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PHOTOLYSIS OF 2,3-DIPHENYLNAPHTHOQUINONE OXIDE: TRAPPING OF A BENZ[d]OXEPINE-1,5-DIONE, A SEVEN-MEMBERED MESOIONIC SYSTEM

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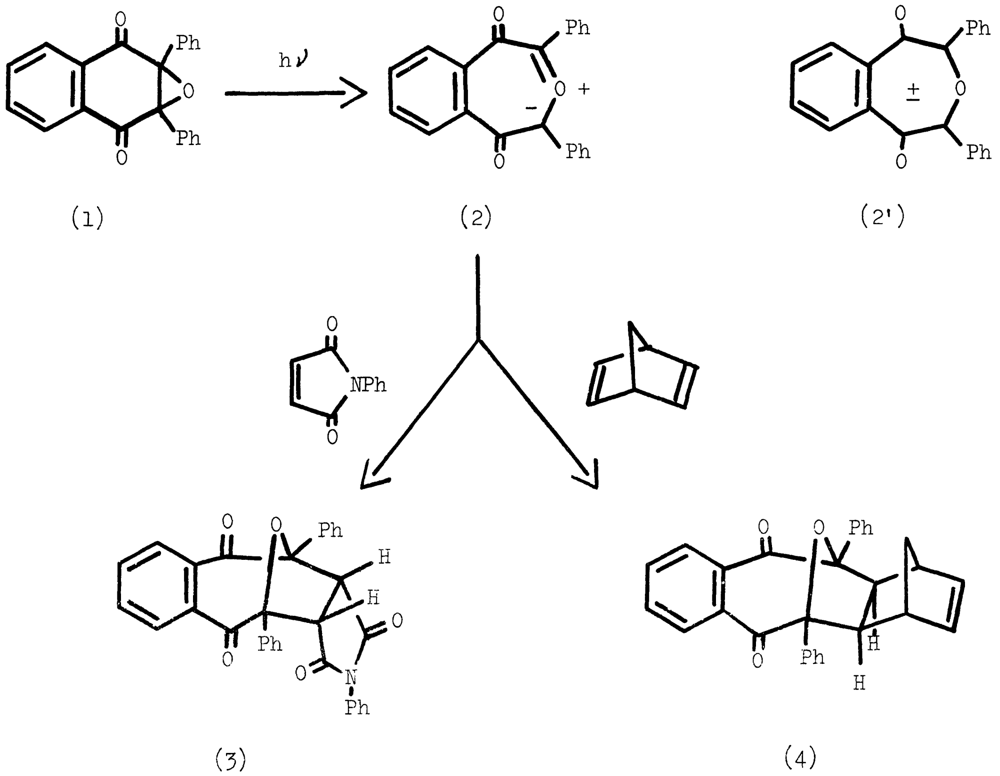
Photolysis of 2,3-diphenylnaphthoquinone oxide resulted in carbon—carbon bond cleavage to give a seven-membered mesoionic benz[d]oxepine-1,5-dione intermediate, which was trapped by N-phenylmaleimide and norbornadiene.

The recent report[1)] on the photo-induced isomerization of 2-acyl-3-methyl-1,4-naphthoquinone oxides prompts us to report our own results on the photolysis of 2,3-diphenylnaphthoquinone oxide (1), which behaved differently from the 2-acyl derivatives.

Irradiation through Pyrex of a benzene solution of 2,3-diphenylnaphthoquinone oxide (1)[2)] [λ_{max}^{EtOH} 237 and 360 nm (log ε 4.57 and 3.38)] in the presence of N-phenylmaleimide gave a 72% yield of a 1 : 1 adduct, mp 237.7—238.2°C (Found: C, 77.17; H, 4.28; N, 2.77%. Calcd. for $C_{32}H_{21}NO_5$: C, 76.94; H, 4.24; N, 2.80%). The adduct showed carbonyl bands at 1780 and 1720 cm^{-1} (KBr), and nmr signals at δ 4.38 (2H, s, methine H) and 7.10—7.90 (19H, m, aromatic H), and is consistent with symmetrical structure (3) with an endo configuration.[3)]

Similar irradiation of (1) in the presence of norbornadiene gave a 68% yield of adduct (4), mp 157°C (Found: C, 82.99; H, 5.40%. Calcd. for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30%). The infrared spectrum of (4) showed only a single carbonyl band at 1760 cm^{-1}, and assignment of its exo-exo configuration is based on nmr signals of angular methine protons at δ 3.20 (2H, s) and methylene bridge protons at 1.12 and 3.10 (1H each, broad d, J = 9 Hz).[3, 4)] [Other nmr signals: 2.99 (2H, broad s, bridgehead H), 6.46 (2H, broad s, olefinic H), 7.20—7.46 (10H, m, Ph), 7.46—8.00 (4H, AA'BB', aromatic H)]. The appearance of the infrared carbonyl bands of (3) and (4) at a high frequency region and a remarkable shielding effect of the bridge oxygen atom on the endo methylene bridge proton of (4) show that the adducts are highly strained. The mass spectrum of (4) showed only a weak (1% rel. intensity) molecular ion peak, and fragment peaks at m/e 352 (M - cyclopentadiene), 220 (diphenylfuran), and 66 (cyclopentadiene) show that a double retro Diels-Alder fragmentation of (4) occurs by electron impact.

These results show that, in contrast to the photolysis of 2-acylnaphthoquinone oxide derivatives,



the photolysis of 2,3-diphenyl derivative (1) resulted in the carbon—carbon bond cleavage[5] to give a cyclic carbonyl ylide (2) or a mesoionic benz[d]oxepine-1,5-dione (2'), which was trapped by added 1,3-dipolarophiles to give the adducts (3) and (4). The intermediate (2) may be regarded as the first example of a seven-membered mesoionic ring system,[6] although it was not stable enough to permit its isolation.

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