551. *The Schmidt Reaction on* 1 : 2-5 : 6-*Dibenzanthra*-3 : 4-*quinone*.

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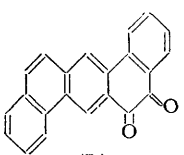
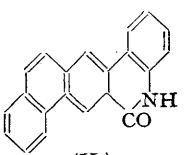
The Schmidt reaction on 1 : 2-5 : 6-dibenzanthra-3 : 4-quinone (I) has been investigated. An improved preparation of (I) has been described and 1 : 2-5 : 6-*dibenzanthra*-3 : 4 : 7 : 8-*di-quinone* (V) isolated as a by-product from this preparation. An alternative preparation of naphtho(1′ : 2′-2 : 3)fluorenone (VIII) from (I) is described.

In an attempt to prepare nitrogen analogues of the potent carcinogen 1 : 2-5 : 6-dibenzanthracene, a Schmidt reaction on 1 : 2-5 : 6-dibenzanthra-3 : 4-quinone (I) was examined with a view to obtaining one or both of the phenanthridones (II) and (III), which could presumably be converted by standard procedures into the corresponding phenanthridines. (I), obtained previously by Cook (*J.*, 1933, 1592) as a by-product of the chromic acid oxidation of



(I.)



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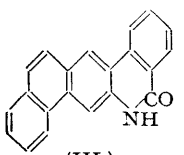

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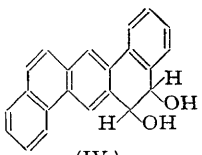

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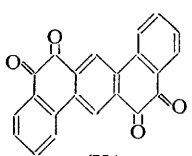

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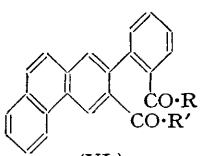
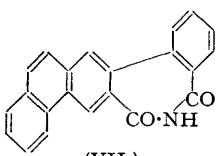
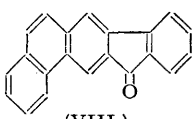


(VI.)



(VII.)



(VIII.)

1 : 2-5 : 6-dibenzanthracene and of 9 : 10-dihydro-1 : 2-5 : 6-dibenzanthracene, was in the present work prepared by chromic acid oxidation of 3 : 4-dihydroxy-3 : 4-dihydro-1 : 2-5 : 6

dibenzanthracene (IV) (Cook and Schoental, *J.*, 1948, 170), when a small amount of a *diquinone* was always formed. The two quinones were separated by cautious fractional sublimation, and the diquinone shown to be a di-*ortho*-quinone, evidently (V), by condensation with 2 moles of *o*-phenylenediamine to give a diquinoxaline derivative.

Caronna (*Gazzetta*, 1941, **71**, 481; *Chem. Abs.*, 1943, **37**, 118) has converted phenanthraquinone into phenanthridone. As Caronna's original paper was not available, some preliminary experiments were carried out with phenanthraquinone and also with diphenic acid to determine suitable experimental conditions. It was found that, with a large excess of sodium azide (10 moles) in an excess of concentrated sulphuric acid, the phenanthridone was obtained in excellent yield. Decrease in the proportion of azide led to the production of a considerable proportion of diphenamic acid and less phenanthridone. With proportions of azide less than 2 moles, much quinone was recovered unchanged. (Further details are discussed in the Experimental section.) Attempts to apply these findings to (I) gave very poor yields of the required products. Use of a large excess of azide converted (I) into intractable resins. Smaller proportions (2·7 moles of azide) gave a small amount of a phenanthridone (II) or (III) and a larger proportion of a mixture of acids [presumably the amic acids (VI; R = OH, R′ = NH_2 and *vice versa*)] which could not be purified directly, but was converted by hydrolysis into the *dicarboxylic acid* (VI; R = R′ = OH) or by vacuum sublimation into its *imide* (VII). (VII) was hydrolysed to (VI; R = R′ = OH) when heated with aqueous sodium hydroxide.

Considerable proportions of resinous material were always formed even under the most favourable experimental conditions, and the amount of phenanthridone obtained was insufficient to serve as a starting material for the preparation of the phenanthridine.

