690. *The Electrophilic Reactivity of Some Polycyclic Ketones. Part III.*[1] *Dibenz*[a,kl]*anthrone.*

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Bromination of dibenz[*a*,*kl*]anthrone (I) under different conditions gives variously a mono-, di-, or tri-bromo-derivative.

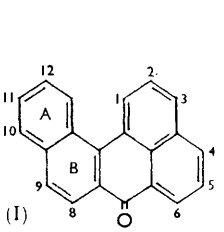
With the nucleophilic reagents potassium hydroxide, sodamide, sodium anilide, and sodium piperidide, but not sodium morpholide, the ketone (I) undergoes self-condensation with formation of quinones. Except in the case of sodium anilide which gives dinaphtho[1,2-*a*:1,2-*l*]peropyrene-11,22-quinone (II), the quinone is mainly dinaphtho[1,2-*a*:2,1-*m*]peropyrene-7,12-quinone (III). In all cases the ketone (I) is also attacked by the reacting anion mainly at the 4-position, except with sodamide which leads to 6-substitution.

Confirmation of the structures of the above quinones is provided by spectroscopic comparison with those obtained by the reaction with alkali of the mono- and tri-bromo-derivatives of the anthrone (I) which gave a dihydroxy-derivative of the quinone (III) and a tetrahydroxy-derivative of the quinone (II), respectively.

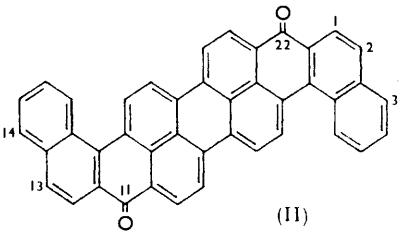
BRADLEY and SUTCLIFFE [1b] briefly investigating the reaction of dibenz[*a*,*kl*]anthrone (10,11-benzomesobenzanthrone) (I) with alcoholic potassium hydroxide at 110° obtained

[1] Parts I and II are to be regarded, respectively, as Bradley and Sutcliffe, *J.*, (*a*) 1951, 2118; (*b*) 1952, 1247.

a dark blue quinone which they assumed to be diphenanthro[2,3,4-*cd*:2′,3′,4′-*lm*]perylene-11,22-quinone (1,2:10,11-dibenzoisoviolanthrone) (II). The assumption was made by analogy with the conversion of benz[*de*]anthrone by alkali into mixtures of violanthrone ("*cis*"-form) and isoviolanthrone ("*trans*"-form) in which the proportion of the latter is higher at lower reaction temperatures.[2]



(I)



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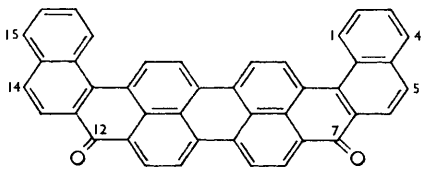


(III)

The present work shows this assumption to be wrong and that the dark blue quinone from (I) is mainly the "*cis*"-form, dinaphtho[1,2-*a*:2,1-*m*]peropyrene-7,12-quinone (III) accompanied by somewhat less of the "*trans*"-form (II).

This conclusion has been reached by comparing the visible absorption spectra (in "AnalaR" sulphuric acid solution) of compounds (II) and (III) with those of products obtained by the action of sundry nucleophilic reagents on the ketone (I) and some of its bromo-derivatives.

Dibenz[*a*,*kl*]anthrone was found to give a bromo-derivative with bromine in boiling acetic acid. Further attack did not occur in that solvent but with two equivalents of the halogen in boiling nitrobenzene a dibromo-derivative was formed. When the original ketone was treated with a large excess of neat bromine it gave a dark brown material which was converted into a tribromo-derivative of the dibenzanthrone (I) by the action of acetic acid.

The complete orientation of these three bromo-compounds was not determined and was not, in fact, required for subsequent argument. It was sufficient to know that the second bromine atom entered position 3 in (I) while the other two did not enter position 1, 2, 3, or 4. This was shown by subjecting the bromo-compounds to oxidative degradation and to the action of alkali.

The mono- and di-bromo-derivatives with chromic acid in acetic acid each gave the same acid whose composition and general behaviour proclaimed it to be a bromobenz[*a*]-anthraquinonecarboxylic acid. Similarly the tribromo-derivative afforded a dibromo-benz[*a*]anthraquinonecarboxylic acid. It would thus seem that, unlike benz[*de*]anthrone,[3] the first attack by bromine in compound (I) is other than at position 3.

With ethanolic potassium hydroxide at 110° the bromo-derivative behaved like its parent, (I),[1b] in giving a dark blue quinonoid substance. This appeared to be a mixture of dihydroxy-derivatives of the quinones (II) and (III) since by continued extraction with hot nitrobenzene there was first extracted material possessing strong light absorption (in sulphuric acid) at 675 mμ while the less readily extracted material had also a pronounced absorption maximum at 730 mμ. In contrast with its behaviour towards potassium hydroxide in ethanol the bromo-compound did not react to any extent with the alkali in

[2] Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259.
[3] Maki and Kikuchi, *J. Soc. Chem. Ind. Japan, Suppl.*, 1939, **42**, 316B.

ethylene glycol but in the absence of solvent, at 240°, afforded a black, intractable solid which was almost insoluble in hot nitrobenzene or in alkaline sodium dithionite.

The tribromo-derivative of dibenz[*a*,*kl*]anthrone (I), on the other hand, with potassium hydroxide in hot ethylene glycol was readily converted into a tetrahydroxyquinone whose main light absorption was at 730 mμ with none at 675 mμ. By analogy with the easy formation of isoviolanthrone from 3-bromo[*de*]anthrone [2] this must be the "*trans*"-quinone and it would thus appear that an absorption maximum at about 730 mμ (in sulphuric acid) is associated with structure (II) and that the preponderating dihydroxy-derivative ($\lambda_{max.}$ 675 mμ) above is derived from structure (III).

