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.[1,2,3] 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.[4] 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

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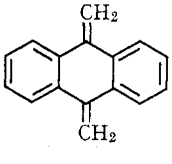
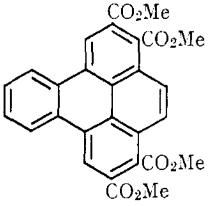
[1] J. M. Tedder, *Ann. Reports*, 1961, 225.
[2] I. T. Millar and K. V. Wilson, *Proc. Chem. Soc.*, 1963, 217.
[3] J. K. Stille and R. T. Foster, *J. Org. Chem.*, 1963, **28**, 2708.
[4] I. T. Millar and K. V. Wilson, *J. Chem. Soc.*, 1964, 2121.

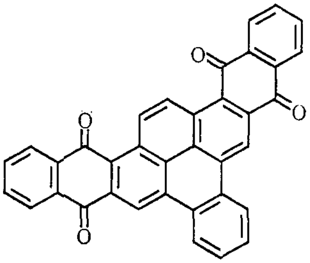
(m.p. >360°). Decarboxylation of the acid gives 4,5-benzopyrene (37% yield), thus excluding the possibility that the initial reaction gives a perylene derivative.



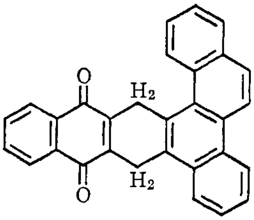
(I)



(II)



(III)



(IV)

In boiling acetic ahydride, 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°, 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-benzodinaphtho[2′,3′ : 1,2] [2″,3″ : 7,8]pyrene-1′,4′ : 1″,4″-diquinone (III) (m.p. >360°, 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 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 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—324°; 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 cm.$^{-1}$ (The infrared spectrum of 9,10-anthraquinone shows an absorption at 692 cm.$^{-1}$ due to aromatic C–H). Reduction of the diquinone (III) gives 4,5-benzodinaphtho[2′,3′ : 1,2]-pyrene thus confirming the structure previously assigned to this hydrocarbon by Clar.[5]

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[5] E. Clar and M. Zander, *Tetrahedron*, 1963, **19**, 521.