Attempts were made to convert naphtho(1′ : 2′-2 : 3)fluorenone (VIII) into (II) or (III) by the action of hydrazoic acid in sulphuric acid (cf., *e.g.*, Walls, *J.*, 1935, 1405; Petrow, *J.*, 1946, 200, 888), but the ketone was either recovered unchanged or converted into resinous materials.

Experimental.

(All m.p.s are uncorrected.)

1 : 2-5 : 6-*Dibenzanthra*-3 : 4-*quinone* (I) *and* 1 : 2-5 : 6-*Dibenzanthra*-3 : 4 : 7 : 8-*diquinone* (V).—3 : 4-Dihydroxy-3 : 4-dihydro-1 : 2-5 : 6-dibenzanthracene (IV) was prepared according to the method of Cook and Schoental (*J.*, 1948, 170). The crude diol had a deep pink colour, due presumably to traces of the 3 : 4-quinone. It was not purified, but was oxidised as follows. A mixture of the diol (1·56 g.) and sodium dichromate (1·74 g.) in water (5 ml.) and acetic acid (180 ml.) was heated under reflux for 20 minutes, whereupon the diol dissolved and the quinone separated. The warm mixture was poured into water, the quinone collected, washed well with water, dried, and crystallised from *o*-dichlorobenzene, giving fine, red needles, m. p. 326—328° (decomp.) (1·08 g.). Even after repeated crystallisations from *p*-dichlorobenzene this quinone gave a low value for carbon on analysis, owing to the presence of the diquinone (V). Cautious fractional sublimation of the contaminated monoquinone (bath temperature, < 250°/0·6—0·8 mm.) gave an orange-red sublimate which after crystallisation from *o*-dichlorobenzene formed light-red needles, m. p. 327—329° (decomp.) (Cook, *loc. cit.*, gives m. p. 326—327°) (Found : C, 85·7; H, 4·1. Calc. for $C_{22}H_{12}O_2$: C, 85·7; H, 3·9%). After sublimation of the monoquinone, sublimation at higher temperatures (mainly 300—330°/0·6 mm.) gave a dark red sublimate (needles) of the diquinone. However, it proved very difficult to separate all traces of the monoquinone from the diquinone, and the latter was boiled under reflux again with excess of dichromate in acetic acid until oxidation of the monoquinone was practically complete. The product was again fractionally sublimed and the sublimate crystallised from diethylene glycol. The *diquinone* (V) separated as tiny, dark red needles, decomp. > 360° (Found : C, 78·2; H, 3·05. $C_{22}H_{10}O_4$ requires C, 78·1; H, 3·0%). When the diethylene glycol solution cooled very slowly, the diquinone separated as large, very dark red needles which in bulk formed a shiny, purple-black crystalline mass. The *diquinoxaline* derivative of (V) was prepared by suspending pure (V) in acetic acid containing excess of pure *o*-phenylenediamine and heating the mixture under reflux for 1 hour. This derivative (small mustard-yellow crystals) had m. p. > 360°, and was too sparingly soluble in the organic solvents tried to allow crystallisation (Found : C, 84·5, 84·45; H, 3·9, 3·9; N, 11·7, 11·55. $C_{34}H_{18}N_4$ requires C, 84·65; H, 3·8; N, 11·6%).

Naphtho(1′ : 2′-2 : 3)*fluorenone* (VIII) (cf. Cook *et al.*, *J.*, 1935, 1319).—Purified (I) was mixed with 7—8 times its weight of litharge and converted into the ketone (VIII) by the method described for similar cases (Cook and Stephenson, *J.*, 1949, 842). The orange sublimate (75 mg.) had m. p. 218·5—219·5°, not altered by crystallisation from alcohol–benzene (3 : 2) (Cook *et al.*, *loc. cit.*, give m. p. 214·5—215°) (Found : C, 90·2; H, 4·55. Calc. for $C_{21}H_{12}O$: C, 90·0; H, 4·3%).

