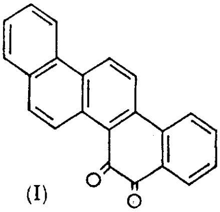
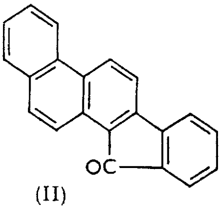
299. *The Synthesis of Polycyclic Aromatic Compounds. Part III.*[1] *The Production of Fluorene Derivatives in the Zinc-dust Distillation of Polycyclic* o-*Quinones related to Phenanthra*-9,10-*quinone.*

By W. Davies and B. C. Ennis.

Zinc oxide with phenanthra-9,10-quinone at 300—320° gives fluorenone, and with chrysene-1,2- and picene-5,6-quinone gives the corresponding fluorenones, all in moderate yields. Zinc-dust distillation of the above and similar quinones shows that such ring contraction followed by reduction to the corresponding fluorene is a general reaction.

Diels–Alder condensation of 1-vinylnaphthalene and 3-bromo-1,2-naphthaquinone gives[1] picene-5,6-quinone (I). However, following this by a zinc-dust distillation we were unable to obtain pure picene despite its reported isolation[2] in this way from "picene-quinone"—formed by oxidation—which contains[1] the quinone (I) and picene-13,14-quinone, both of which might be expected to yield picene. The quinone (I) is now found to yield, not picene, but naphtho(2′,1′:1,2)fluorenone (II) mixed with the corresponding fluorene which has been identified by its ultraviolet absorption. Picene, m. p. 365°, does not depress[3] the m. p. 338° of this fluorene derivative, and moreover the analytical differences are only C 0·23 and H 0·23%: hence the previously unsuspected confusion between the two hydrocarbons. This was possibly accentuated by the presence of a little residual picene shown to be present[1] (by a chromatographic method not available to Bamberger and Chattaway) in their "picene quinone."[2] Since the structure of the present authors' synthetic quinone was not determined by converting it into picene, the quinone was also prepared by oxidising picene, thus removing the possibility that the synthetic quinone was a derivative of 5,6-benzochrysene.


(I)



(II)

It is known that hot solutions of strong bases convert phenanthra-9,10-quinone into fluorenone by a benzilic acid type of rearrangement, and the weak base litharge is a favoured reagent in the dry way for this kind of change,[4] especially with large *o*-quinones sparingly soluble in alcoholic solutions of alkali. It is now found that litharge can be replaced by the slower-acting zinc oxide, for from a mixture of this and the above-mentioned quinones of phenanthrene, chrysene, and picene at 300—320° the corresponding fluorenones sublime or distil at atmospheric pressure in yields varying from 40 to 50%. A smaller yield is obtained from picene-13,14-quinone, but none from retene-9,10-quinone. Here no volatile material is formed, presumably owing to condensation of alkyl and carbonyl groups under the influence of the basic zinc oxide.

Commercial, freshly prepared zinc dust always contains zinc oxide which moreover is always formed by the removal of oxygen in organic compounds as the zinc-dust distillation proceeds. This explains the formation of the fluorenone in all instances when zinc dust is heated with *o*-quinones of phenanthrene, retene, chrysene, and picene, but with the 4- and 5-ring quinones the fluorene was also observed. These conditions afford little or none

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[1] Part II, Davies and Ennis, *J.*, 1959, 915.
[2] Bamberger and Chattaway, *Annalen*, 1895, **284**, 52.
[3] Cook, *J.*, 1941, 685.
[4] "Beilsteins Handbuch der Organischen Chemie," 4th edn., Vol. VII, pp. 797, 819, 827, 839.

of the formerly expected hydrocarbon consisting of six-membered rings only. However, chrysene, as well as the related fluorene and fluorenone derivatives, are formed from chrysenequinone and hot zinc dust in a stream of hydrogen. These three are also formed when the zinc oxide in the zinc dust has previously been converted into metallic zinc *in situ* by a stream of hydrogen. In this case the zinc dust was initially supported on pumice, and afforded the best yield (9%) of chrysene obtained in our work.

In general the presence of zinc oxide in zinc dust seems advantageous in zinc-dust distillations without the use of externally supplied hydrogen. For example, when ordinary zinc dust is heated in a tube the infusible zinc oxide hinders the coalescing of the minute droplets of molten zinc. In this way a large surface of molten zinc on the "carrier" zinc oxide is exposed to the action of the hot steam formed by the high-temperature decomposition of part of the organic compound to be reduced. It seems likely that it is the hot hydrogen thus produced which effects reduction to the hydrocarbon, since we found that when the zinc-dust distillation of phenanthrene- and chrysenequinone is effected in the presence of starch, which readily forms much steam, the only pure compounds isolated are the hydrocarbons fluorene and "chrysenofluorene."

