186. *The Synthesis of Polycyclic Aromatic Compounds. Part II.*[1] *Picene-5 : 6- and -13 : 14-quinone and Picene-5 : 6 : 7 : 8-diquinone.*

By W. Davies and B. C. Ennis.

A new application of the Diels–Alder reaction is the use of *o*-quinones with vinylarenes. 1-Vinylnaphthalene and 3-bromo-1 : 2-naphthaquinone form picene-5 : 6-quinone (III) which, together with a smaller amount of picene-13 : 14-quinone, is now separated from the " picene quinone " described in the literature. Oxidation of the monoquinone (III) gives picene 5 : 6 : 7 : 8-diquinone.

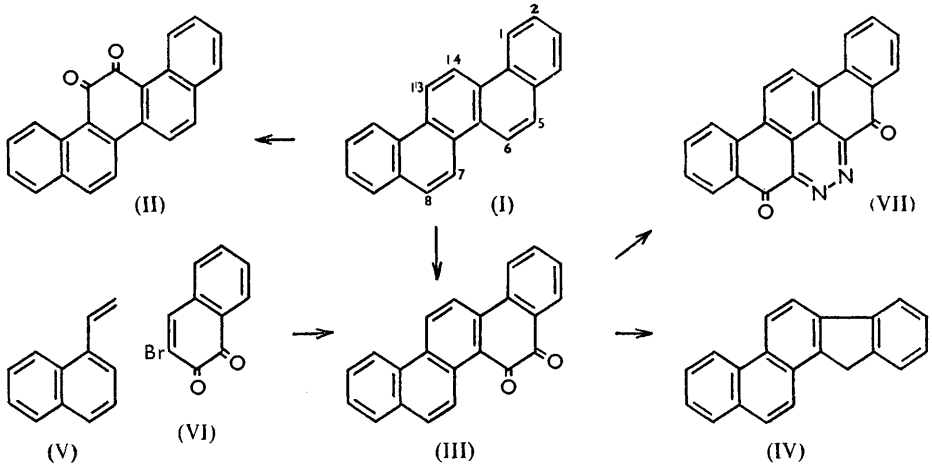
The synthesis of polycyclic quinones, and thence of their parent aromatic hydrocarbons, by the Diels–Alder reaction of *p*-quinones with 1-vinylnaphthalene and related dienes (Part I [1]) suggests a similar synthetic rôle for *o*-quinones. Though some substituted *o*-benzoquinones will react with active dienes, their instability often leads to low yields (and more than one adduct).[2] However, the use of relatively stable *o*-quinones was more hopeful

[1] Part I, Davies and Porter, *J.*, 1957, 4967.

[2] Smith and Hac, *J. Amer. Chem. Soc.*, 1936, **58**, 229; Horner and Merz, *Annalen*, 1950, **570**, 89; Horner and Spietschka, *ibid.*, 1953, **579**, 159; Barltrop and Jeffreys, *J.*, 1954, 154.

as satisfactory yields had been reported [3] from 2 : 3-dimethylbutadiene and 1 : 2- and 3 : 4-phenanthraquinone and substituted 1 : 2-naphthaquinones.

" Picenequinone," of obscure structure, was obtained by Bamberger and Chattaway [4] by oxidation of picene (I) with chromic acid; it was degraded through a ketone and an acid to 2 : 2′-dinaphthyl, and so was assigned structure (II). On the other hand, Cook,[5] using the original specimen of ketone prepared [4] by heating " picenequinone " with litharge, found it to be a complex mixture from which he chromatographically isolated naphtho(2′ : 1′-1 : 2)fluorenone, which was reduced with hydrazine hydrate to naphtho(2′ : 1′-1 : 2)-fluorene (IV). Cook accordingly accepted the structure of " picenequinone " as essentially (III), and attributed the isolation of 2 : 2′-dinaphthyl " to the presence of impurity in the ' picenic acid ' used by Bamberger and Chattaway."



1-Vinylnaphthalene (V) reacts with 1 : 2 naphthaquinone in acetic acid to form a tar, but with 3-bromo-1 : 2-naphthaquinone (VI) gives >30% of picene-5 : 6-quinone (III), m. p. 310°, which is the only new product isolated. Excess of quinone was used and the initial product was formed, dehydrobrominated, and dehydrogenated in the one operation, as in the self-condensation of 3-bromothionaphthen 1 : 1-dioxide.[6] The compound of m. p. 310° might theoretically be an unknown quinone of 5 : 6-benzochrysene or a quinone of picene; unfortunately reduction yielded neither hydrocarbon. It could not be compared with the " picenequinone " of the literature, as no m. p. is recorded for this compound, or its phenazine derivative [7] [whose recorded nitrogen content (7·9%) agrees poorly with the theoretical value (7·4%; erroneously given by Meyer *et al.*[7] as 8·2%)], or for the " yellow brown precipitate " produced by reductive acetylation (whose acetyl content [7] was the only basis for its formulation as 9 : 10-diacetoxy-9 : 10-dihydro-1 : 2 : 7 : 8-dibenzophenanthrene, $C_{26}H_{20}O_4$).