Naphtho(1′ : 2′-2 : 3)*fluorene*.—Sublimed (VIII) (70 mg.) and 50% hydrazine hydrate (0·2 ml.) were heated in a sealed tube at 200—210° for 7¼ hours. The crude product was collected, washed well with water, dried, and dissolved in light petroleum (b. p. 60—80°), and this solution passed through a column of alumina. Coloured impurities were strongly adsorbed and the colourless, weakly fluorescent hydrocarbon passed readily into the eluate. The colourless product (35 mg.) recovered from the eluate had m. p. 225—227·5°, raised to 230—231° by crystallisation from alcohol–benzene (4 : 1), from which it separated as colourless plates (lit., 226—226·5°).

Action of Hydrazoic Acid and Concentrated Sulphuric Acid on Phenanthraquinone.—(*a*) Phenanthraquinone (0·208 g., 0·001 mol.) dissolved in concentrated sulphuric acid (10 ml.) was treated with finely

powdered sodium azide (technical; 0·65 g., 0·01 mol.), the mixture being cooled in an ice-bath so that the temperature was maintained at 0—10°. The mixture was then kept at room temperature until gas evolution had subsided and the original deep green colour of the solution had faded to a pale green (2—3 hours). Phenanthridone (m. p. 287—288°; 180 mg.) was precipitated when the reaction mixture was poured into ice-water. No other products were isolated.

(*b*) Essentially the same results were obtained when the quantity of sulphuric acid was reduced to 1 ml., and the mixture was covered with 10 ml. of pure chloroform.

(*c*) The same results as in (*a*) were obtained when the reaction was carried out at 30—40°.

(*d*) When the experiment was carried out as under (*a*) but using 0·325 g. (0·005 mol.) of sodium azide, only 35 mg. of phenanthridone and 120 mg. of diphenamic acid were obtained. The latter is readily converted into diphenimide by sublimation *in vacuo*.

(*e*) When equimolar proportions of azide and quinone were used under the conditions of (*a*), (*b*), or (*c*), much quinone was recovered unchanged.

Action of Hydrazoic Acid and Concentrated Sulphuric Acid on Diphenic Acid.—Caronna (*Gazzetta*, **1941**, **71**, 475; *Chem. Abs.*, 1943, **37**, 118) reports that diphenic acid is converted mainly into phenanthridone when treated with hydrazoic acid and concentrated sulphuric acid, very little 2 : 2′-diaminodiphenyl being obtained. When the reaction was carried out as follows, 2 : 2′-diaminodiphenyl was the main product. Diphenic acid (2·4 g., 0·01 mol.) in concentrated sulphuric acid (10 ml.), overlaid with chloroform (50 ml.), was treated with finely powdered sodium azide (6·5 g., 0·1 mol.) at such a rate that the temperature was maintained at 30—40° (20—25 minutes). After heating for another hour at 30—40°, the mixture was poured on crushed ice, the chloroform evaporated, and the insoluble phenanthridone (0·28 g., m. p. 287—288°) [lit., m. p. 293° (corr.)] collected. The acid filtrate was made alkaline with sodium hydroxide, 2 : 2′-diaminodiphenyl (1·4 g., m. p. 80—81·5°) (lit., m. p. 81°) being obtained. The chloroform may be omitted in the above experiment, and a larger volume of sulphuric acid employed.