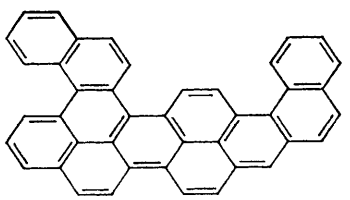
Repetition of the work of Bradley and Sutcliffe [1b] confirmed the production of a dark blue vat-dye but it was found possible to separate it roughly into two fractions by prolonged extraction first with benzene and then with nitrobenzene. The more soluble fraction was substantially pure "*cis*"-form (III) ($\lambda_{max.}$ 650 mμ). The "*trans*"-form (II) was present in the less soluble fraction ($\lambda_{max.}$ 650—660, 730 mμ) but was not obtained from it in a pure state.

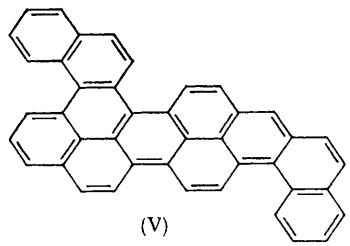
In addition to the quinones a trace of phenolic material was formed. This was obtained in increased yield, still accompanied by quinones, when the dibenzanthrone (I) was fused with potassium hydroxide and manganese dioxide at 240°. Its mode of formation and general properties and the fact that its alkaline solution had a strong green fluorescence [4] indicated that it was 4-hydroxydibenz[*a*,*kl*]anthrone, m. p. 302—303°. Bradley and Jadhav [5] found that a similar alkaline oxidation of benz[*de*]anthrone produced, in addition to the 4-hydroxy-derivative, a 6-hydroxy-derivative which, owing to the hydrogen-bonding between hydroxyl and carbonyl groups, was insoluble in alkali and of comparatively low melting point and formed a boroacetate with Dimroth's reagent. Chromatographic analysis on alumina of the benzene-soluble fraction in the present experiment yielded a small amount of highly adsorbed material which gave correct analyses for the 6-hydroxy-derivative of the starting ketone (I), and was insoluble in alkali, of comparatively low m. p. (200—201°), and identical with the product of hydrolysis of an amine later obtained by the action of sodamide on the ketone (I).

Also of interest was the isolation from the chromatogram of two weakly adsorbed, golden to brownish-yellow hydrocarbons, $C_{42}H_{22}$, m. p.s 332—334° and 344—346°. These were not the isomeric aromatic hydrocarbons corresponding to the quinones (II) and (III), which were prepared by the Clar reduction [6] of the tetrahydroxy-derivative of (II), and of (III), respectively, and which were both red and of considerably higher m. p.

The close resemblance between the absorption spectra of the two hydrocarbons and those of the two analogous ones obtained by Clar *et al.*[7] by the action of phosphoryl chloride

(IV)





(V)

on benz[*de*]anthrone suggests that they are one or the other of dinaphtho[1,2-*a*:1,2-*p*]-(IV) or dinaphtho[1,2-*a*:2,1-*i*]-peropyrene (V) although the presence of the two other possibly formed dinaphthoperopyrenes cannot be excluded.

[4] Bradley, *J.*, 1948, 1175.
[5] Bradley and Jadhav, *J.*, 1937, 1791.
[6] Clar, *Ber.*, 1939, **72**, 1645; 1943, **76**, 458.
[7] Clar, Fell, Ironside, and Balsillie, *Tetrahedron*, 1960, **10**, 26.

The formation of quinones by the action of ethanolic potassium hydroxide at 110° on the dibenzanthrone (I) is one example of its higher reactivity towards nucleophilic reagents than that of benz[*de*]anthrone which affords bi(benz[*de*]anthron-4-yl) under the same conditions.[2] Other examples are the production of quinones with sodamide and sodium anilide which give none with benz[*de*]anthrone.[2,4]

Bradley [4] studied the reaction of benz[*de*]anthrone with sodamide in dimethylaniline under oxygen and obtained a mixture of 6-amino- and 6-hydroxy-benz[*de*]anthrone and di(benz[*de*]anthron-6-yl)amine. No 4-substituted compound was obtained in substance. When dibenz[*a*,*kl*]anthrone (I) was heated with sodamide and dimethylaniline under nitrogen the main product was the "*cis*"-quinone (III) ($\lambda_{max.}$ 645 mμ). Under oxygen, in addition to this, there was formed a mixture of amines which was chromatographically separated into 6-amino- and 6-*N*-methylanilino-dibenz[*a*,*kl*]anthrone. The former was identified by its alkaline hydrolysis to the 6-hydroxy-derivative, previously obtained by the action of potassium hydroxide and manganese dioxide on ketone (I). The structure of the latter amine follows from its analysis and comparatively low m. p. (159—160°), compared with the subsequently prepared 4-anilino-derivative (m. p. 257—258°). Its formation must have involved reaction of the preformed sodium derivative of the 6-amino-compound with solvent, rather than prior interaction of sodamide and solvent, giving sodium *N*-methylanilide, followed by attack of this on ketone (I) because the latter mechanism would be expected to lead to 4-substitution as happens when sodium anilide [2] or sodium diphenylamide [8] react with benz[*de*]anthrone.

4-Aminodibenz[*a*,*kl*]anthrone was obtained by ammonolysis of the 4-hydroxy-derivative at 230° with a copper bronze catalyst. Without the catalyst no reaction took place although Perkin and Spencer [9] were able to obtain 4-aminobenz[*de*]anthrone from the 4-hydroxy-compound with ammonia alone in a sealed tube at 220°.