The structure of the compound of m. p. 310° has, however, been determined by repeating the oxidation [4] of picene: the product was separated chromatographically into unchanged picene and a quinone identical with the Diels–Alder product which must therefore be the 5 : 6-quinone (III). There is also formed an isomeric quinone which gives a diacetoxypicene and a phenazine very much more slowly: we believe this to be the 13 : 14-quinone (II), whose quinone group would be sterically hindered. It is isolated in less than one-third the yield of the 5 : 6-quinone (III), but the amount initially formed may be much larger since excess of the oxidant (chromic acid) rapidly converts it into soluble products.

[3] Fieser and Dunn, *J. Amer. Chem. Soc.*, 1937, **59**, 1016.
[4] Bamberger and Chattaway, *Annalen*, 1895, **284**, 52.
[5] Cook, *J.*, 1941, 685.
[6] Davies, James, Middleton, and Porter, *J.*, 1955, 1565.
[7] Meyer and Hoffman, *Monatsh.*, 1916, **37**, 681.

On the other hand, the isomeric 5 : 6-quinone is only partly destroyed under these conditions and is readily oxidised to a diquinone; this is assigned the structure picene-5 : 6 : 7 : 8-diquinone, since with hydrazine hydrate it gives an azine considered to be (VII).

Experimental

3-Bromo-1 : 2-naphthaquinone, prepared by bromination [8] of 1 : 2-naphthaquinone,[9] was recrystallised from benzene immediately before use. 1-Vinylnaphthalene was made from crude 1-1′-naphthyl ethanol.[10] Picene, m. p. 365°, was a product of Rütgerswerke-Aktiengesellschaft Castrop-Rauxel 2.

Picene-5 : 6-quinone (III).—3-Bromo-1 : 2-naphthaquinone (7·3 g.) and 1-vinylnaphthalene (2·3 g.) in *sym*-tetrachloroethane (200 ml.) were heated in a boiling-water bath for 5 hr.; the solvent was then removed at reduced pressure and the oily residue triturated with acetone (50 ml.) to give crystalline *picene-5 : 6-quinone* (2·0 g.), sparingly soluble in acetone, slightly soluble in boiling benzene, or chloroform, and conveniently recrystallising from boiling xylene or acetic acid as orange-red needles, m. p. 310° (1·5 g., 33%, calc. on 1-vinylnaphthalene) (Found: C, 85·4; H, 4·0. $C_{22}H_{12}O_2$ requires C, 85·7; H, 3·9%). A slightly lower yield (30%) separated from the cooled solution when glacial acetic acid was substituted for tetrachloroethane. In cold concentrated sulphuric acid it gives a deep green, slowly changing to a permanent navy-blue, colour.

The *phenazine derivative*, yellow needles (from acetic acid), m. p. 278—278·5° (Found: N, 7·3. $C_{28}H_{16}N_2$ requires N, 7·4%), was obtained in good yield when the quinone was boiled for 15 min. with the theoretical quantity of *o*-phenylenediamine in acetic acid. It dissolves in cold concentrated sulphuric acid to a stable olive-green solution.

Oxidation of Picene.—To a suspension of picene (2·5 g.) in boiling acetic acid (200 ml.), previously distilled from chromic acid, was added chromic acid (3·2 g.) in acetic acid (100 ml.) during 10 hr. After a further 4 hours' boiling, the mixture was concentrated to 30 ml. The product was collected, washed with dilute sodium carbonate at 50°, and recrystallised from acetic acid to give ill-defined crystals, m. p. 260—280°. Sublimation of this product at 200°/0·04 mm. caused extensive decomposition and the sublimate, m. p. 270—285°, was still impure. The original product was dissolved in chlorobenzene (300 ml.) and chromatographed on deactivated silica [11] containing 7% of water. The first, colourless band was blue-fluorescent under ultraviolet light and on concentration yielded picene as colourless plates (0·07 g.), m. p. 363—365°. The eluate from the first dark brown, non-fluorescent band, on concentration, gave *picene-13 : 14-quinone* (II) (0·25 g.), red plates (from acetic acid or benzene), m. p. 285° unchanged by sublimation at 220°/1 mm. (Found: C, 85·8; H, 4·0. $C_{22}H_{12}O_2$ requires C, 85·7; H, 3·9%). It was destroyed on an attempted conversion into a diquinone under the conditions which succeeded with the isomer (III). In cold concentrated sulphuric acid there is a stable royal-blue coloration.

