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PHOTOCHEMICAL RING CONTRACTION REACTIONS OF SOME 9,10-ANTHRAQUINONE ORTHO - QUINONE DIAZIDES

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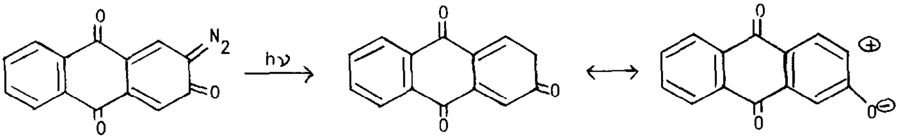
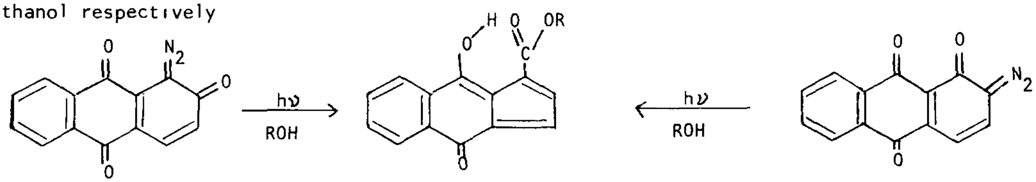
The photochemical ring contraction of *ortho*-benzoquinone diazides is a well known reaction of considerable synthetic value, leading to cyclopentadiene derivatives (the Sus reaction). The benzoquinone diazide system may be substituted or even annelated with other aromatic rings. However, very few examples are known where the benzoquinone diazide ring forms part of another quinone system, and in the anthraquinone series the only compound thus far examined (I) did not appear to undergo photochemical ring contraction[1]. The failure of this reaction was attributed to the high electrophilic character of the intermediate carbene (II), best represented by the resonance structure (IIb). The sole photochemical products obtained from (I) arose by insertion of the carbene into C-H bonds of the solvent[1].



(I) (IIa) (IIb)

Because of the potential synthetic value of the Sus reaction for the conversion of 9,10-anthraquinone *ortho* - quinone diazides to cyclopentadiene analogues of anthraquinone, we have re-examined this reaction and also investigated the photochemical behaviour of other positional isomers of (I). We wish to report that whereas (I) does not undergo photochemical rearrangement, the isomeric quinone diazides (III) and (IV) give high yields of the ring contraction products (V) and (VI) when irradiated in the presence of water and methanol respectively

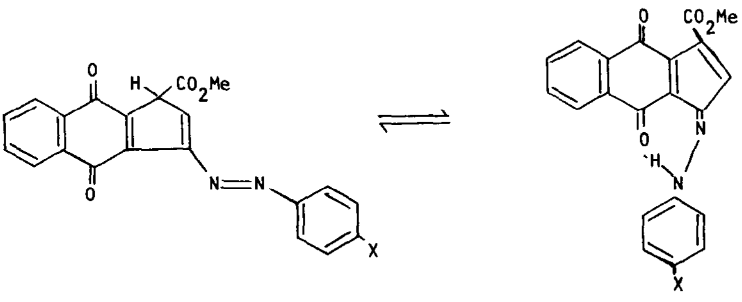


(III) (V) R= H, (VI) R= Me (IV)

1,2,9,10-Anthradiquinone-1-diazide (III)[2] was prepared by diazotisation of 1-amino-2-hydroxyanthraquinone In aqueous acetonitrile, (III) underwent a rapid reaction when exposed to u v or visible radiation ($\lambda <$ 500nm) The product, isolated in 63% yield, was shown to be the cyclopentadiene carboxylic acid derivative (V),[3] and was converted to the methyl ester (VI) with diazomethane The same ester was isolated in 78% yield, m p 145-146° (dec) by irradiation of (III) in methanol The mass spectrum of (VI) showed a strong molecular ion peak at m/e 254, and the n m r spectrum (CDCl$_3$) showed aromatic protons at τ 1 9-2 5 (4H,m), cyclopentadiene protons at τ 2 89 (1H, d, J 3Hz), methoxyl protons at τ 6 04 (3H, s), and a sharp hydroxyl signal τ -5 49 The last is indicative of strong intramolecular hydrogen bonding, as depicted in (VI) A substituted derivative of (V) has been prepared by a non-photochemical route, and showed a similar hydroxyl absorption at τ -6 4[4] The ester (VI) is an acidic compound, dissolving readily in dilute alkali The anion is sufficiently nucleophilic to undergo coupling with various diazonium ions Thus p-NO$_2$-, p-H-, p-Cl-, but not p-MeO-, benzenediazonium chlorides gave red crystalline azo dyes, which were shown to be direct coupling products by elemental analysis