With sodium anilide in aniline under nitrogen Lüttringhaus and Neresheimer [2] found that benz[*de*]anthrone afforded the 4-anilino-derivative and bibenz[*de*]anthron-4-yl, but no quinone. Under similar conditions the dibenzanthrone (I) gave a small amount of quinone ($\lambda_{max.}$ 733 mμ) which, though not obtained analytically pure, must have been mainly the "*trans*"-form (II) free from the previously preponderant "*cis*"-form (III) since the 650—675 mμ peak is absent. The main products of the reaction were, however, 4-anilinodibenz[*a*,*kl*]anthrone and bi(dibenz[*a*,*kl*]anthron-4-yl). The former suffered alkaline hydrolysis to the previously obtained 4-hydroxy-compound, while the latter with hot ethanolic potassium hydroxide afforded the expected "*cis*"-quinone (III) ($\lambda_{max.}$ 675 mμ). The reaction also produced, in small yield, a compound which, from its analysis and comparatively low m. p. (193—194°), was the 6-anilino-derivative of the ketone (I).

Sodamide–piperidine (sodium piperidide) [10,11] and sodamide–morpholine (sodium morpholide) [11] have been shown to possess some activity as nucleophilic reagents, although to a smaller degree than those used above.

With the former reagent, our compound (I) gave mainly 4-piperidinodibenz[*a*,*kl*]-anthrone, which underwent alkaline hydrolysis to the 4-hydroxy-derivative. A secondary product was an amorphous reddish-brown material which could not be obtained pure but had a considerably higher nitrogen content than had the piperidino-derivative; it may have been a piperidine–(I) adduct of the type encountered by Bradley [10] when working with piperidine and benz[*de*]anthrone. Only a trace of quinonoid material was obtained and its absorption spectrum ($\lambda_{max.}$ 670 mμ) indicated that it was mainly the "*cis*"-quinone (III).

4-Substitution again was the main effect on the dibenzanthrone (I) of the sodamide–morpholine reagent, and the resulting 4-morpholinodibenz[*a*,*kl*]anthrone was hydrolysed

[8] Bradley and Sutcliffe, *J.*, 1954, 708.
[9] Perkin and Spencer, *J.*, 1922, 479.
[10] Bradley, *J.*, 1937, 1091.
[11] Bradley and Bruce, *J.*, 1954, 1894.

by alkali to the 4-hydroxy-derivative. There was no evidence of quinone formation, but a small amount of a compound was isolated whose analysis and absorption spectrum proclaimed it to be an isomeric morpholino-derivative. Despite the fact that its m. p. is about 30° higher, it is considered to be the 6-morpholino-derivative because the m. p.-lowering due to hydrogen-bonding no longer applies and generalisations on this basis cannot be made here.

Experimental

Absorption spectra were measured in a Unicam S.P. 500 spectrophotometer for " AnalaR " sulphuric acid solutions unless otherwise specified. Where no m. p. is recorded for a new compound the compound did not melt below 450°. Chromatography was carried out on a chromatographic grade of aluminium oxide from B.D.H. or May and Baker.

Dibenz[a,kl]*anthrone*.—The procedure described by Bradley and Sutcliffe [1b] was improved as follows: 1,1′-Binaphthyl-8,8′-dicarboxylic acid (1 kg.; technical grade) in 10% sodium hydroxide solution (2340 c.c.) was stirred overnight. The sodium salt was filtered off, washed with brine, and redissolved in boiling water, the solution was acidified with concentrated hydrochloric acid, and the precipitated acid (221 g.), m. p. 308—310°, was washed with water and dried at 110°. It (100 g.) was triturated with 48% v/v sulphuric acid (480 g.), the mixture was cooled in ice, and concentrated sulphuric acid (1800—2000 g.) was added until a test portion, when added to dilute alkali, showed that insoluble anthanthrone was beginning to be formed. The addition was effected at 25—30° and, on completion, the solution was poured on ice (10 kg.), and the golden-yellow solid was collected and washed with water. It was dissolved in 10% sodium hydroxide solution, anthanthrone was removed by filtration, the clear solution was acidified with concentrated hydrochloric acid, and the precipitated dibenz-[*a,kl*]anthrone-13-carboxylic acid was filtered off, washed with water, and dried at 110°. All this acid (85 g.) was stirred under reflux with copper bronze (8·5 g.) in freshly distilled quinoline (600 c.c.) for 22 hr., then cooled, and added to an excess of 10% hydrochloric acid. This mixture was stirred for 2 hr. and the brown solid was filtered off, washed with dilute hydrochloric acid and then water, and then digested and washed with 5% sodium carbonate solution until free from acid. The solid (75 g.) was washed with water, dried at 110°, and stirred with 80% sulphuric acid (1 l.); a little 1,1′-binaphthyl remained insoluble and was filtered off. The filtrate was added to ice (5 kg.), and the precipitate was filtered off, washed with dilute ammonia, and dried. This solid was sublimed at 180°/0·001 mm. and the sublimate recrystallised from toluene, to give the anthrone, pure enough for further use, m. p. 189—190° (lit.,[1b] m. p. 181—182°). In " AnalaR " sulphuric acid it was deep red, with $\lambda_{max.}$ 328, 373, 440, 535 mμ (log ε 4·29, 3·83, 4·32, 3·68), and in 95% ethanol, yellow, with $\lambda_{max.}$ 265, 298, 339, 429 mμ (log ε 4·27, 4·34, 4·03, 3·83).

Bromodibenz[a,kl]*anthrone*.—Bromine (3·84 g.) in glacial acetic acid (15 c.c.) was added slowly to a warm solution of the anthrone (6 g.) in the same solvent (210 c.c.). A brown precipitate was formed which became yellow and evolved hydrogen bromide during the subsequent 5 hours' heating under reflux. After the mixture had been cooled, the solid (5·5 g.) was filtered off and recrystallised from toluene and then glacial acetic acid, affording the *bromo-derivative* as golden-yellow platelets, m. p. 237—238°, $\lambda_{max.}$ (red) 375, 455, 560 mμ (log ε 4·03, 4·52, 3·63) (Found: C, 69·8; H, 2·9; Br, 22·4. $C_{21}H_{11}BrO$ requires C, 70·2; H, 3·05; Br, 22·3%).