In the present work four compounds with a 1,2-quinone group in the "*K* region" of phenanthrene have been distilled with zinc dust, and in all cases ring contraction has taken place. Since this seems to be the rule its occurrence need no longer be a source of confusion but may actually be evidence for the structure of the quinone and its parent, completely aromatic, hydrocarbon. The ready formation of the fluorenone from picene-13,14-quinone (which reacts with *o*-phenylenediamine with difficulty [1]) suggests that this reaction may find use in the recognition of *o*-quinones subject to even greater steric hindrance.

EXPERIMENTAL

Reactions of o-*Quinones with Zinc Oxide*.—A mixture of the quinone with three parts of zinc oxide was heated at 300—320° until there was no further sublimation, usually for about 1 hr.

Phenanthra-9,10-quinone (0·50 g.) yielded fluorenone (0·17 g., 40%), yellow needles (from aqueous ethanol), m. p. and mixed m. p. 84°. The oxide residue was extracted with benzene, and the extract chromatographed on alumina, to yield colourless needles, m. p. 314° (presumably diphenanthrofuran, m. p. 310°,[5] 306° [6]) as the only discrete material (Found: C, 91·2; H, 4·5. Calc. for $C_{28}H_{16}O$: C, 91·3; H, 4·35%).

Chrysene-1,2-quinone (0·50 g.) produced a sublimate of yellow-orange needles of 1,2-benzofluorenone (0·25 g., 52%), m. p. 132° (from ethanol). There was no depression when admixed with a sample prepared from chrysene-1,2-quinone.[7]

Picene-5,6-quinone (0·20 g.) gave plates which after chromatography on alumina in benzene solution yielded naphtho(2′,1′:1,2)fluorenone, golden-yellow plates (from ethanol), m. p. 210° (lit.,[8] m. p. 210°) (Found: O, 6·0. Calc. for $C_{21}H_{12}O$: O, 5·7%). Picene-13,14-quinone similarly yielded 1,2:7,8-dibenzofluorenone (0·05 g., 27%), brown-orange plates, m. p. 270—270·5° (lit., m. p. 272°,[8] 265—266° [9]) (Found: C, 90·4; H, 4·3. Calc. for $C_{21}H_{12}O$: C, 90·0; H, 4·3%).

Retenequinone gave no sublimate and no discrete compound could be isolated from the oxide residue. Benzil (b. p. 347°) distilled unchanged from zinc oxide.

Reaction of Picene-5,6-quinone with Litharge.—Picene-5,6-quinone (0·10 g.) was heated with lead oxide (0·8 g.) at 280° for 2 min. Vacuum was then applied. Naphtho(2′,1′:1,2)fluorenone, m. p. 210° (0·06 g.), sublimed. Vacuum-methods are not so suitable to reactions with zinc oxide since a considerable amount of the quinone sublimed with the fluorenone.

Zinc-dust Distillation of o-*Quinones*.—Unless otherwise indicated an intimate mixture of the quinone with five parts of zinc dust was lightly packed in a horizontal test tube and covered with the same amount of zinc dust. The zinc dust was commercial material containing

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[5] Dutt and Sen, *J.*, 1923, **123**, 3420.
[6] Japp and Findlay, *J.*, 1897, **71**, 1115.
[7] Bamberger and Kranzfeld, *Ber.*, 1885, **18**, 1931.
[8] Wanscheidt, *Ber.*, 1926, **59**, 2092.
[9] Swain and Todd, *J.*, 1941, 674.

approximately 86% of metallic zinc and 14% of zinc oxide. The mixture was then heated to dull red heat for 5—10 min. and the resultant sublimate extracted with a suitable solvent and chromatographed on alumina.

Phenanthraquinone. (i) The sublimate was extracted with light petroleum (b. p. 56°) and chromatographed on alumina. The first band, fluorescing pale blue under ultraviolet light, yielded on concentration a small amount of phenanthrene, m. p. and mixed m. p. 99°. The second band, pale yellow and non-fluorescent, gave a small amount of fluorenone, m. p. and mixed m. p. 84°.

(ii) The distillation was repeated but with an equal weight of quinone and starch in the first layer of zinc dust. The distillation took about twice the time required in the absence of starch. The sublimate was chromatographed as before and the first band, weakly fluorescent under ultraviolet light, yielded on concentration fluorene, m. p. and mixed m. p. 113°, in very low yield. No other product was isolated.

