

## Diels–Alder Reactions of 9,10-Anthraquinodimethane

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REACTION of an *o*-quinodimethane with a dienophile usually gives a 1:1 Diels–Alder adduct.<sup>1,2,3</sup> Investigation of the addition reactions of 9,10-anthraquinodimethane (I), a *p*-quinodimethane, with various dienophiles, shows that this reactive intermediate reacts with two molecules of the dienophile. Other cases of *p*-quinodimethanes reacting in this way do not appear to have been reported. The intermediate (I) is liberated from *cis*- or *trans*-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene, by dehydration in a suitable

solvent, in the presence of an excess of the dienophile.<sup>4</sup> Even with a large excess of the intermediate (I) no product other than a di-adduct was isolated; or, in nitrobenzene as solvent, the product of its aromatization.

Reaction with dimethyl acetylenedicarboxylate in boiling nitrobenzene gives tetramethyl 4,5-benzopyrene-1,2,7,8-tetracarboxylate (II) (m.p. 321°, 23% yield). Alkaline hydrolysis gives 4,5-benzopyrene-1,2,7,8-tetracarboxylic acid which readily gives the corresponding dianhydride

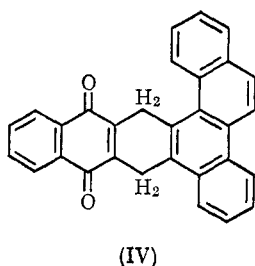
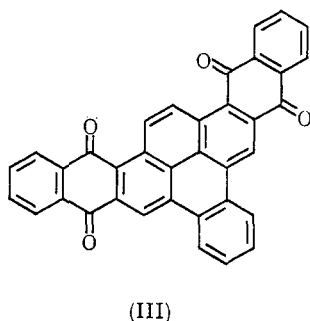
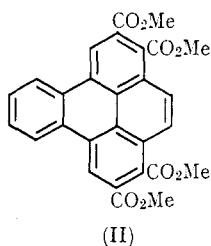
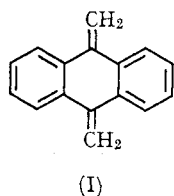
<sup>1</sup> J. M. Tedder, *Ann. Reports*, 1961, 225.

<sup>2</sup> I. T. Millar and K. V. Wilson, *Proc. Chem. Soc.*, 1963, 217.

<sup>3</sup> J. K. Stille and R. T. Foster, *J. Org. Chem.*, 1963, 28, 2708.

<sup>4</sup> I. T. Millar and K. V. Wilson, *J. Chem. Soc.*, 1964, 2121.

(m.p.  $>360^\circ$ ). Decarboxylation of the acid gives 4,5-benzopyrene (37% yield), thus excluding the



possibility that the initial reaction gives a perylene derivative.

In boiling acetic anhydride, 9,10-anthraquinodimethane reacts with excess of maleic anhydride to give 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (m.p.  $230^\circ$ , 60% yield) which on dehydrogenation gives the fully aromatic dianhydride identical with that prepared as described above.

With 1,4-naphthaquinone, in boiling nitrobenzene, 9,10-anthraquinodimethane gives 4,5-benzodimethylenepyrene-1,2:7,8-dicarboxylic anhydride (m.p.  $>360^\circ$ , 46% yield). If the reaction is stopped after 10 minutes a mixture of (III) and its hydrogenated derivatives is obtained. The progress of aromatization may be followed by the increase in intensity of a very strong absorption band at  $707\text{ cm}^{-1}$  which we attribute to the out-of-plane deformation absorption of the four adjacent aromatic C-H bonds on the terminal rings adjacent to the *p*-quinone rings. The frequency of this band is outside that normally attributed to four adjacent aromatic C-H bonds ( $770$  to  $735\text{ cm}^{-1}$ ), but we base our assignment on analogy with 5,12-dihydro-3,4-benzonaphtho-[1',2':1,2]naphthacene-6,11-quinone (IV) (m.p.  $322\text{--}324^\circ$ ; prepared in 56% yield by the reaction of 5,6-chrysaquinodimethane with 1,4-naphthaquinone in diethyl phthalate) which shows a similar very strong band at  $707\text{ cm}^{-1}$  (The infrared spectrum of 9,10-anthraquinone shows an absorption at  $692\text{ cm}^{-1}$  due to aromatic C-H). Reduction of the diquinone (III) gives 4,5-benzodimethylenepyrene thus confirming the structure previously assigned to this hydrocarbon by Clar.<sup>5</sup>

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<sup>5</sup> E. Clar and M. Zander, *Tetrahedron*, 1963, **19**, 521.