

Photochemical Addition of 1,2-Naphthaquinones to *p*-Dioxen

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THE cycloaddition of *o*-quinones to olefins giving dioxans is a thoroughly investigated reaction as far as its scope¹ is concerned but as yet few proposals have been made regarding the multiplicity of the reacting excited state.²

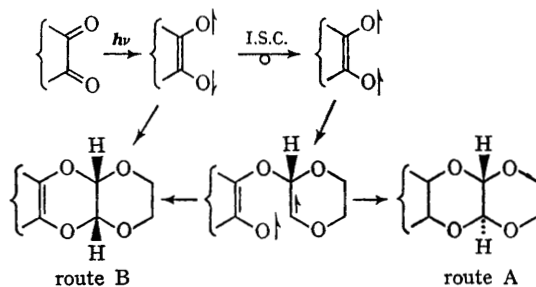
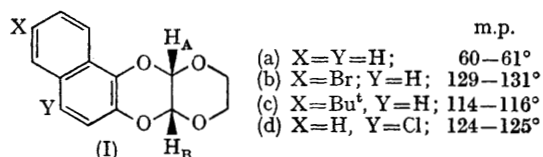
We report the photochemical addition of *p*-dioxen to some 1,2-naphthaquinones to give adducts† (I). The 1,2-quinones were readily prepared by oxidation of the corresponding 2-naphthol or 4-substituted 1-naphthol by potassium nitrosodisulphonate.³ Photolysis‡ of the quinone and olefin in benzene solution gave reasonable yields of the products (I) which were isolated by column chromatography.

Initial light absorption by the 1,2-quinone is envisaged as producing a diradical but the multiplicity of the excited state is never stated. Consideration of the consequence of triplet intermediacy indicates that, due to the necessary spin relaxation step, the products arising from cycloaddition with a cyclic olefin will probably be a mixture of *cis*- and *trans*-fused dioxans (Route A). When a singlet state is operational the addition will be concerted giving rise, exclusively, to a *cis*-product (Route B).

The observed spectra (60 Mc./sec.) of protons H_A and H_B appear as a typical AB pattern, the two protons being magnetically non-equivalent, and are tabulated below.

The decision whether the addition is concerted or a two-step process depends upon the low value of the coupling constant $J_{AB} \approx 1$ c./sec. and upon

the fact that n.m.r. studies do not show any additional complexity of the AB system which could be attributed to the presence of another isomer. The observed value of J_{AB} for (I) is



much lower than that encountered in *p*-dioxan where values of 3 c./sec. are recorded for *cis*-coupling constants.⁴ The reduction in value of J_{AB} can, however, be accounted for by (i) the increase in electronegativity of the substituents on the C–C bond and (ii) models show that the additional dioxen ring in (I) tends to distort the other ring thus diminishing the dihedral angle.

† Satisfactory elemental analyses were obtained for new compounds reported.

‡ Photolyses were carried out in an immersion apparatus using a Hanovia 125 w medium pressure mercury arc lamp and a Pyrex filter.

Both of these factors are well known to influence values of J_{AB} .⁵ Therefore it is not unreasonable

to assume that $J_{AB} \approx 1$ c./sec. is indeed a *cis*-coupling constant.

The above reaction scheme is a simplification of the ways of producing the observed *cis*-configuration in (I). Product formation could be due to reaction of an excited singlet state,[§] vibrationally excited ground state or by way of a triplet state where there is a means of transference of spin within the molecule.[¶] Experiments are in progress to try to differentiate between these pathways.

(Received, September 18th, 1967; Com. 999.)

TABLE

(Spectra were measured in $CDCl_3$ with internal Me_4Si)

Compound	Spectrum of ring junction Protons (H_A and H_B)		
	τ	J_{AB}	$\Delta\nu_{AB}$
(I) (a) X=Y=H	4.94	1.2 c./sec.	5.0 c./sec.
(b) X=Br; Y=H	4.66	1.3	4.7
(c) X=Bu ^t ; Y=H	4.61	1.3	4.7
(d) X=H; Y=Cl	4.60	1.3	4.7

§ The lifetime of the excited singlet state of 1,2-quinones is short which could exclude this pathway.

¶ It may be possible for transference of spin from oxygen to the naphthalene moiety if the energy considerations are favourable.

¹ J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405 and references contained therein; P. de Mayo in *Adv. Org. Chem.*, 1960, **2**, 367.

² D. C. Neckers in "Mechanistic Organic Photochemistry", Reinhold, 1967.

³ H.-J. Teuber and N. Gotz, *Chem. Ber.*, 1954, **87**, 1236.

⁴ J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836.

⁵ M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870.