Dibromodibenz[a,kl]*anthrone*.—To a solution of the above bromo-compound (1 g.) in hot nitrobenzene (35 c.c.) was added bromine (0·54 g.) in nitrobenzene (5 c.c.) and the mixture was refluxed for 1 hr. Benzene was added to the cooled solution, and the brown solid (0·6 g.) was filtered off, washed with benzene and then ethanol; it then became yellow; it had m. p. 232—270°. Several recrystallisations from glacial acetic acid yielded the *dibromo-compound*, m. p. 325—326°, $\lambda_{max.}$ (olive-green) 380, 468, 590 mμ (log ε 4·13, 4·295, 3·68) (Found: C, 58·3; H, 2·35; Br, 36·3. $C_{21}H_{10}Br_2O$ requires C, 57·5; H, 2·3; Br, 36·5%).

In a similar experiment, where the nitrobenzene was replaced with glacial acetic acid, the monobromo-compound was not affected.

Bromobenz[a]*anthraquinone-11-carboxylic Acid*.—(*a*) Bromodibenz[*a,kl*]anthrone (0·36 g.), chromic oxide (1·2 g.), and 80% acetic acid (25 c.c.) were refluxed together for 1 hr., the green mixture was added to water, and the yellow precipitate (0·17 g.) was filtered off. When recrystallised from glacial acetic acid it afforded the yellow, microcrystalline *acid*, m. p. 298—300° (decomp.) (Found: C, 59·8; H, 2·35; Br, 21·6. $C_{19}H_9BrO_4$ requires C, 59·8; H, 2·35;

Br, 21·0%). In hot dilute sodium carbonate solution it was yellow, and the yellow sodium salt separated on cooling. With alkaline sodium dithionite solution it formed a red vat.

(*b*) The dibromodibenzanthrone (0·06 g.) was refluxed with chromic oxide (0·3 g.) in 80% acetic acid (10 c.c.) for 4 hr., during which bromine was evolved. The mixture was added to water, and the precipitate (0·02 g.) was washed, dried, and then recrystallised from glacial acetic acid, giving the same acid, m. p. and mixed m. p. 298° (decomp.), as that obtained in (*a*).

Tribromodibenz[a,kl]*anthrone*.—Bromine (27 c.c.) was slowly added to the dibenzanthrone (4·5 g.) so that the temperature of the mixture was kept below 30° with the aid of water cooling. The mixture was left overnight at room-temperature, then diluted with glacial acetic acid, and the dark brown solid was filtered off and washed with acetic acid until free from bromine. When boiled with water it became yellow and after being recrystallised from nitrobenzene afforded the *tribromo-derivative* as golden-yellow needles, m. p. 302—304°, $\lambda_{max.}$ (green) 390, 462, 600 mμ (log ε 4·25, 4·53, 3·79) (Found: C, 48·6; H, 1·65; Br, 46·5. $C_{21}H_9Br_3O$ requires C, 48·7; H, 1·75; Br, 46·4%).

Dibromobenz[a]*anthraquinone*-11-*carboxylic Acid*.—The above tribromo-derivative (0·599 g.) and chromic oxide (2·4 g.) in 80% acetic acid (60 c.c.) were refluxed for 4 hr., during which bromine vapour was evolved. After dilution of the mixture with water, the resulting greenish-yellow precipitate was collected and recrystallised from glacial acetic acid, giving the *acid* as golden-yellow needles, m. p. 292° (decomp.) (Found: C, 49·3; H, 2·0; Br, 34·8. $C_{19}H_8Br_2O_4$ requires C, 49·6; H, 1·75; Br, 34·8%).

Reaction of Bromodibenz[a,kl]*anthrone with Alkali*.—(*a*) The bromo-compound (0·5 g.) was heated under reflux with a solution of potassium hydroxide (5 g.) and potassium acetate (0·5 g.) in 95% ethanol (10 c.c.) for 2½ hr., the internal temperature being 110—120°. The resulting dark blue mixture was poured into water which was then aerated, and the black solid (0·45 g.) was filtered off, washed with dilute alkali and with water, and dried at 110°. It was extracted (Soxhlet) first with benzene, removing a little starting material, and then with nitrobenzene until the percolate had changed from blue-black to a clear blue. The process was continued with fresh solvent until the percolate was almost colourless.

The first nitrobenzene extract was concentrated and, on cooling, afforded *dihydroxydinaphtho*[1,2-*a*:2,1-*m*]*peropyrene*-7,12-*quinone* (0·1 g.) as microscopic black needles, $\lambda_{max.}$ (deep, slightly bluish green) 410, 675 mμ (log ε 4·27, 4·62) (Found: C, 85·9; H, 3·4. $C_{42}H_{20}O_4$ requires C, 85·7; H, 3·4%).

The second nitrobenzene extract, similarly treated, gave a black, microcrystalline solid (0·05 g.), $\lambda_{max.}$ (bluish-green) 410, 650, 730 mμ (log ε 4·29, 4·52, 4·55).

(*b*) The bromo-compound (0·75 g.) was refluxed for 3 hr. with a solution of potassium hydroxide (5 g.) and potassium acetate (0·5 g.) in ethylene glycol (25 c.c.), the cooled solution was added to water, and the precipitate collected. When this was extracted with alkaline sodium dithionite solution containing a little pyridine the extract was green with a red fluorescence but only a trace of black solid was deposited on aeration. The residue from the extraction constituted almost the whole of the starting material.

(*c*) The bromo-compound (1 g.) was added in portions during several minutes to a melt of potassium hydroxide (5 g.) and potassium acetate (0·5 g.) in a nickel crucible at 250°. The thick greyish-brown paste was stirred for 15 min., then added to water (100 c.c.), and the mixture was aerated and filtered. The residual black solid was virtually insoluble in boiling nitrobenzene or in pyridinised dithionite solution.

