

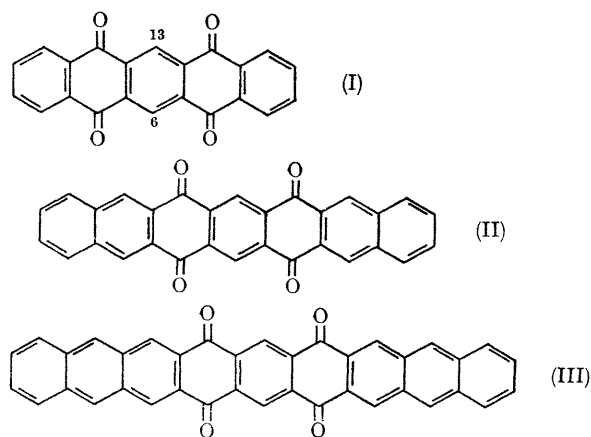
Formation of some Linear Polycyclic Diquinones *via* Novel Dimerization

By I. BAXTER,* D. W. CAMERON, and R. B. TITMAN
(University Chemical Laboratory, Cambridge CB2 1EW)

Summary Certain 2-methyl-1,4-quinones undergo dimerization in the presence of *N*-methylcyclohexylamine to yield linear diquinones.

A SOLUTION of 2-methyl-1,4-naphthaquinone and *N*-methylcyclohexylamine in ethanol deposited, after 24 hr., a sparingly soluble pale yellow product, m.p. > 350° which was assigned structure (I) on the basis of its spectral characteristics [λ_{max} . (CHCl₃) 270 and 343 nm. (ϵ 113,500 and 13,350); ν_{max} . (KBr) 1695 and 1680 cm.⁻¹; τ (H₂SO₄) 1.69 (2H, s, 6-H and 13-H) and 2.4—2.9 (8H, m, adjacent aromatic H) and M^+ at m/e 338] and confirmed by comparison with authentic material.¹ The yield (15%) was not improved by the use of a wide variety of other bases in place of *N*-methylcyclohexylamine, amination of the quinone being a competitive reaction in some cases.^{2,3} 3-Bromo- and 3-chloro-2-methyl-1,4-naphthaquinones also yielded the diquinone (I) on treatment with ethanolic *N*-methylcyclohexylamine in 11 and 4% yield, respectively, but the 3-ethoxy-, 3-methylamino-, and 3-anilino-derivatives failed to react in this way. These observations are consistent with a dimerization process involving two base-catalysed addition (displacement) reactions and a series of oxidation steps affording aromatisation of the system.

The relative reluctance of *N*-methylcyclohexylamine to effect nuclear amination of certain quinones has been noted



before.³ Similar self-coupling of 2-methyl-1,4-anthraquinone (made by treatment of $\alpha\alpha\alpha\alpha$ -tetrabromo-*o*-xylene with 1,4-toluquinone in the presence of sodium iodide in

dimethylformamide; *cf.* ref. 4) furnished a 24% yield of the golden yellow heptacene diquinone (II)⁵ which gave satisfactory analytical data and had λ_{max} (H₂SO₄) 231, 271, 323, and 590 nm. (ϵ 26,600, 25,600, 58,000, and 15,200), λ_{inf} 427 and 470 nm. (ϵ 10,050 and 10,900), ν_{max} (KBr) 1675 and 1660 cm.⁻¹ and M^+ at m/e 438.[†]

2-Methyl-1,4-tetracenequinone⁶ was too insoluble in ethanol for the coupling conditions above to be employed. It nevertheless reacted smoothly when suspended in a more

concentrated ethanolic solution of *N*-methylcyclohexylamine to give, after 5 days, a red product (35%) m.p. >350° presumed to be the diquinone (III), on account of spectroscopic data and its mode of formation [λ_{max} (H₂SO₄) 300, 390, 745, and 829 nm. (ϵ 35,000, 63,400, 29,900, and 28,800), ν_{max} (KBr) 1670, 1655 cm.⁻¹, M^+ at m/e 538·122 (required 538·121)].[†]

The formation of other polycyclic systems from alkyl-1,2 and 1,4-quinones is under investigation.

(Received, March 17th, 1969; Com. 385.)

[†] Owing to extreme insolubility no n.m.r. data for this compound could be obtained.

¹ W. H. Mills and M. Mills, *J. Chem. Soc.*, 1912, 2194.

² D. W. Cameron, P. M. Scott, and Lord Todd, *J. Chem. Soc.*, 1964, 42.

³ D. W. Cameron, R. G. F. Giles, and R. B. Titman, *J. Chem. Soc. (C)*, 1969, 1245.

⁴ M. P. Cava, A. A. Deana, and K. Muth, *J. Amer. Chem. Soc.*, 1959, **81**, 6458.

⁵ A. N. Grinev and V. L. Florent'ev, *Soviet Inventions Illustrated, Sect. 1 (Chemical)* 167,859 (Sept. 1965) (*Chem. Abs.*, 1965, **62**, 16166, describe the preparation of this compound but give no analytical or spectroscopic data.

⁶ A. Cohen and J. Deschamps, *Tetrahedron Letters*, 1968, 4409.