Photochemical Synthesis of 2-Benzimidoyl-3-hydroxy-1,4-naphthoquinone and its Analogues. A New Type of Plant Growth Regulator

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Summary The photochemical synthesis of 2-benzimidoyl-3-hydroxy-1,4-naphthoquinone and related compounds having plant growth regulating activity is described.

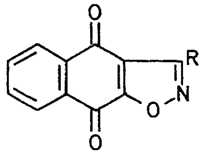
DURING an investigation of the photochemistry of 50 ml naphthoquinones,[1] we obtained a series of derivatives, some of which [(I), (III), (IX), (IV), and (VI)] have plant growth regulating activity. Here, we describe the synthesis of these naphthoquinone derivatives involving a novel photochemical N–O bond cleavage of the isoxazole ring.

Irradiation of the dione (I)[2] in methanol with a high-pressure mercury arc lamp under argon at room temperature afforded a product (III) [71%, m.p. 258—260°; λ_{max} (MeOH) (log ϵ) 240 (4·37), 282 (4·15), and 319 (4·22) nm; i.r. (Nujol) 3300, 1697, and 1631 cm^{-1}; τ (Me_2SO) $-0·8$br (2H, exchangeable with D_2O) and 0·8—2·5 (9H, ArH). After similar photolysis, both the dione (VIII)[3] and the spiro-compound (IX)[2b] were converted into (III) (57 and 34% respectively). Irradiation of (I) in aqueous tetrahydrofuran with a low-pressure mercury arc lamp under argon also gave (III) (39%). Hydrolysis of (III) with K_2CO_3 in aqueous ethanol yielded the known naphthoquinone (IV)[4] (64%). From these results, the photoproduct was assigned structure (III).

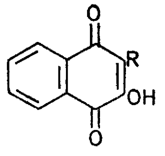
Similar photolysis of the dione (II)† m.p. 184—185°, prepared from 1,4-naphthoquinone, nitroethane, and phenyl isocyanate, afforded the naphthoquinone (V) [m.p. 284° (decomp.); i.r. (Nujol) 3200, 1684, and 1631 cm^{-1}] (70%).

Irradiation of (I) in dioxan containing dimethylamine through a Pyrex filter with a high-pressure mercury arc lamp under argon afforded the *N*-methyl compound (VI) (24%), m.p. 235—237°; i.r. (Nujol) 1685 and 1638 cm^{-1}; τ (Me_2SO) 7·13 (s, 3H, *N*-Me) and recovered starting material. Similar photolysis of (VIII) also gave (VI) (30%). When mono- or tri-methylamine was used instead of dimethylamine, (I) afforded a trace of (VI) (*ca.* 2%) (*ca.* 20% recovery). Structure (VI) was assigned on the following evidence. Hydrolysis of (VI) with sodium hydroxide in aqueous ethanol gave (IV) (40%). Photolysis of an ethanolic solution of the naphthoquinone (VII),‡ m.p. 171—173° (decomp.), prepared from benzaldehyde, methylamine, and 2-hydroxy-1,4-naphthoquinone, gave (VI) (7%), thus confirming assignment of structure (VI).

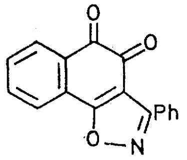
Compounds (III), (V), and (VI) have been found to have avena section straight-growth effect§ at concentrations of *ca.* 0·1—10 μg/ml, and compounds (I), (III), (IV), (VI), and (IX) have parthenocarpy-stimulating activity§ in tomato and eggplant.



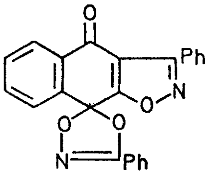
(I) R = Ph
(II) R = Me



(III) R = C(Ph)=NH
(IV) R = COPh
(V) R = C(Me)=NH
(VI) R = C(Ph)=NMe
(VII) R = CH(Ph)NHMe



(VIII)



(IX)

Analytical data obtained for all compounds were in agreement with the structures assigned.

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† Synthesised by Mukaiyama's procedure; T. Mukaiyama and T. Hoshino, *J. Amer. Chem. Soc.*, 1960, **82**, 5339.

‡ Synthesised by Leffler's procedure; M. Y. Leffler and R. T. Hathaway, *J. Amer. Chem. Soc.*, 1949, **71**, 1697.

§ Details of the biological test will be published elsewhere. Photolysis (sunlight) of (I) in aqueous dioxan afforded (III) (55%).

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[2] (a) A. Quilico and S. D'Alcontres, *Gazzetta*, 1950, **80**, 140; (b) S. Morrochi, A. Quilico, A. Ricca, and A. Selva, *ibid.*, 1968, **98**, 891.
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[4] M. G. Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 3666.