Stabilised 2,3-Naphthoquinodimethanes *via* Transient 1,3-Diphenylbenz[*f*]inden-2-one

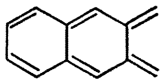
By DAVID W. JONES*, ALAN POMFRET, and RICHARD L. WIFE

(*Department of Organic Chemistry, The University, Leeds* LS2 9JT)

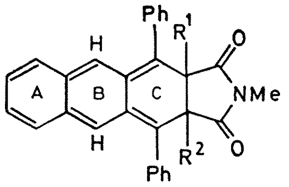
Summary 1,3-Diphenylbenz[*f*]inden-2-one (**5**) reversibly generated by thermal dissociation of its ($_{\pi}4 + {}_{\pi}4$)-dimer (**4**) adds stereospecifically to *cis*- and *trans*-but-2-ene; the related adducts (**6**) and (**7**) undergo smooth photodecarbonylation to the long-lived 2,3-naphthoquinodimethanes (**2**; $R^1 = R^2 =$ Me) and (**2**; $R^1,R^2 = [CH_2]_4$).

2,3-NAPHTHOQUINODIMETHANE (**1**) and a simple bridged derivative have been observed only at low temperature in a rigid matrix and are extremely reactive towards oligomerisation and autoxidation.[1] We describe preparation of the 2,3-naphthoquinodimethanes (**2**; $R^1 = R^2 =$ Me) and (**2**; $R^1,R^2 = [CH_2]_4$) which are long-lived in fluid solution at 20 °C.

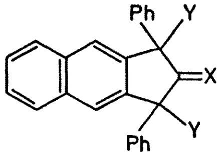
The 2-oxime of benz[*f*]indane-1,2,3-trione was prepared by reaction of benz[*f*]indane-1,3-dione with nitrous acid; with phenyl-lithium it gave a mixture of the stereoisomeric diols (**3**; X = NOH; Y = OH). With hydrogen iodide this mixture gave (**3**; X = O; Y = H) which, with bromine (CCl_4; 20 °C; 17 h), was converted into the dibromoketone (**3**; X = O; Y = Br) (m.p. 158—160 °C from benzene–petroleum). With sodium iodide in boiling acetone the



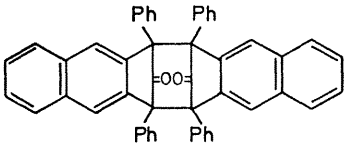
(1)



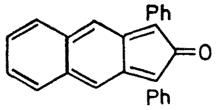
(2)



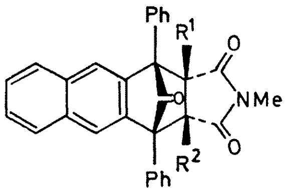
(3)



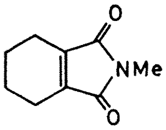
(4)



(5)



(6) $R^1 = R^2 = Me$
(7) $R^1, R^2 = [CH_2]_4$



(8)

dibromide afforded the insoluble dimer (**4**) (96%) ν_{max}(Nujol) 1 770 cm^{-1}.† As judged by trapping experiments with various olefins (**4**) reversibly dissociates into (**5**) in *o*-dichlorobenzene at 155—160 °C. Trapping with *cis*- and *trans*-but-2-ene is stereospecific indicating a singlet ground state for (**5**) and concerted Diels–Alder addition to these olefins. Trapping with trimethylmaleimide gave the *endo*-adduct (**6**) (56%), ν_{max}(Nujol) 1 755(s) and 1 695(s) cm^{-1}, in which the NMe group is strongly shielded (δ 2·37). Similar trapping with (**8**) gave the *endo*-adduct (**7**). On irradiation (medium pressure mercury lamp, 20 °C, benzene solution) (**6**) and (**8**) gave deep-blue solutions of the 2,3-naphthoquinodimethanes (**2**; $R^1 = R^2 = Me$) and (**2**; $R^1,R^2 = [CH_2]_4$) respectively. The long wavelength u.v. bands of these compounds [(**2**; $R^1 = R^2 = Me$) has λ_{max} (CH_2Cl_2) 594 nm] are similar in form to the spectra of (**1**)[1a] and a simple derivative[1b] but are displaced to longer wavelength by *ca.* 50 nm. The derivatives (**2**) survive for longer than 1 h in fluid solution at 20 °C. They are therefore much more stable than (**1**) and a bridged derivative, neither of which survive above −75 °C in fluid solution.[1b] The stability of the 2,3-naphthoquinodimethanes (**2**) is attributed to protection of the reactive ring-C diene system by the phenyl and other ring-C substituents. It is likely that the phenyl groups are prevented from effective conjugation with the quinonoid system owing to steric clash with the ring-B hydrogens and other ring-C substituents. Accordingly they probably lie orthogonal to the quinonoid system so that their *ortho*-hydrogens protect the ring-C diene system.

The stability of the derivatives (**2**) does not match that of the corresponding *o*-quinodimethanes (**2**; lacking ring-A) which are isolable[2] and stable in air. This relative instability is associated with the ring-B diene system, which is unprotected; blue solutions of the derivatives (**2**) may be titrated to a colourless end-point with phenyltriazolinedione to give adducts derived by addition to the ring-B diene system, and on prolonged irradiation (**2**; R^1, $R^2 = [CH_2]_4$) gives a ($_{\pi}4 + _{\pi}4$)-dimer where the two monomer units (**2**) have joined using their ring-B diene systems.

(*Received*, 14*th February* 1980; *Com.* 165.)

---

† The spectrum shows no band at *ca.* 1 700 cm^{-1} expected for a dimer of Diels–Alder type. The structure of the dimer is proposed by analogy with the dimer of (**5**; lacking ring-A), which has ν_{max} 1 768 cm^{-1}; the carbon skeleton of the latter was established chemically [J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1971, 608].

[1] (a) M. Gisin and J. Wirz, *Helv. Chim. Acta*, **1976**, **59**, 2273; (b) R. P. Steiner, R. D. Miller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, 1979, **101**, 1820.

[2] D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans.* 1, 1975, 171.

Printed by Heffers Printers Ltd Cambridge England