

993. *The Synthesis of Polycyclic Aromatic Compounds. Part I. The Reaction of Quinones with Vinylnaphthalenes and Related Dienes.*

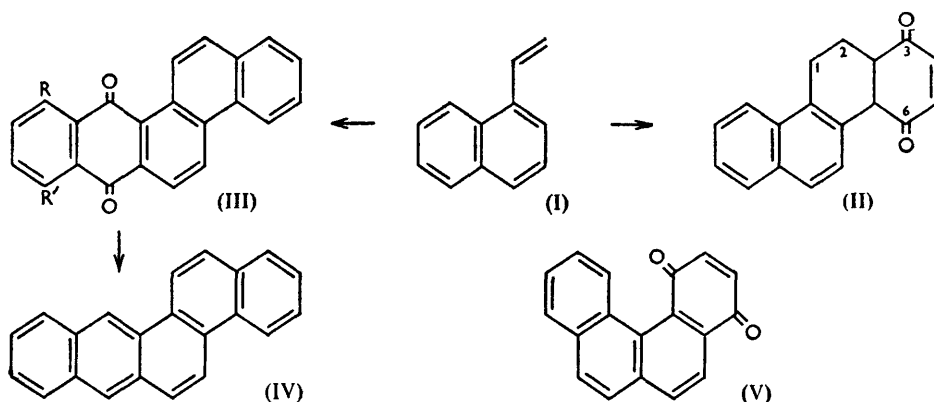
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Convenient syntheses are described of chrysene-1 : 4-quinone, 3 : 4-benzophenanthrene-1' : 4'-quinone, and naphtho(2' : 1'-1 : 2)anthracene-9 : 10-quinone, and of the corresponding aromatic hydrocarbons. A practical advance is the direct removal, by lithium aluminium hydride, of the oxygen atoms in a quinone group in an outermost ring, to afford the aromatic hydrocarbon.

POLYCYCLIC aromatic compounds are often made starting from an aliphatic diene and a *p*-quinone (*e.g.*, butadiene and 1 : 4-naphthaquinone^{1,2}) or from a vinylaromatic diene and an aliphatic dieneophil (*e.g.*, 1-vinylnaphthalene and maleic anhydride^{2,3}), but there are few records of interaction of vinyl aromatic dienes with quinones prior to our use⁴ of 2-vinylthiophen and 3-vinylthionaphthen. A known instance of such a reaction in the aromatic series is that⁵ between 1-vinylnaphthalene (I) and *p*-benzoquinone to give a high yield of chrysene-1 : 4-quinone, excess of quinone having oxidised the original adduct (II) which was not isolated. It is now found that this pale yellow compound can be isolated if excess of 1-vinylnaphthalene is warmed with *p*-benzoquinone in glacial acetic acid for a short time and then kept for some days: it is formed much more slowly than the corresponding adduct from the isosteric 3-vinylthionaphthen and benzoquinone.⁴ The adduct (II) is easily dehydrogenated by benzoquinone or chloranil to chrysene-3 : 6-quinone, which is reduced in one operation and in high yield (70%) to chrysene by lithium aluminium hydride (*cf.* ref. 4).

¹ Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337.² Cf. Norton, *Chem. Rev.*, 1942, **31**, 319; Kloetzel, "Organic Reactions," Wiley, New York, 1954, Vol. IV, p. 1; Holmes, *op. cit.*, p. 60; Butz and Rytina, *op. cit.*, Vol. V, p. 136.³ Cohen and Warren, *J.*, 1937, 1315.⁴ Davies and Porter, preceding papers; Davies, Porter, and Wilmshurst, *J.*, 1957, 3366.⁵ Bachmann and Deno, *J. Amer. Chem. Soc.*, 1949, **71**, 3062.

Although 2-vinylnaphthalene is known³ to give an adduct with maleic anhydride, it was apparently not known to react with quinones. With excess of *p*-benzoquinone, however, 3:4-benzophenanthrene-1':4'-quinone (V) is produced in 47% yield. The intermediate hydrogenated adduct could not be isolated, the reaction is slower than that with 1-vinylnaphthalene, and the product is more coloured (bright red) than any quinone derived from 1-vinylnaphthalene. Fischer atomic models indicate that 3:4-benzophenanthrene-1':4'-quinone is considerably strained owing to the proximity of the



1'-oxygen atom to the neighbouring six-membered ring and it seems unlikely that the molecule is planar. Steric hindrance is probably responsible for the lower yield of adduct in this case, and for the relatively low (50%) yield of 3:4-benzophenanthrene formed by the reduction of the quinone with lithium aluminium hydride. No adduct has so far been isolated after reaction of 2-vinylnaphthalene and 1:4-naphthaquinone, the only product being 2:2'-dinaphthyl-1:4:1':4'-diquinone, previously isolated from 1:4-naphthaquinone and acetic acid containing pyridine.⁶

The synthetical value of this process is seen in the preparation of naphtho(2':1'-1:2)-anthracene-9:10-quinone (III; R = R' = H) and thence by our general methods naphtho(2':1'-1:2)-anthracene (IV), previous syntheses⁷ of which are less satisfactory in yield, convenience, or lack of ambiguity.