Tetrahydroxydinaphtho[1,2-*a*:1,2-*l*]*peropyrene*-11,22-*quinone*.—The tribromoanthrone (1 g.) was refluxed for 7 hr. with a solution of potassium hydroxide (20 g.) and potassium acetate (2 g.) in ethylene glycol (100 c.c.). the dark blue mixture was cooled, then added to water, and the suspension was aerated. The black solid (0·6 g.) was collected and extracted (Soxhlet) with benzene and then with nitrobenzene. On cooling, the latter extract deposited microscopic black needles of the *compound*, $\lambda_{max.}$ (slightly bluish-green) 320, 405, 730 mμ (log ε 4·63, 4·38, 4·84) (Found: C, 81·9; H, 3·35. $C_{42}H_{20}O_6$ requires C, 81·3; H, 3·25%).

Dinaphtho[1,2-*a*:2,1-*m*]*peropyrene*-7,12-*quinone*.—Dibenz[*a*,*kl*]anthrone (2 g.) was stirred under reflux for 2½ hr. with a solution of potassium hydroxide (25 g.) and potassium acetate (2·5 g.) in 95% ethanol (50 c.c.), the dark blue reaction mixture was added to water (250 c.c.), the mixture was aerated, and the black solid was filtered off, washed with dilute alkali and water, and dried at 110°. The combined filtrate and washings were yellow with a green fluorescence but yielded only a trace of brown solid when acidified. The black solid (2 g.) was

extracted with benzene (Soxhlet) until the percolate was colourless, and then similarly with nitrobenzene. The benzene extract, when cooled and filtered, yielded a bluish-black solid (0·3 g.) which recrystallised from nitrobenzene, giving the *quinone* as microscopic black needles, $\lambda_{max.}$ (bluish-green) 365, 650 mμ (log ε 4·40, 4·53) (Found: C, 89·6; H, 3·75. $C_{42}H_{20}O_2$ requires C, 90·7; H, 3·6%).

The nitrobenzene extract, when cooled, gave a bluish-black solid (0·4 g.), $\lambda_{max.}$ (bluish-green) 370, 650, 730 mμ (log ε 4·47, 4·55, 4·27) (Found: C, 88·0; H, 3·7. $C_{42}H_{30}O$ requires C, 90·7; H, 3·6%). Both solids were blue with a red fluorescence in alkaline sodium dithionite solution containing a little pyridine.

Reaction of Dibenz[a,kl]*anthrone with Potassium Hydroxide and Manganese Dioxide.*—An intimate mixture of the anthrone (20 g.) with manganese dioxide (20 g.; precipitated) was added during 10 min. to a melt of potassium hydroxide (200 g.) and potassium acetate (20 g.) at 210° in a nickel crucible. The temperature was raised to 240° and maintained for 1 hr., the pasty mixture being stirred meanwhile. After being cooled, the melt was digested with hot water (aeration) and filtered, and the insoluble material was washed with 1% potassium hydroxide solution until the washings were colourless, leaving a black residue (A). The combined extract and washings were reddish-brown with a slight green fluorescence and when acidified with hydrochloric acid gave a yellowish-brown precipitate (7 g.). This sublimed at 300—320°/0·001 mm. and the sublimate crystallised from 1,2,4-trichlorobenzene to yield 4-*hydroxydibenz*[a,kl]-*anthrone* as yellow crystals of indefinite form, m. p. 302—303° (Found: C, 84·7; H, 4·1. $C_{21}H_{12}O_2$ requires C, 85·2; H, 4·05%). Its solutions were coloured: red in sulphuric acid, $\lambda_{max.}$ (335), 460 mμ (log ε 3·99, 4·46); yellow in 95% ethanol, $\lambda_{max.}$ 270, 430 mμ (log ε 4,52, 4·00); yellow in 0·1N-sodium hydroxide, $\lambda_{max.}$ 280, 465, 495 mμ (log ε 4·57, 4·29, 4·40); and yellow in pyridine, changing to orange-red with a vivid fluorescence on addition of a drop of 25% methanolic potassium hydroxide. Its *acetyl derivative* crystallised from 95% ethanol as silky yellow needles, m. p. 220—222°, $\lambda_{max.}$ (yellow) 340, 455 mμ (log ε 4·06, 4·50) (Found: C, 81·5; H, 4·0. $C_{23}H_{14}O_3$ requires C, 81·6; H, 4·1%).

The residue (A) was extracted with benzene in a Soxhlet apparatus until the percolate had changed from a fluorescent yellow to blue, the residue (B) was kept, and the extract was run through a column of alumina (5·4 × 30 cm.). The resulting chromatogram was developed with benzene until four main bands were apparent, which, in increasing intensity of adsorption, were (*a*) greenish-yellow, (*b*) golden-yellow, (*c*) brown, and (*d*) black. Bands (*a*) and (*b*) were washed out of the column during the benzene development; the other two were mechanically separated and eluted with ethanol. The four solutions were severally evaporated, yielding the four corresponding solids:

(*a*) (0·2 g.) Golden-yellow, m. p. 340—360° (decomp.). Recrystallisation from toluene afforded a *substance* as golden-yellow needles, m. p. 344—346° (Found: C, 95·2; H, 4·15. $C_{42}H_{22}$ requires C, 95·8; H, 4·2%). It was insoluble in cold concentrated sulphuric acid although the surface of the solid darkened; in benzene it was yellow with a green fluorescence, $\lambda_{max.}$ 350, (365), 450, 465, 478 mμ (log ε 4·54, 4·47, 4·59, 4·57, 4·74).

(*b*) (0·08 g.) Brownish-red, m. p. 310—330° (decomp.). When recrystallised from toluene it gave a *substance* as orange needles, m. p. 332—334° (decomp.) (Found: C, 95·7; H, 4·15. $C_{42}H_{22}$ requires C, 95·8; H, 4·2%). In sulphuric acid and benzene it behaved like the previous compound; it had $\lambda_{max.}$ 315, 330, 362, 380, (410), 463, 495 mμ (log ε 4·74, 4·83, 4·56, 4·73) 4·28, 4·73, 4·95).

