^{3,9},0^{4,8}]decane-2,5-dione ring system.

IRRADIATION of the readily available *p*-benzoquinone-butadiene Diels–Alder adduct (I) does not give the unknown cage photoproduct (II),^{1,2} but instead, irradiation of the adduct (I) and a number of its alkyl derivatives leads to novel products best formulated as arising *via* intramolecular allylic hydrogen abstraction from C-5 or C-8.²

We now report that a reaction analogous to the (I) → (II) conversion can be brought about provided that substituents are introduced which impede the normally favoured hydrogen abstraction processes. This approach thus holds promise for the synthesis of a variety of substituted tetracyclo[4.4.0.0^{3,8}.0^{4,9}]decane-2,5-dione derivatives.



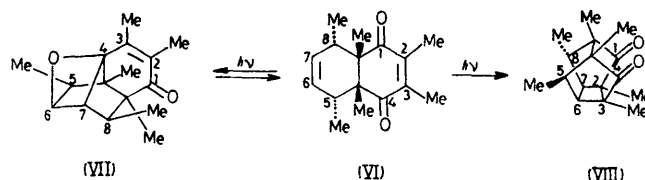
We have studied the epimeric Diels–Alder adducts (III), m.p. 103–104 °C and (VI), m.p. 57–58 °C formed between duroquinone and *trans,trans*-hexa-2,4-diene.[†] Irradiation[‡] of the adduct (III) gave a 1:2 ratio of the photoproducts (IV), m.p. 156.5–157 °C and (V) (oil) in 80% overall isolated yield. The photochemistry observed for (III) thus parallels that observed² for the duroquinone-2,3-dimethylbutadiene Diels–Alder adduct and very likely involves the competitive processes of allylic (C-5) hydrogen abstraction by either the C-1 carbonyl oxygen or the C-3 enone carbon atom leading, after collapse of the diradicals so produced, to (IV) and (V) respectively.



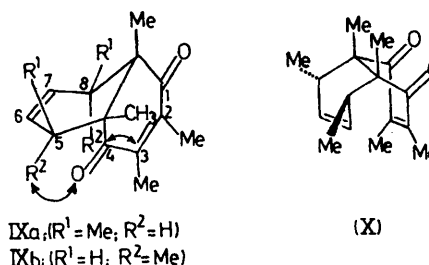
In contrast to these results, photolysis of the *endo* Diels Alder adduct (VI) leads to the intramolecular oxetan (VII) m.p. 59.5–60 °C, and the cage compound (VIII), m.p. 144–146 °C. The (VII): (VIII) ratio depends on the length of irradiation since (VII) is transformed into (VI) and (VIII) under the conditions of the experiment. Prolonged photolysis affords (VIII) in quantitative yield.

The structures of the photoisomers (VII) and (VIII) rest on their spectral data. Compound (VIII) showed λ_{max} (cyclohexane) 301 (ϵ 46) and 315 nm (ϵ 35); τ (CCl_4) 7.40 (2H, q, J 7 Hz, 5- and 8-H), 7.60 (2H, s, 6- and 7-H), 8.97

(6H, s, Me), 9.07 (6H, s, Me), and 9.33 (6H, d, J 7 Hz, 5- and 8-Me); ν_{max} (CCl_4) 5.68 and 5.75 ($\text{C}=\text{O}$) μm . Similar 'split' carbonyl i.r. peaks have been observed for the analogous C-5–C-8 bridged cage compounds.¹ The oxetan (VII) showed an $\alpha\beta$ -unsaturated carbonyl i.r. stretch (KBr) at 6.04 μm and exhibited the following definitive n.m.r. spectrum: τ (CCl_4) 5.64 (1H, d, J 4 Hz, 6-H), 7.40 (1H, d, J 4 Hz, 7-H), 7.78 (1H, q, J 7 Hz, 5- or 8-H), 8.03 and 8.33 (each 3H, br s, vinyl-Me), 8.35 (1H, q, J 7.5 Hz, 8- or 5-H), 8.97 (3H, s, 4a- or 8a-Me), 9.01 (3H, d, J 7 Hz, 5- or 8-Me), 9.30 (3H, s, 8a- or 4a-Me), and 9.46 (3H, d, J 7.5 Hz, 8- or 5-Me).



The differences in photochemical reactivity observed for the Diels–Alder adducts (III) and (VI) are explicable in terms of their respective 'twist' conformers (IXa) and (IXb) in which the bridgehead methyl groups are non-eclipsed. X-Ray crystallographic studies³ have shown this conformation to be preferred in the solid state (and hence very likely also in solution⁴) for analogous duroquinone–Diels–Alder adducts. As can be seen, conformation (IXa) allows for allylic hydrogen abstraction by either oxygen or carbon (arrows) whereas its epimer (IXb) does not. As a result, the alternative process of intramolecular oxetan formation is observed in the case of (IXb) (*i.e.*, VI), probably through initial overlap of the proximate and favourably disposed *p*-orbitals on C-4 and C-7. It seems likely that cage product formation also originates from conformation (IXb) since the only alternative, conformation (X), is disfavoured by bridgehead methyl eclipsing.



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[†] Satisfactory elemental analyses were obtained for all compounds described. The structural and stereochemical assignments for compounds (III)–(VI) are based on spectral data and analogy with previous work² and will be discussed in detail in the full paper.

[‡] Photolyses were performed at a concentration of 2 mg/ml in benzene using light filtered through a Corning # 7380 glass filter (transmitting $\lambda > 340$ nm) from an externally situated 450 W Hanovia lamp.

¹ R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudc, *J. Chem. Soc.*, 1964, 3062.

² J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. A. Wostradowski, *J. Amer. Chem. Soc.*, 1975, **97**, 2178.

³ S. E. Phillips, J. R. Scheffer, and J. Trotter, unpublished results.

⁴ F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, 1969, **91**, 3223; F. R. Jensen and R. A. Neese, *ibid.*, 1971, **93**, 6329.