The second brown, non-fluorescent band was more strongly adsorbed and attempts to speed elution by addition of ethyl acetate or alcohol to the solvent resulted in precipitation of the quinone. The column was extruded and the relevant portion extracted with chlorobenzene. Concentration of the extract yielded orange needles which recrystallised from acetic acid and from benzene to give picene-5 : 6-quinone (III) (0·89 g.), m. p. 309—309·5°, unchanged by sublimation at 200°/0·002 mm. (Found: C, 85·7; H, 4·2%). The m. p. was unchanged on admixture with the previous specimen of m. p. 310°. The phenazine derivative, m. p. 278·5—278·7°, was also identical (mixed m. p.): it is difficult to burn, 50% more than the normal time being required in its combustion (Found: C, 88·0; H, 4·3. $C_{28}H_{16}N_2$ requires C, 88·4; H, 4·2%).

Reductive Acetylation of the Quinone (III).—Picene-5 : 6-quinone (0·1 g.), anhydrous sodium acetate (0·1 g.), and zinc dust (0·2 g.) were heated under reflux in acetic anhydride (5 ml.) for 1 hr. The anhydride was hydrolysed by warm water; the resulting product gave an excellent yield of *5 : 6-diacetoxypicene*, colourless needles (from benzene–light petroleum), m. p. 224—225° (Found: C, 79·3; H, 4·5; O, 16·4. $C_{26}H_{18}O_4$ requires C, 79·2; H, 4·6; O, 16·2%). Its almost colourless solution in concentrated sulphuric acid gradually became navy blue. Its solution in benzene gave a blue-violet fluorescence in ultraviolet light.

[8] Zincke, *Ber.*, 1894, **27**, 733.
[9] Fieser, *Org. Synth.*, Coll. Vol. II, p. 430.
[10] Davies and Porter, *J.*, 1957, 459.
[11] Cahnmann, *Analyt. Chem.*, 1957, **29**, 1307.

Derivatives of Picene-13 : 14-*quinone*.—Reductive acetylation as above gave 13 : 14-*diacetoxypicene*, colourless needles (from ethanol), m. p. 236—237°, in poor yield (Found: C, 79·0; H, 4·7%). Its fluorescence resembled that of the isomer. Its sulphuric acid solution gradually became royal-blue.

The *phenazine derivative* is formed with difficulty from the quinone (0·05 g.) and *o*-phenylenediamine (0·05 g.) in refluxing acetic acid (10 ml.). Crystals appeared in 1 hr.; 0·02 g. was collected after 4 hr., and after a further 10 hr. additional phenazine (0·03 g.) separated in golden needles, m. p. 258—258·5° (from acetic acid in which it is very sparingly soluble) (Found, after extra time for combustion: C, 88·4; H, 4·2; N, 7·7%). It colours cold concentrated sulphuric acid navy-blue.

Picene-5 : 6 : 7 : 8-*diquinone*.—Chromic oxide (0·11 g.) in acetic acid was added to a boiling solution of picene-5 : 6-quinone (0·11 g.) in acetic acid (60 ml.). In about 30 seconds a precipitate of the diquinone appeared. The mixture was immediately cooled and filtered, to give the *picene*-5 : 6 : 7 : 8-*diquinone* (0·07 g.), reddish-brown needles (from *o*-dichlorobenzene), m. p. 386° (Found: C, 77·6; H, 3·2. $C_{22}H_{10}O_4$ requires C, 78·1; H, 3·0%). Its solution in cold sulphuric acid is brown and stable. It is extremely insoluble in hot acetic or heptanoic acid, and its solution in hot phenylacetic acid gave no phenazine with *o*-phenylenediamine despite apparent reaction. Under these conditions the phenazine from the monoquinone (III) is rapidly obtained in good yield after subsequent dilution with alcohol.

6 : 7-*Diazabenzo*[fgh]*picene*-5 : 8-*quinone* (VII) was formed when the diquinone (0·07 g.) was heated under reflux for 1½ hr. in pyridine (7 ml.) with 90% hydrazine hydrate (0·7 ml.); the deep blue reaction mixture was cooled and the precipitate recrystallised from boiling nitrobenzene as brown-violet needles, m. p. >450° (Found: N, 8·5. $C_{22}H_{10}O_2N_2$ requires N, 8·4%). Its solution in cold concentrated sulphuric acid is dark green, its smear is brown-violet, and its solution in organic solvents, in which it is very sparingly soluble, is orange-brown.

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