

Conversion of Benzoin into 9,10-Phenanthrenequinone by Photocyclisation

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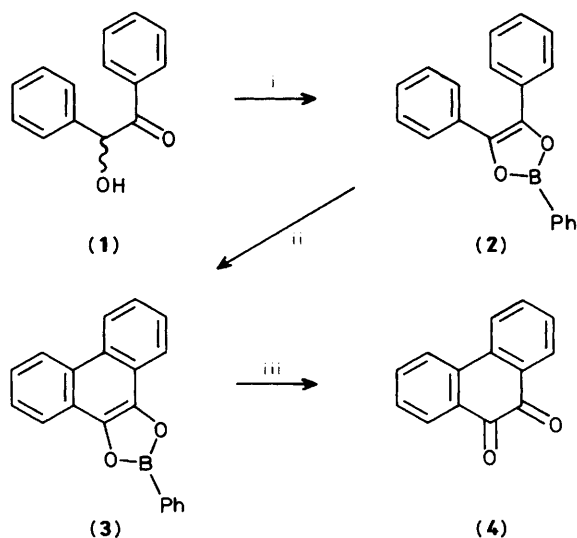
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Benzoin is converted into 9,10-phenanthrenequinone by photocyclisation of its adduct with phenylboric acid, followed by hydrolysis of the photoproduct.

In connection with our efforts towards a short total synthesis of methoxatin,¹ the coenzyme of quinoproteins,² we needed a mild procedure to effect the conversion of a stilbene derivative into the analogous 9,10-phenanthrenequinone. Classically, this is done by oxidative photocyclisation of stilbene³ followed by oxidation of the resulting phenanthrene to 9,10-phenanthrenequinone using CrO_3 or similar aggressive oxidants.⁴ As

the latter conditions were not suitable for our purpose we tried to devise a method in which a stilbene, already carrying at least one oxygen substituent on its double bond, is cyclised to the analogous phenanthrene which is now easily oxidised with Fremy's salt⁵ or other mild oxidants⁴ to the 9,10-phenanthrenequinone.

We have now developed a route which converts benzoin (**1**) into 9,10-phenanthrenequinone (**4**) in two simple steps (Scheme 1). Reaction of (**1**) with phenylboric acid gave the known 2,4,5-triphenyl-1,3-dioxaborole (**2**)⁶ in excellent yield.[†] As this compound is forced into a *cis* conformation the *trans*-*cis* isomerisation which must precede the photocyclisation of *trans*-stilbenes is now effectively bypassed. Indeed, photocyclisation of (**2**)⁷ in benzene with diphenyl diselenide as mild oxidant[‡] proceeded readily to give the crystalline phenanthrene (**3**) (m.p. 200–204 °C) in 54% yield (work-up A).[§]



Scheme 1. Reagents and conditions: i, PhB(OH)_2 ; ii, $h\nu$, PhSeSePh ; iii, $\text{NaOH/H}_2\text{O}$, air.

[†] Reagents and conditions: Benzene, azeotropic reflux, 4 h.

[‡] Use of air as oxidant led to rapid decomposition.

[§] Reagents and conditions: A solution of (**2**) (200 mg) and diphenyl diselenide (472 mg) in dry benzene (300 ml), sparged with argon 20 min before and during the reaction, was irradiated in a photochemical apparatus (Applied Photophysics) with a 450 W medium pressure mercury lamp through a pyrex sleeve (cutoff region: 290–330 nm) for 2 h 40 min. Work-up A: the solvent was evaporated and the residue crystallised from hexane. Work-up B: the solution was extracted with 1 M aq. NaOH , dried (Na_2SO_4) and evaporated, and the residue was crystallised from hexane.

Interestingly, upon hydrolysis of (3) with methanol, aqueous base, or even on t.l.c. plates the only product observed was (4) and not a trace of the analogous dihydro compound was found. The instantaneous autoxidation of 9,10-dihydroxyphenanthrene has been observed before.⁸ As a consequence (4) could be isolated directly from the photolysis mixture in 84% yield after an aqueous work up which removed boric acid and simultaneously served to oxidise the presumed dihydroquinone to (4) (work-up B).§ Melting point (204—208 °C) and mixed melting point with an authentic sample (205—209 °C) confirmed its identity, as did the i.r. spectrum.

We are currently attempting to apply this methodology to the synthesis of methoxatin.

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