Conversion of Benzoin into 9,10-Phenanthrenequinone by Photocyclisation

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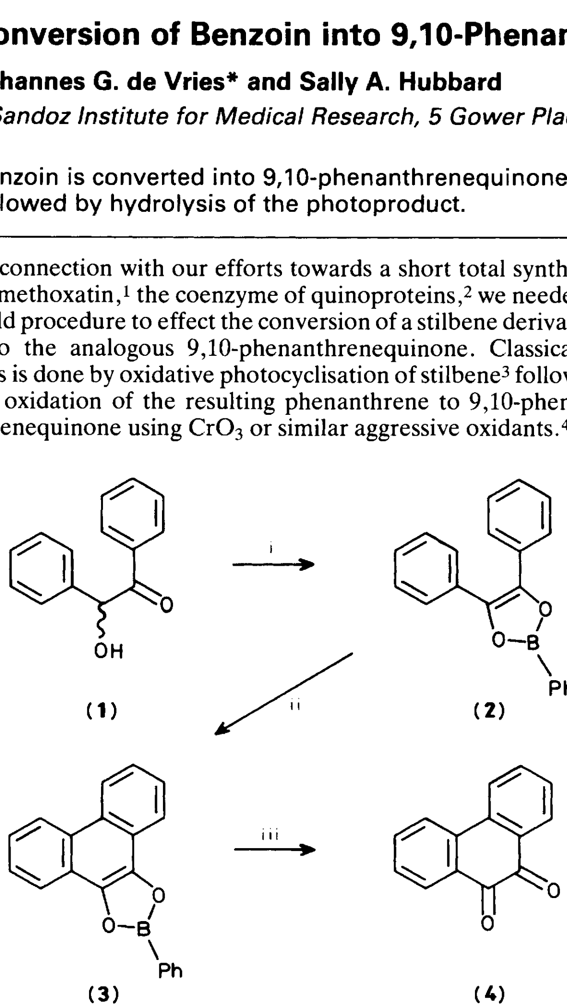
Benzoin is converted into 9,10-phenanthrenequinone by photocyclisation of its adduct with phenylboric acid, followed by hydrolysis of the photoproduct.

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 stilbene[3] 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 salt[5] or other mild oxidants[4] to the 9,10-phenanthrenequinone.



Scheme 1. *Reagents and conditions*: i, $PhB(OH)_2$; ii, *hv*, PhSeSePh; iii, $NaOH/H_2O$, air.

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-dioxoborole (**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).§

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† *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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References

1 J. B. Hendrickson and J. G. de Vries, *J. Org. Chem.*, 1985, **50**, 1688.

2 J. A. Duine, J. Frank, Jzn., and J. A. Jongejan, *Adv. Enzymol. Relat. Areas Mol. Biol.*, 1987, 169.

3 F. B. Mallory and C. W. Mallory, *Org. React.* (*N.Y.*), 1984, **30**, 1.

4 R. H. Thomas, in 'The Chemistry of the Quinonoid Compounds,' vol. 1, ed. S. Patai, J. Wiley & Sons, New York, 1974, p. 111; C. Grundmann in 'Houben-Weyl, Methoden der Organische Chemie,' vol. 7/3b, Georg Thieme Verlag, Stuttgart, 4th edn., 1979, p. 1.

5 H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, 1971, **71**, 229.

6 R. L. Letsinger and S. B. Hamilton, *J. Org. Chem.*, 1959, **25**, 592.

7 For the photocyclisation of the analogous cyclic carbonate see: K.-R. Stahlke, H.-G. Heine, and W. Hartmann, *Justus Liebigs Ann. Chem.*, 1972, **764**, 116; T. Hiyama, S. Fujitas, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2797; I. Lantos, *Tetrahedron Lett.*, 1978, 2761.

8 F. Mayer, *Ber.*, 1912, **45**, 1105.