Formation of some Linear Polycyclic Diquinones *via* Novel Dimerization

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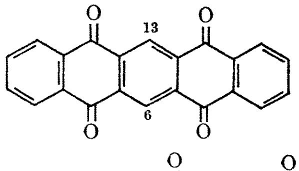
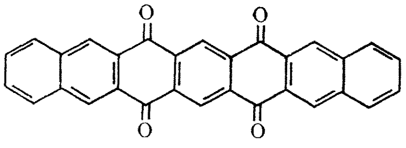
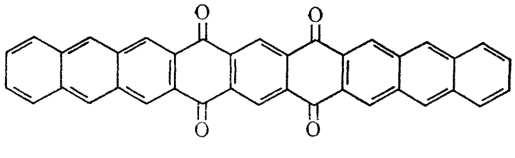
Summary Certain 2-methyl-1,4-quinones undergo dimerization in the presence of *N*-methylcyclohexylamine to yield linear diquinones.



(I)



(II)



(III)

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 [$\lambda_{max.}$ ($CHCl_3$) 270 and 343 nm. (ϵ 113,500 and 13,650); $\nu_{max.}$ (KBr) 1695 and 1680 cm.$^{-1}$; τ (H_2SO_4) 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 $\alpha\alpha^1\alpha^1$-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} (H_2SO_4) 231, 271, 323, and 590 nm. (ϵ 26,600, 25,600, 58,000, and 15,200), λ_{infl} 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-tetracenequinone[6] 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} (H_2SO_4) 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.

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† 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.