Action of Hydrazoic Acid and Concentrated Sulphuric Acid on (I).—The yields of the required products were always poor. To avoid complete resinification of the quinone or products, it was necessary to maintain the temperature at 0—10° and avoid a large excess of sodium azide and prolonged contact with the concentrated sulphuric acid. In some of the experiments, the proportion of sulphuric acid was somewhat decreased and the mixture overlaid with pure chloroform, but this is probably no improvement. In a typical experiment, the quinone (1·03 g.) and concentrated sulphuric acid (25—30 ml.) were mixed and cooled to 0—5° in an ice-bath. Sodium azide (0·585 g.) in distilled water (3 ml.) was added dropwise so that the temperature was maintained at 0—10° (*ca.* 1 hour). After 2 hours, the original deep blue colour of the solution had faded to deep purple, and after 3—3½ hours gas evolution had practically ceased. Without delay the mixture was poured on crushed ice and the acid partly neutralised with sodium hydroxide solution. The discoloured precipitate was collected (by centrifuging) and shaken with sodium carbonate solution, in which it was partly soluble. The carbonate-insoluble fraction was dried and submitted to sublimation under reduced pressure, a yellowish sublimate being collected at 280—310° (bath temperature)/0·6 mm., and a dark, charred residue remaining in the tube. Yields varied from 70 to 200 mg. To remove yellow impurities, the sublimate was digested with warm benzene, cooled, filtered, and washed with benzene until the washings were colourless. (There was insufficient of these benzene-soluble yellow by-products to allow of their complete purification.) The benzene-insoluble material was crystallised from *n*-butanol, with filtration hot from a small amount of a sparingly soluble by-product (this by-product could be crystallised from acetic acid and had m. p. > 350° but was not in sufficient quantity to be obtained analytically pure). After repeated crystallisations from *n*-butanol, the benzene-insoluble *compound* formed cream-coloured needles or plates, m. p. 327—330° (Found: C, 85·3; H, 4·3; N, 4·8. $C_{21}H_{13}ON$ requires C, 85·4; H, 4·4; N, 4·7%). This substance is insoluble in hot or cold 2N-sodium hydroxide and in dilute hydrochloric acid. From its analysis and method of formation it should be (II) or (III). The pale brown sodium carbonate extract (see above) on acidification gave a discoloured gelatinous precipitate which was collected (by centrifuging) and dried (550 mg.). This product could not be purified directly and is probably a mixture of the acids (VI; R = OH, R′ = NH_2 and *vice versa*) since on being heated with aqueous sodium hydroxide it was converted (in yields of 85—90%) into 2-o-*carboxyphenylphenanthrene*-3-*carboxylic acid* (VI; R = R′ = OH) which, crystallised from acetic acid (charcoal, Supercel), gave a pale yellow crystalline powder, m. p. 311—313° (decomp.; gas evolution), identical with the acid obtained by hydrolysis of the imide (VII) (see below) (Found: C, 77·1; H, 4·2. $C_{22}H_{14}O_4$ requires C, 77·2; H, 4·1%). The crude product from the carbonate extract was also submitted to sublimation *in vacuo*; much decomposition took place [at 200—250° (bath temperature)/0·6 mm.]. A dark charred residue remained in the tube, and a crystalline sublimate with a bright yellow encrustation collected. To remove the yellow impurities, the sublimate was treated with benzene as described for the phenanthridone. 400 Mg. of crude mixed acids gave 210—230 mg. of sublimate after benzene treatment.*

The sublimate insoluble in benzene was crystallised repeatedly from *n*-butanol. The resulting *imide* (VII) formed faint cream-coloured prisms, m. p. 239—240° (Found: C, 81·8, 82·0; H, 4·0, 4·4; N, 4·55. $C_{22}H_{13}O_2N$ requires C, 81·7; H, 4·05; N, 4·3%). This substance is insoluble in sodium carbonate solution but soluble in 2N-sodium hydroxide and reprecipitated by acids (provided that the solution is not heated). It is moderately soluble in *n*-butanol, less soluble in ethanol, and sparingly soluble in benzene. When boiled with sodium hydroxide solution, it gave the acid (VI; R = R′ = OH) (identified by m. p. and mixed m. p.). (This hydrolysis was first carried out by Mr. J. M. L. Cameron.)

* The yellow benzene extract from this sublimate was chromatographed on alumina, several bands separating. One bright yellow band gave an eluate which yielded a bright yellow crystalline product which accounted for the bulk of the original material. After several crystallisations from benzene–alcohol (3 : 2), it gave bright yellow needles, m. p. 280·5—282·5° (Found: C, 86·6; H, 3·4; N, 5·9%). There was insufficient material to allow its final identification. This substance was not attacked by 2N-sodium hydroxide or by dilute hydrochloric acid.

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