These dyes exhibited an interesting tautomeric behaviour The spectroscopic properties suggest that coupling occurs in the 3-position of (VI), although coupling in the 2-position cannot yet be excluded unequivocally If 3-coupling is assumed, then since the dyes are deeply coloured, the arylazo residue must be conjugated to the chromophore of (VI) This leads to the two possible tautomeric structures (VII) and (VIII) The n m r spectrum showed no sharp hydroxyl absorption analogous to (VI), but did show a typically broad hydrazone N-H signal at low field (τ -6 6 for X = Cl, in CDCl$_3$), exchangeable with D$_2$O The low field value again suggests intramolecular hydrogen bonding, as in (VIII)

The i r spectrum of the solid dye (VII or VIII, X = Cl), (KBr) showed two carbonyl bands at 1730 and 1710 cm^{-1}, and a quinone band at 1660 cm^{-1}, suggesting a mixture of the saturated and unsaturated esters (VII) and (VIII) Differential thermal analysis showed two sharp endotherms at ca 215° and 226°, and rapid cooling and reheating gave only one endotherm at 226° The i r spectrum of the product showed a single peak at 1730 cm^{-1}, presumably due to (VII) The other pure tautomer, ν_{max}(KBr) 1710 cm^{-1}, was obtained by careful recrystallisation from ligroin Both were interconvertible in solution Work is in progress to confirm the position of coupling in (VI)

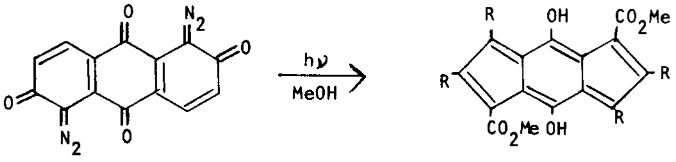


(VII) (VIII)

Irradiation of (I)[5] in methanol gave no trace of any compounds analogous to (VI) and 2-hydroxyanthraquinone was the only isolable product from the very slow photochemical reaction. This behaviour contrasted so markedly with (III) that the positional isomer (IV) was also investigated. This compound[5] was prepared by diazotisation of 1-chloro-2-aminoanthraquinone with nitrosylsulphuric acid, followed by hydrolysis in boiling water. Irradiation of (IV) in methanol resulted in its rapid conversion to the cyclopentadiene (VI) in 65% yield.

The photochemical rearrangement of (III) and (IV) proceeded equally efficiently with light sufficient to excite the first absorption bands only (λ 400-500 nm) or with radiation of shorter wavelengths. Benzophenone retarded the latter reactions, suggesting that triplet sensitisation had little effect, and that benzophenone was merely acting as an internal filter Thermolysis of (III) and (IV) in various solvents containing water or methanol gave no trace of (V) or (VI), and it seems likely that the photochemical rearrangement proceeds from the first excited singlet state of the quinone diazides

The generality of the rearrangement reaction was demonstrated by the photochemical conversion of 1,2,5,6,9,10-anthratriquinone-1,5-bis-diazide (IX)[6] to the _s_-indacene derivative (X), a reaction involving the contraction of two six-membered rings within the same molecule



(IX)

(X) R = H

(XI) R = CO_2Me

The product (X) was isolated as a deep purple solid in 12% yield, and its properties were in accord with the assigned structure.[3] The n m.r. spectrum ($CDCl_3$) showed a highly symmetrical structure, with cyclopentadiene protons at τ 3.56 (2H,d, _J_ 3.5Hz), 3 70 (2H,d, _J_ 3.5Hz), methoxyl protons at τ 6.15 (6H,s) and chelated hydroxyl protons at τ -4.12 (2H,s). The electronic spectrum of (X) was very similar to that of the closely related _s_-indacene derivative (XI), prepared by a non-photochemical route.[7] Photolysis of the bis-diazide for short intervals gave no detectable traces of intermediates containing one cyclopentadiene ring.

As the anthraquinone quinone diazides are readily accessible compounds, the described photochemical ring contraction reactions appear to have synthetic value for the preparation of 1H-benz[f]indene and s-indacene derivatives. The anomalous behaviour of the carbene (II) cannot be interpreted in terms of the dominating resonance form (IIb), since those factors that might favour (IIb) (e.g. retention of the anthraquinone π system) also apply to the carbenes derived from (III) and (IV). In addition, there is no significant variation in the i.r. diazo stretching frequencies (ca. 2150 cm^{-1}) of the compounds studied, indicating that there are no major ground state differences among these compounds The anthraquinone ortho-quinone diazide system appears to be unique in showing such a pronounced photochemical dependence on positional isomerism. This problem, and the thermolytic reactions of the diazides will be the subject of another paper.

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