# An Expeditious Synthesis of Benz[*a*]anthracene and some of Its Oxygenated Derivatives

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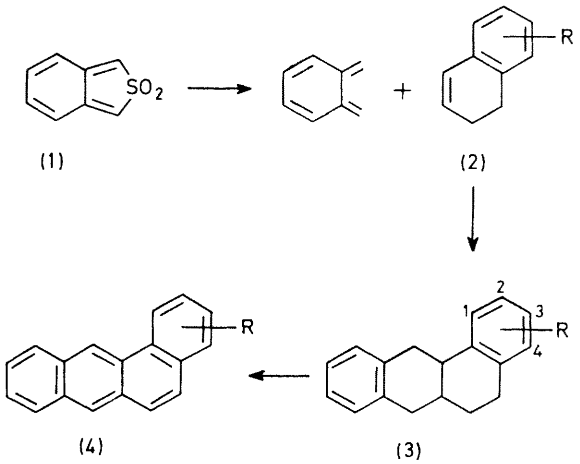
*Summary* Benz[*a*]anthracenes were synthesized by reaction of *ortho*-quinodimethane and 1,2-dihydronaphthalenes.

THE considerable current interest in the mechanism of carcinogenesis by polynuclear aromatic hydrocarbons[1] has led to a number of approaches to the synthesis of these compounds and their oxygenated metabolites. Several recent syntheses have used the Diels–Alder reaction, with a variety of diene–dieneophile combinations, to build up the benz[*a*]anthracene nucleus.[2] However, in some of these examples, isomeric mixtures, low yields, or extremely long reaction times do not recommend their preparative utility. Our own retrosynthetic analysis suggested that the cycloaddition of an *ortho*-quinodimethane to a 1,2-dihydronaphthalene would lead directly to the reduced benz[*a*]anthracene which could be expected to be easily oxidized to the fully aromatic hydrocarbon.



(1) (2)

(4) (3)

(2) **a**, R = H
**b**, R = 6-OMe
**c**, R = 7-OMe
**d**, R = 8-OMe

(3) and (4) **a**, R = H
**b**, R = 2-OMe
**c**, R = 3-OMe
**d**, R = 4-OMe

A mixture of the *ortho*-quinodimethane precursor, 1,3-dihydrobenzo[*c*]thiophen *SS*-dioxide (**1**)[3] and 1,2-dihydronaphthalene (**2a**) in refluxing 1,3,5-trichlorobenzene for 14 h produced, in 92% yield, the hexahydrobenz[*a*]anthracene (**3a**). The solvent and any excess of olefin were easily removed by simple chromatography (hexane). That the structure of the product is as formulated was suggested by its mass spectrum, which in addition to a strong molecular ion (70%) exhibited peaks at *m/e* 104 (100%) and 130 (25%) indicative of a Diels–Alder process which is the reverse of that of product formation. Confirmation of the structural assignment was obtained by oxidation of (**3a**) with dichlorodicyanoquinone (DDQ) in refluxing toluene for 1 h to the known benz[*a*]anthracene, identical with an authentic sample. In a similar manner reaction of the diene precursor (**1**) with the methoxy-substituted dihydronaphthalenes (**2b**, **d**),† yielded the corresponding reduced benz[*a*]anthracenes, (**3b**, **d**) (Table).

Table Yields/% of benz[*a*]anthracenes (**3**) and (**4**)

| | G.l.c./Isolated | | Isolated |
|---|---|---|---|
| (**3a**) | 92/73 | (**4a**) | 89 |
| (**3b**) | 80/67 | (**4b**) | 93 |
| (**3c**) | 78/66 | (**4c**) | 84 |
| (**3d**) | 90/65 | (**4d**) | 88 |

After oxidation with DDQ the resulting benzanthracene derivatives (**4b**, **d**), identified by congruence of their melting point with published values,[4] were easily isolated by chromatography (benzene).

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† The substituted dihydronaphthalenes were obtained from the appropriate benzyl alcohol by warming briefly in HCl–HOAc solution. In each case, pure material exhibited the spectral characteristics (i.r., n.m.r., and mass spectroscopy) appropriate to its assigned structure.

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[3] M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, 1959, **81**, 4266.

[4] G. M. Muschik, J. E. Tomaszewski, R. I. Sato, and W. B. Manning, *J. Org. Chem.*, 1979, **44**, 2150.