# Thermal Decomposition of the Diphenyldiazomethane Adducts of 1,4-Naphthaquinone

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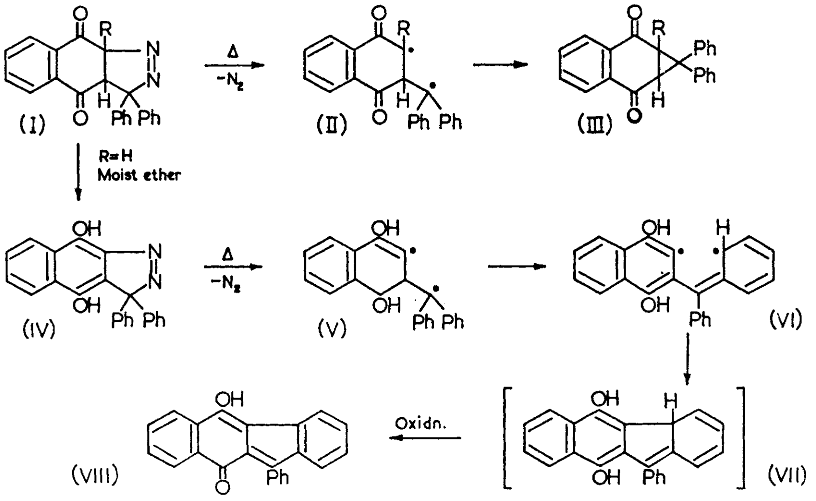
DIPHENYLDIAZOMETHANE is known to react with 1,4-naphthaquinone in benzene solution giving the isopyrazolo-1,4-naphthahydroquinone (IV), m.p. 203° decomp., which evolves nitrogen at its melting point[1] affording the benzofluorene derivative (VIII) and 2-diphenylmethyl-1,4-naphthaquinone as two of the decomposition products.[2] In the present work these results have been confirmed and it has been established also that the tricyclic dione (III: R=H) is absent from the product mixture. The benzofluorene derivative (VIII) supposedly arises by oxidation of the hypothetical intermediate (VII) which would be the expected product following rearrangement of the postulated biradical (V) to the fully conjugated *ortho* resonance form (VI).

The dioxoindazole (I: R=H), from which (IV) was assumed to be formed by rearrangement, has now been isolated as colourless needles, m.p. 102—103° decomp. [$\nu_{max}$ 1680 (C=O), 1585 (aromatic), 1550 cm.$^{-1}$ (N=N)]. This initial adduct is unstable and, when treated with moist ether, rearranges rapidly giving the adduct (IV) in quantitative yield. When the dry adduct (I: R=H) is heated it does not rearrange but suffers complete loss of nitrogen at the decomposition point giving, as sole products, the tricyclic dione (III: R=H), m.p. 138° [$\nu_{max}$ 3060 (cyclopropane CH), 1685 (C=O), 1595 cm.$^{-1}$ (aromatic), $\lambda_{max}$ (EtOH) 223, 306 m$\mu$ (log $\epsilon$ 4·55, 3·51), $\tau$ 2·1—3·1 (multiplet, 14H, aromatic hydrogen) and 6·6 (singlet, 2H, tertiary hydrogen)] together with a small amount of 2-diphenylmethyl-1,4-naphthaquinone, m.p. and mixed m.p. 185°. These decomposition products can be accounted for on the basis of the biradical intermediate (II: R=H) which, unlike (V), is not expected to lead to benzofluorenes since the *ortho* resonance form of the diphenylmethyl radical in this case lacks the conjugative stabilisation apparent in (VI).

Support for the above mechanism is provided by the isolation of the colourless diphenyldiazomethane adduct of 2-methyl-1,4-naphthaquinone (I: R=Me), m.p. 119—121° decomp., [$\nu_{max}$ 1685 (C=O), 1585 (aromatic), 1560 cm.$^{-1}$ (N=N)] in which the methyl group serves as a blocking



substituent to aromatisation. This adduct, therefore, cannot rearrange but, when heated, loses nitrogen yielding the expected tricyclic dione[3] (III: R=Me), m.p. 213° [$\nu_{max}$ 3055 (cyclopropane CH), 1680 (C=O), 1595 cm.$^{-1}$ (aromatic), $\lambda_{max}$ (EtOH) 224, 306 m$\mu$ (log $\epsilon$ 4·63, 3·47), $\tau$ 2·1—3·1 multiplet, 14H, aromatic hydrogen), 6·7 (singlet, 1H, tertiary hydrogen) and 8·6 (singlet, 3H, tertiary methyl group)] as well as a trace amount of 2-diphenylmethyl-3-methyl-1,4-naphthaquinone, m.p. and mixed m.p. 162°.

The kinetics of the thermal decompositions of these adducts are being investigated.

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[1] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **1931**, **53**, 4080.

[2] A. R. Bader and M. G. Ettlinger, *J. Amer. Chem. Soc.*, **1953**, **75**, 730.

[3] F. M. Dean, P. G. Jones, R. B. Morton, and P. Sidisunthorn, *J. Chem. Soc.* 1963, 5336. The tricyclic dione (III: R=Me) was originally obtained by heating a mixture of diphenyldiazomethane and 2-methyl-1,4-naphthaquinone but, since the initial adduct was not isolated, it was argued that the product could have resulted from biradicals formed by preliminary loss of nitrogen from the diazo-compound.