(*c*) (0·9 g.) Starting material.

(*d*) (0·5 g.) Black. Sublimation at 160—180°/0·005 mm. gave an orange-yellow solid (0·1 g.), m. p. 196—198° which, after being crystallised from 95% ethanol, formed silky, golden-yellow needles of 6-*hydroxydibenz*[a,kl]*anthrone*, m. p. 200—201°, $\lambda_{max.}$ (yellow) 315, 420, 495 mμ (log ε 4·40, 4·37, 3·75) (Found: C, 85·1; H, 4·15. $C_{21}H_{12}O_2$ requires C, 85·1; H, 4·05%).

The residue (B) (8·4 g.) was freed from manganese dioxide by the action of sulphur dioxide and dilute hydrochloric acid. It was partly soluble in warm alkaline sodium dithionite solution with a deep magenta colour; and in boiling nitrobenzene, from which solution, on being cooled, was deposited a black solid, $\lambda_{max.}$ (bluish-green) 653, 730 mμ (log ε 4·47, 4·33).

Dinaphtho[1,2-*a*:1,2-*l*]*peropyrene.*—An intimate mixture of tetrahydroxydinaphthoperopyrenequinone (0·5 g.), sodium chloride (1 g.), zinc dust (1 g.), and fused zinc chloride (5 g.) was heated to 290° during 5 min. and the melt was stirred at this temperature for a further 25 min. After being cooled, the mixture was digested with 10% hydrochloric acid, and the

brown, insoluble matter (0·3 g.) was filtered off, washed with water, and dried at 110°. It was subjected to two different treatments: (*a*) The material was sublimed at 450°/0·001 mm. and the red sublimate crystallised from 1,2,4-trichlorobenzene, giving the *dinaphthoperopyrene* as small, dark red needles, m. p. 440—444° (Found: C, 95·7; H, 4·1. $C_{42}H_{22}$ requires C, 95·8; H, 4·2%). In pyridine, it was yellow with a green fluorescence, $\lambda_{max.}$ 320, 337, 366, 384, (412), 450, 455, 486, 520 mμ (log ε 4·75, 4·87, 4·71, 4·98, 3·76, 4·32, 4·31, 4·79, 5·07). (*b*) The material (0·2 g.) was extracted with benzene (200 c.c.), the extract was run through a column of alumina (5·4 × 30 cm.), and the chromatogram was developed with benzene. A prominent yellow band separated and passed out of the column, giving a yellow solution with a strong green fluorescence. The solid obtained by evaporation of this solution recrystallised from toluene, affording orange crystals, m. p. 328—330° (decomp.), not depressed on admixture with the substance, m. p. 332—334° (decomp.), previously described.

Dinaphtho[1,2-*a*:2,1-*m*]*peropyrene*.—The dinaphthoperopyrene-7,12-quinone (1 g.), sodium chloride (2 g.), zinc dust (2 g.), and zinc chloride (12 g.) were treated in the manner described above. Sublimation of the crude product followed by recrystallisation of the sublimate from xylene gave the *hydrocarbon* as small red needles, m. p. 374—376° (Found: C, 95·4; H, 4·5. $C_{42}H_{22}$ requires C, 95·8; H, 4·2%). In pyridine, it was yellow with a green fluorescence, having $\lambda_{max.}$ 328, 344, 367, 388, 418, 444, 475, 509 mμ (log ε 4·82, 4·94, 4·46, 4·49, 3·94, 4·42, 4·88, 5·13).

Reaction of Dibenz[a,kl]*anthrone with Sodamide*.—(*a*) *Under nitrogen.* Sodamide (1·5 g.) was finely ground under *NN*-dimethylaniline (15 c.c.; free from *N*-methylaniline [12]) and the suspension was added to a mixture of the anthrone (4 g.) with dimethylaniline (20 c.c.). This was heated, with stirring, to about 120°; an exothermic reaction then set in and the temperature was kept at this level by the judicious use of external heat until the main reaction was over, after which it was kept at 140° for 1 hr. The cooled, dark green mixture was added to water (300 c.c.), aerated for 2 hr. at 70—90°, and filtered, giving a two-phase filtrate and a black residue. Neither layer of the filtrate, deeply coloured though they were, yielded an identifiable material.

The black residue was freed from starting material by extraction with benzene, leaving impure *dinaphtho*[1,2-*a*:2,1-*m*]*peropyrene*-7,12-*quinone*, $\lambda_{max.}$ (bluish-green) 420, 645 mμ (log ε 4·32, 4·52).

(*b*) *Under oxygen.* Under similar conditions to those described, but with oxygen in place of nitrogen, the anthrone (17 g.), sodamide (5 g.), and dimethylaniline (170 c.c.), after being heated for 3 hr. at 140°, gave a dark brown mixture which was deprived of solvent by distillation in steam. The residual amorphous black solid was powdered, washed with hot 1% sodium hydroxide solution and water, and dried. The combined alkaline liquor was brown with a slight green fluorescence but no definite compound could be isolated from the solid which was precipitated on acidification.

The black solid (17·4 g.) was extracted with benzene (Soxhlet), giving a dark brown extract and a residue (A). The extract was run through a column of alumina (5·4 × 30 cm.), and the resulting chromatogram was developed with benzene. A strong reddish-brown band containing starting material (6·6 g.) passed out of the column which was then drained and the lower, crimson, and the upper, orange, band were mechanically separated and eluted with ethanol, and the eluates were freed from solvent.

From the lower band there was thus obtained a dark resin (0·4 g.) which, after having been triturated with ether and recrystallised from 95% ethanol, afforded 6-N-*methylanilinodibenz*-[a,kl]*anthrone* as greenish-yellow plates, m. p. 159—160° (decomp.), $\lambda_{max.}$ (olive-green) 315, 384, 460, 600 mμ (log ε 4·21, 4·14, 4·40, 3·49) (Found: C, 87·3; H, 4·75; N, 3·65%).