Retenequinone. The yellow sublimate was chromatographed in light petroleum (b. p. 56°) on alumina. The first band eluted fluoresced blue under ultraviolet light and its colourless solution on concentration yielded a very small amount of non-crystalline material. This formed an orange 2,4,7-trinitrofluorenone complex, needles (from benzene), m. p. 167° undepressed when admixed with retene–2,4,7-trinitrofluorenone complex (m. p. 167°). The second band, pale yellow and non-fluorescent, yielded on concentration yellow crystals, m. p. 88—89° alone or mixed with retenequinone.[10]

Chrysenequinone. (i) The orange sublimate from the zinc-dust distillation of the quinone (1·0 g.) was dissolved in benzene, and this solution was diluted with two volumes of light petroleum (b. p. 56°) and chromatographed on alumina. The first band, fluorescing blue under ultraviolet light, yielded on concentration a small amount of 1,2-benzofluorene, white plates, m. p. 185—187° (lit.,[11] m. p. 188°) [complex with 2,4,7-trinitrofluorenone, m. p. 215° (lit.,[12] m. p. 215°) (Found: C, 67·7; H, 3·3. Calc. for $C_{30}H_{17}N_3O_7$: C, 67·8; H, 3·4%]. The second, yellow, band yielded 1,2-benzofluorenone, m. p. 132°.

(ii) When starch was mixed with the quinone and zinc dust the only pure material obtained was 1,2-benzofluorene, in very low yield.

(iii) The quinone (1·0 g.) was distilled with zinc dust in a stream of hydrogen. The product was purified as before. The first band contained a mixture of chrysene and 1,2-benzofluorene. The mixture in benzene was treated with 2,4,7-trinitrofluorenone in benzene and the first crop of crystals (orange needles) recrystallised from benzene to give the chrysene–2,4,7-trinitrofluorenone complex, m. p. 249° (lit.,[13] m. p. 249°). The filtrate from the first crop was concentrated and diluted with ethanol, to yield red-orange needles of the 1,2-benzofluorene–2,4,7-trinitrofluorenone complex, m. p. 215°. The complexes in benzene solution were decomposed by passage through an alumina column, yielding chrysene (0·03 g.) and 1,2-benzofluorene (0·03 g.). The second band yielded 1,2-benzofluorenone (0·12 g.).

(iv) Zinc dust was mixed with powdered pumice and heated in a stream of hydrogen at 550° for 2 hr. The quinone (1·0 g.), also suspended on pumice, was then heated to drive it through the zinc dust in a stream of hydrogen. From this, chrysene (0·09 g.), 1,2-benzofluorene (0·03 g.), and 1,2-benzfluorenone (0·02 g.) were isolated as in (iii).

Picene-5,6-*quinone.* The sublimate and the residue from the distillation of the quinone (0·50 g.) were extracted with boiling xylene, and the extract was concentrated to 5 ml. Sublimation of the yellow crystals gave a mixture of white needles and yellow plates which could not be separated by chromatography on either silica or alumina. The material was extracted with boiling ethanol, and the residue recrystallised repeatedly from chloroform and from toluene, to yield colourless needles of naphtho(2′,1′:1,2)fluorene, m. p. 333—334° (lit., m. p. 338°,[3] 327—328° [14]), undepressed when admixed with picene (Found: C, 94·4; H, 5·1. Calc. for $C_{21}H_{14}$: C, 94·7; H, 5·3. Calc. for $C_{22}H_{14}$: C, 94·9; H, 5·1%). The ultraviolet spectrum of this material agrees well with that of naphtho(2′,1′:1,2)fluorene [14] but differs markedly from that of picene.[14] No 2,4,7-trinitrofluorenone complex could be prepared under conditions where picene readily gave such a derivative.[13] The filtrate from the original xylene extraction and

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[10] Bamberger and Hooker, *Annalen*, 1885, **229**, 102.
[11] Graebe, *Ber.*, 1894, **27**, 952.
[12] Woolfolk and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002.
[13] Woolfolk and Orchin, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.
[14] Cook, Hewett, Mayneord, and Roe, *J.*, 1934, 1727.

the above alcohol washings, when combined and evaporated to dryness, gave a very small yield of yellow plates (from ethanol), m. p. 204—206°, not depressed when admixed with naphtho(2′,1′:1,2)fluorenone, m. p. 210°.

The microanalyses were carried out by Dr. W. Zimmermann and his staff. One of us (B. C. E.) thanks the Vacuum Oil Co. Pty. Ltd. for a scholarship. Some equipment was provided from the Anti-Cancer Council of Victoria.

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[*Received, October 6th,* 1959.]