Juglone reacts with 3-vinylthionaphthen, but not with 1-vinylnaphthalene; its acetyl derivative, however, on prolonged heating gives the adduct (III; R = OAc, R' = H, or *vice versa*) (cf. the ready reaction with 3-vinylthionaphthen⁴). The same trend is seen in the inactivity of the acetate of lawsone (2-hydroxy-1:4-naphthaquinone) towards 1-vinylnaphthalene, though it reacts with 3-vinylthionaphthen.⁴ This difference is probably due to the lower aromaticity of 3-vinylthionaphthen. It is of interest that all the polycyclic quinones from 3-vinylthionaphthen are considerably paler than the isosteric quinones from 1-vinylthionaphthen.

1-cyclohex-1'-enylnaphthalene is stated⁸ not to give an adduct with maleic anhydride, and its 3'- and 4'-methyl derivatives are reported not to react with benzoquinone.⁹ It is now found that with excess of *p*-benzoquinone in acetic acid, 1-cyclohex-1'-enylnaphthalene is dehydrogenated to 1-phenylnaphthalene and no adduct is formed, as previously found for reaction with chloranil.¹⁰ No adducts were isolated on treatment of *p*-benzoquinone

⁶ Rosenhauer, Braun, Pummerer, and Riegelbauer, *Ber.*, 1937, **70**, 2281.

⁷ Clar, *Ber.*, 1929, **62**, 1574; Buu-Hoi, Hoan, and Jacquignon, *J.*, 1951, 1381; Martin, *Bull. Soc. chim. belges*, 1949, **58**, 87.

⁸ Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1940, **62**, 1699.

⁹ Bergmann and Weitzmann, *J. Org. Chem.*, 1944, **9**, 352.

¹⁰ Arnold, Collins, and Zenk, *J. Amer. Chem. Soc.*, 1940, **62**, 983.

(3—4 mols.) in acetic acid at 100° with styrene, 1-propenylnaphthalene, or 1-isopropenylnaphthalene, although in each case considerable quantities of quinhydrone (dehydrogenation) and polymer were formed; it is possible that partial dehydrogenation of the polymer by benzoquinone accounts for the quinhydrone formed.

The one-stage reduction of quinones to hydrocarbons by lithium aluminium hydride⁴ failed except when the quinone grouping was on the outermost ring and unfortunately even then the reaction is sometimes subject to steric effects which hinder or even prevent it.

EXPERIMENTAL

M. p. determinations were made in Pyrex tubes.

Reaction of 1-Vinylnaphthalene and Benzoquinone.—(a) *p*-Benzoquinone (0.3 g.) and 1-vinylnaphthalene¹¹ (1.0 g.) were kept at 80° for 15 min., then at room temperature for 5 days, and the crystalline product was recrystallised from benzene-ligroin, giving yellow prisms of 1 : 2 : 2a : 6a-tetrahydrochrysene-3 : 6-quinone (II) (0.25 g.), m. p. 188—189° (decomp.) (Found: C, 82.0; H, 5.0. C₁₈H₁₄O₂ requires C, 82.4; H, 5.3%).

This quinone was converted into chrysene-3 : 6-quinone, m. p. and mixed m. p. 213—214°, when heated with benzoquinone (3 mol.) in acetic acid at 100° for 4 hr., or refluxed with chloranil (2.1 mol.) in xylene for 30 min.

(b) 1-Vinylnaphthalene (1.5 g.) and *p*-benzoquinone (4.0 g.) in acetic acid (50 ml.) were heated on the water-bath for 5 hr., then cooled, and the precipitate recrystallised from acetic acid in orange needles of chrysene-3 : 6-quinone, m. p. 213.5—214° (2.0 g., 77%) (Bachmann and Deno⁵ report m. p. 206.5—207.5° and 78% yield (Found: C, 83.5; H, 3.95. Calc. for C₁₈H₁₀O₂: C, 83.7; H, 3.9%).

Reduction of Chrysene-3 : 6-quinone.—The quinone (0.88 g.) was extracted (Soxhlet) into a solution of lithium aluminium hydride (1.0 g.) in boiling tetrahydrofuran (150 ml.) for 10 hr. The excess of hydride was decomposed with moist ether, and dilute hydrochloric acid added; the dried ethereal layer yielded a yellow solid (0.7 g.) which on recrystallisation from acetic acid (charcoal) gave chrysene (0.55 g., 70%), m. p. and mixed m. p. 253—254° (Found: C, 94.4; H, 5.4. Calc. for C₁₈H₁₂: C, 94.7; H, 5.3%).

Reaction of 2-Vinylnaphthalene with p-Benzoquinone.—2-Vinylnaphthalene¹¹ (1.5 g.) and *p*-benzoquinone (4.0 g.) in acetic acid (30 ml.) were heated on the water-bath for 12 hr. and the black needles, deposited on cooling, were washed with cold ethanol to remove quinhydrone. The residue recrystallised from acetic acid in red needles of 3 : 4-benzophenanthrene-1' : 4'-quinone (V), m. p. 229.5—230° (1.42 g., 37%) (Found: C, 83.4; H, 3.9%). It (0.5 g.) was reduced with lithium aluminium hydride as described for chrysenequinone, giving 3 : 4-benzophenanthrene, needles (from ethanol), m. p. 67.5—68° (lit.,¹² m. p. 68°) (0.23 g., 50%) (Found: C, 94.6; H, 5.3%).