The solid (0·5 g.) from the upper band, after having sublimed at 160—180°/0·001 mm. and recrystallised from toluene, formed golden-yellow needles of 6-*aminodibenz*[a,kl]*anthrone*, m. p. 219—221°, $\lambda_{max.}$ (yellowish-green) 320, 340, 478, 610 mμ (log ε 4·18, 4·15, 4·22, 3·51) (Found: C, 85·4; H, 4·45; N, 4·75. $C_{21}H_{13}NO$ requires C, 85·4; H, 4·4; N, 4·75%). It was greenish-yellow in pyridine, changing to golden-yellow after addition of a drop of 25% methanolic potassium hydroxide.

The black residue (A) (2·4 g.) was impure dinaphtho[1,2-*a*:2,1-*m*]peropyrene-7,12-quinone, $\lambda_{max.}$ (green) 420, 648 mμ (log ε 4·32, 4·39), blue with a red fluorescence in alkaline sodium dithionite solution containing a little pyridine.

[12] Vogel, " A Text Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 550.

6-*Hydroxydibenz*[a,kl]*anthrone by Hydrolysis of the* 6-*Amino-compound.*—The amino-compound (0·2 g.) and potassium hydroxide (2·5 g.) in isopentyl alcohol (50 c.c.) were stirred under reflux for 1½ hr. The alcohol was removed in steam, and the residual solid recrystallised from 95% ethanol, to give golden-yellow needles of the 6-hydroxy-derivative, m. p. 198—199° (not depressed on admixture with the 6-hydroxy-derivative, m. p. 200—201°, obtained as above).

4-*Aminodibenz*[a,kl]*anthrone from the* 4-*Hydroxy-compound.*—The 4-hydroxy-compound (0·15 g.), copper bronze (0·015 g.), and ammonia (70 c.c.; *d* 0·88) were heated in an autoclave for 15 hr. at 230°. The reddish-brown solid (0·05 g.) thus produced was washed with 2% sodium hydroxide solution and water, and recrystallised from 95% ethanol (charcoal), to give the *amine* as brownish-red rosettes, m. p. 244—245° (Found: N, 5·05. $C_{21}H_{13}NO$ requires N, 4·75%).

If copper bronze was omitted from this experiment no reaction occurred.

Reaction of Dibenz[a,kl]*anthrone with Sodium Anilide.*—The anthrone (7·5 g.) in aniline (50 c.c.) was added at room temperature to a solution of sodium anilide in aniline [prepared [2] from sodium (2·5 g.), nickel oxide (0·01 g.), copper bronze (0·01 g.), and freshly distilled aniline (50 c.c.), under nitrogen]. No temperature rise was noticed and, after having been stirred for 2 hr., the reddish-violet mixture was added to water (200 c.c.). The mixture was aerated and then made acid to Congo Red by addition of hydrochloric acid, and the dark brown solid (8·4 g.) was filtered off, washed with water, and dried at 110°. It was extracted with portions of acetone (11 × 100 c.c.) at room temperature, leaving a reddish-brown solid (A) (3·4 g.). The first three extracts were combined (B), as were the last eight (C), and the solvent was removed from the two combinations on the steam-bath.

The dark brown solid (2·3 g.) from (B) was run in toluene, through a column of alumina (1·4 × 40 cm.), and the chromatogram was developed with toluene. A yellow band was washed out of the column, and the solution, after being evaporated, left an orange-yellow solid (0·4 g.) which recrystallised from 95% ethanol, giving 6-*anilinodibenz*[a,kl]*anthrone* as orange needles, m. p. 193—194°, $\lambda_{max.}$ (green, becoming orange in 10 min.) 380, 465 mμ (log ε 4·02, 4·42) (Found: C, 87·3; H, 4·55; N, 4·0. $C_{27}H_{17}NO$ requires C, 87·3; H, 4·6; N, 3·75%). In pyridine it was yellow, changing wine-red on addition of one drop of 25% methanolic potassium hydroxide. The material remaining adsorbed on the column was removed by elution with hot toluene and proved to be starting material.

The brown solid (2 g.) from (C) sublimed at 0·001 mm. At 160—180°, starting material (0·5 g.) passed over, and at 200—220° a red sublimate (0·6 g.) was formed. The latter recrystallised from toluene, affording 4-*anilinodibenz*[a,kl]*anthrone* as elongated, red plates, m. p. 257—258°, $\lambda_{max.}$ (green, changing within 10 min. to reddish-brown, and then during several hr. to brownish-violet) 508, 635 mμ (log ε 4·66, 3·47) (Found: C, 87·2; H, 4·55; N, 3·5. $C_{27}H_{17}NO$ requires C, 87·3; H, 4·6; N, 3·75%). In pyridine it was yellowish-orange, changing to royal blue on addition of a drop of 25% methanolic potassium hydroxide.

A further quantity (0·9 g.) of the 4-anilino-compound was obtained by extracting the residue (A) with ethanol in a Soxhlet apparatus; continued extraction with *o*-dichlorobenzene then produced a green solution which was cooled and run through a column of alumina (1·4 × 4·0 cm.). When the chromatogram was developed with *o*-dichlorobenzene containing 1% of ethanol the main orange-red band was rapidly washed out; the yellow eluate was concentrated under reduced pressure and the crystallising solid (0·6 g.) was collected. It was recrystallised thrice from chlorobenzene, yielding *bi*(*dibenz*[a,kl]*anthron*-4-*yl*) as stout yellow needles, m. p. 349—350°, $\lambda_{max.}$ (yellowish-brown) 338, 380, 480 mμ (log ε 4·36, 4·42, 4·76) (Found: C, 90·0; H, 3·95. $C_{42}H_{22}O$ requires C, 90·3; H, 3·95%). It was yellow in pyridine and addition of a drop of 25% methanolic potassium hydroxide had no effect on the colour.

The residue from the *o*-dichlorobenzene extraction was a black solid (0·2 g.) which was further extracted with nitrobenzene. The blue extract, on being cooled, deposited fine, black needles of *dinaphtho*[1,2-*a*:1,2-*l*]*peropyrene*-11,22-*quinone*, $\lambda_{max.}$ 320, 420, 733 mμ (log ε 4·54, 4·28, 4·80) (Found: C, 89·4; H, 3·65. $C_{42}H_{20}O_2$ requires C, 90·7; H, 3·6%).

Hydrolysis of 4-*Anilinodibenz*[a,kl]*anthrone.*—The anilino-compound (0·18 g.), potassium hydroxide (2·5 g.), and isopentyl alcohol (70 c.c.) were refluxed for 12 hr. The cooled solution was added to water, and the alcohol was removed in steam, leaving a yellow fluorescent solution and a black tar; the tar was discarded. The solution was acidified, and the precipitate was collected and recrystallised from 1,2,4-trichlorobenzene, giving yellow needles, m. p. 300—304°,

which was not depressed on admixture with the 4-hydroxy-compound, m. p. 302—303°, described above. Their absorption spectra in 95% ethanol were virtually identical.

Action of Alkali on Bi(dibenz[a,kl]*anthron-4-yl*).—The compound (0·05 g.) was refluxed for 2 hr. with potassium hydroxide (5 g.) and potassium acetate (0·5 g.) in 95% ethanol (10 c.c.), and the resulting blue mixture was added to water (150 c.c.). The suspension was aerated and the blue precipitate of dinaphtho[1,2-*a*:2,1-*m*]peropyrene-7,12-quinone was filtered off, washed, and dried; it had $\lambda_{max.}$ (slightly bluish-green) 420, 675 mμ (log ε 4·19, 4·57). In alkaline sodium dithionite solution containing a little pyridine it was blue with a red fluorescence.

Reaction of Dibenz[a,kl]*anthrone with Sodamide and Piperidine.*—Dry oxygen was passed through a stirred mixture of the ketone (5·6 g.), finely powdered sodamide (2 g.), and piperidine (26 g.; dried for 48 hr. over potassium hydroxide and then fractionated; b. p. 106—106·5°) which was slowly heated in an oil-bath from room-temperature. At 80° (bath) a reaction set in, with darkening and ammonia evolution, and heating was discontinued until its completion. The temperature was then raised to about 100° and held there for 2½ hr. After being cooled, the mixture was diluted with benzene (200 c.c.), water (300 c.c.) was cautiously added, and the dark tarry solid filtered off and extracted with fresh benzene (Soxhlet), producing a brown solution and a black residue (A).

The solution was run through a column of alumina (6·4 × 30 cm.), and the chromatogram developed with benzene until a prominent red band passed out of the column. The washings were concentrated and the resulting solid (2·4 g.) was purified by sublimation at 180—220°/0·001 mm., followed by recrystallisation from toluene, giving 4-*piperidinodibenz*[a,kl]*anthrone* as orange crystals, m. p. 228—230°, $\lambda_{max.}$ (apple-green) 325, 380, 460, 590 mμ (log ε 4·19, 4·17, 4·44, 3·51) (Found: C, 86·2; H, 5·8; N, 4·1. $C_{26}H_{21}NO$ requires C, 86·2; H, 5·8; N, 3·85%).

The material present in a bluish-red band surmounting the red one was eluted with hot benzene after mechanical division of the drained column. It was a dark, semi-crystallising oil which afforded a reddish-brown powder (0·5 g.) on being stirred with ether. No identifiable substance could be isolated from this solid, m. p. 206—216° (decomp.) (Found: N, 5·15%).

The black residue (A) was extracted with hot *o*-dichlorobenzene, leaving, undissolved, a little of the 7,12-quinone, $\lambda_{max.}$ (slightly bluish-green) 420, 670 mμ (log ε 4·13, 4·34).

Hydrolysis of 4-*Piperidinodibenz*[a,kl]*anthrone.*—This reaction was accomplished as already described for the 4-anilino-derivative and produced the same 4-hydroxy-derivative.

Reaction of Dibenz[a,kl]*anthrone with Sodamide and Morpholine.*—The ketone (5·6 g.), sodamide (2 g.), and morpholine (50 c.c.; dried for several days over potassium hydroxide and then fractionated; b. p. 126—130°), treated as described in the above piperidine experiment, gave a reddish-brown alkali-insoluble solid. The benzene extract (Soxhlet) from this, when chromatographed on alumina (6·4 × 30 cm.), gave, *inter alia*, a lower, bluish-red, and an upper, orange, band. The lower band yielded an orange-red solid (0·07 g.) which, on recrystallisation from ligroin (b. p. 100—120°), afforded dark red needles of 6-*morpholinodibenz*[a,kl]*anthrone*, m. p. 210—215°, $\lambda_{max.}$ (olive-brown) 340, 380, 460, 570 mμ (log ε 4·18, 4·21, 4·38, 3·47) (Found: C, 82·7; H, 5·25; N, 3·95. $C_{25}H_{19}NO_2$ requires C, 82·2; H, 5·2; N, 3·85%).

The upper band gave yellowish-brown crystals (2 g.) which were recrystallised (charcoal) from ligroin (b. p. 100—120°), giving the 4-*morpholino-derivative* as golden-yellow platelets, m. p. 197—198·5°, $\lambda_{max.}$ (apple-green) 325, 380, 460, 600 mμ (log ε 4·21, 4·16, 4·37, 3·62) (Found: C, 82·0; H, 5·05; N, 4·15. $C_{25}H_{19}NO_2$ requires C, 82·2; H, 5·2; N, 3·85%).

The black solid remaining after benzene extraction showed no evidence of quinonoid character in its reaction with pyridinised alkaline sodium dithionite solution or in its light absorption characteristics.

Hydrolysis of 4-*Morpholinodibenz*[a,kl]*anthrone.*—This substance gave the 4-hydroxy-derivative when treated in the manner already described for the 4-anilino-compound.

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