Reaction of 1-Vinylnaphthalene and 1 : 4-Naphthaquinone.—The quinone (6.0 g.) and 1-vinylnaphthalene (2.0 g.) in acetic acid (50 ml.) were heated on the water-bath for 5 hr., and the precipitate formed on cooling was recrystallised from xylene, giving pale-yellow needles of naphtho(2' : 1'-1 : 2)anthracene-9 : 10-quinone (III; R = R' = H), m. p. 288—288.5° (lit.,⁷ m. p. 269—270°) (3.4 g., 74%) (Found: C, 85.55; H, 4.0. Calc. for C₂₂H₁₂O₂: C, 85.7; H, 3.9%).

This quinone (0.2 g.), zinc dust (0.4 g.), and anhydrous sodium acetate (0.2 g.) were refluxed in acetic anhydride (10 ml.) for 30 min. The solution was added to water (100 ml.), and the product recrystallised from benzene, giving pale cream needles of 9 : 10-diacetoxynaphtho-(2' : 1'-1 : 2)anthracene, m. p. 273—274° (0.17 g.) (Found: C, 79.1; H, 4.8. C₂₄H₁₆O₄ requires C, 79.1; H, 4.6%).

Naphtho(2' : 1'-1 : 2)anthracene (IV).—The preceding quinone (1.0 g.) in refluxing acetic acid (150 ml.) was treated dropwise with stannous chloride (4.0 g.) in concentrated hydrochloric acid (10 ml.), and the mixture then refluxed for 1½ hr., concentrated to 100 ml., and cooled. The product that separated recrystallised from benzene, giving yellow prisms of the anthrone, m. p. 227—228° (0.73 g.) (Found: C, 89.8; H, 4.8. C₂₂H₁₄O requires C, 89.8; H, 4.8%).

The anthrone (0.5 g.) and zinc dust activated by brief treatment with 0.1% copper sulphate solution were refluxed in 2N-sodium hydroxide (25 ml.) under toluene (10 ml.) for 12 hr. Extra

¹¹ Davies and Porter, *J.*, 1957, 459.

¹² Cook, *J.*, 1931, 2524.

toluene (50 ml.) was added and the aqueous phase separated from the hot solution. The toluene layer was decolorised (charcoal) and concentrated, giving pale cream plates of naphtho(2':1'-1:2)anthracene, m. p. 303—304° (0.47 g.) (lit.,⁷ m. p. 293—294°) (Found: C, 94.8; H, 5.05. Calc. for C₂₂H₁₄: C, 95.0; H, 5.0%).

The hydrocarbon was also produced (65%) by reducing the quinone directly by the modified Clemmensen reduction,¹³ without first forming the anthrone.

Reaction of 2-Vinylnaphthalene and 1:4-Naphthaquinone.—The quinone (3.0 g.) and 2-vinylnaphthalene (1.0 g.) in acetic acid (20 ml.) were heated on the water-bath for 12 hr. The product that separated recrystallised from benzene as yellow needles (0.9 g.), m. p. 271—273° (decomp.: darkening at 240°) (Found: C, 76.2; H, 3.3. Calc. for C₂₀H₁₀O₄: C, 76.4; H, 3.2%). Rosenhauer *et al.*⁸ report m. p. 274—275° (decomp.) for 2:2'-dinaphthyl-1:4-1':4'-diquinone.

Reaction of 1-Vinylnaphthalene with Juglone Acetate.—The quinone (2.5 g.) and 1-vinylnaphthalene (0.8 g.) in acetic acid (15 ml.) were heated on the water-bath for 8 hr. The product crystallised from benzene, giving yellow needles of 5'(or 8'-)acetoxynaphtho(2':1'-1:2)anthracene (III; R = H, R' = OAc, or *vice versa*), m. p. 268—269° (0.92 g.) (Found: C, 78.7; H, 3.6. C₂₄H₁₄O₄ requires C, 78.8; H, 3.8%).

Reaction of 1-cycloHex-1'-enylnaphthalene and Benzoquinone.—The quinone (4.5 g.) and 1-cyclohex-1'-enylnaphthalene (3.0 g.) were heated in acetic acid (60 ml.) on the water-bath for 12 hr. Quinhydrone, m. p. and mixed m. p. 171°, separated on cooling. The filtrate was evaporated under reduced pressure (water-bath), excess of benzoquinone removed by sublimation, and the residue steam-distilled. The distillate, extracted with ether, gave 1-phenylnaphthalene (1.6 g.), b. p. 186—188°/22 mm. (no picrate; 4-bromo-derivative,¹⁴ m. p. 75—76°).

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¹³ Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

¹⁴ Weiss and Woiditch, *Monatsh.* 1925, **46**, 453.