*Cyclisation of 3-Aroyl*meso*benzanthrones to 4 : 5-9 : 10-Dibenzopyrene-3 : 8-quinone and Its Derivatives.*

By Alan J. Backhouse and William Bradley.

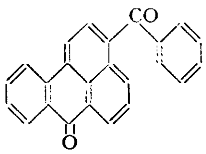
[Reprint Order No. 5869.]

A study of the action of potassium hydroxide on 3-benzoyl-, 3-*m*-nitrobenzoyl-, and 3-α-naphthoyl-*meso*benzanthrone has shown the occurrence of three concurrent reactions, (*a*) hydrolysis of acyl groups, yielding *meso*benzanthrone and a carboxylic acid, (*b*) cyclisation of the ketones to 4 : 5-9 : 10-dibenzopyrenequinone or a derivative thereof, and (*c*) nuclear hydroxylation.

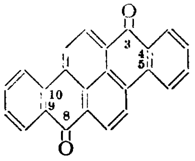
Many examples have been reported of the symmetrical union of two molecules of aromatic cyclic monoketones, such as 1 : 9-pyrazoloanthrone or *meso*benzanthrone, to form quinonoid diketones. The most general characteristic of these reactions is the coupling of carbon atoms situated *para* to carbonyl groups, the reaction depending on the presence of a strong base, such as sodioaniline or potassium hydroxide (Bradley and Bruce, *J.*, 1954, 1894). In G.P. 446,187 the self-condensation reaction has been extended to include the cyclisation of 3-α-naphthoyl*meso*benzanthrone (I; α-$C_{10}H_7$ for Ph) to a benzo-derivative of 4 : 5-9 : 10-dibenzopyrene-3 : 8-quinone (II). In this example the reaction is intramolecular and one of the nuclei becomes coupled through a carbon atom *ortho* to a carbonyl group.

In the present work the formation of a quinonoid diketone from 3-α-naphthoyl*meso*benzanthrone and potassium hydroxide has been confirmed under different conditions from those reported in G.P. 446,187, and some additional examples of the cyclisation reaction have been studied.

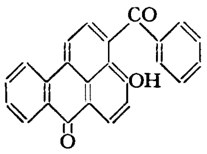
Heating 3-benzoyl*meso*benzanthrone (I) with potassium hydroxide and potassium acetate at 180° gave benzoic acid, *meso*benzanthrone, 4-hydroxy*meso*benzanthrone, violanthrone, and 4 : 5-9 : 10-dibenzopyrene-3 : 8-quinone (II), identical with the compound prepared from *meso*benzanthrone and benzoyl chloride (G.P. 412,053), or 1 : 5-dibenzoylnaphthalene (G.P. 426,710) and aluminium chloride. It is apparent that heating with alkali causes fission of (I) to benzoic acid and *meso*benzanthrone, and that the latter can yield both 4-hydroxy*meso*benzanthrone and violanthrone. Not the whole of the 4-hydroxy-derivative can arise in this way, however.



(I)



(II)



(III)

The yields of 4-hydroxy*meso*benzanthrone obtainable from *meso*benzanthrone and potassium hydroxide are known to be small in comparison with the amount of violanthrone produced (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259), and for this reason the much higher yields which result from the action of alkalis on (I) can arise only in some other way. The most probable explanation is that (I) yields 3-benzoyl-4-hydroxy-*meso*benzanthrone (III), by a reaction analogous to the direct hydroxylation of *meso*benzanthrone (Perkin and Spencer, *J.*, 1922, **121**, 479), which then undergoes hydrolysis with loss of the benzoyl group as benzoic acid and formation of 4-hydroxy*meso*benzanthrone. On this assumption the yields of (II) and 4-hydroxy*meso*benzanthrone obtained indicate that the relative importance of the cyclisation and hydroxylation reactions under the conditions used is 4 : 5. In other experiments manganese dioxide was added to the reactants, and this led to an increase in the amount and proportion of 4-hydroxy*meso*benzanthrone and a reduction in the yield of 4 : 5-9 : 10-dibenzopyrene-3 : 8-quinone, the ratio cyclisation : hydroxylation being 1 : 6. The effect of manganese dioxide in aiding hydroxylation is in agreement with the results of earlier work (Bradley, *J.*, 1937, 1791; Bradley and Waller, *J.*, 1953, 3778), and the reduction in the amount of the dibenzopyrenequinone produced indicates that (III) is an intermediate in the formation of 4-hydroxy*meso*benzanthrone, since the yield of the quinone could not be reduced by the presence of manganese dioxide unless direct hydroxylation of 3-benzoyl*meso*benzanthrone occurred and was facilitated by the addition of the oxidant.

*meso*Benzanthrone and *m*-nitrobenzoyl chloride gave two isomeric compounds, m. p. 223° and 262°, of which the first gave 4-hydroxy*meso*benzanthrone and a quinone, considered to be a nitro-derivative of (II), when heated with potassium hydroxide. For this reason the compound, m. p. 223°, was considered to be 3-*m*-nitrobenzoyl*meso*benzanthrone. The isomer, m. p. 262°, afforded a small amount of a phenolic product when heated with alkali, but there was no indication of the formation of a quinone. The compound, m. p. 262°, may be 9-*m*-nitrobenzoyl*meso*benzanthrone, since benzoyl chloride and *meso*benzanthrone afford 9-benzoyl*meso*benzanthrone as well as the 3-isomer (Moschinskaya, *Chem. Abs.*, 1941, **35**, 5488). The presence of the nitro-group greatly facilitates cyclisation, the yield of the dibenzopyrenequinone derivative being 27—28%. With 3-benzoyl*meso*benzanthrone the yield of this quinone was 10%. G.P. 412,053 describes the direct formation of nitro-derivatives of (II) from nitrobenzoyl chlorides and *meso*benzanthrone, but the formation of nitro-derivatives of (I) has not been described.

3-α-Naphthoyl*meso*benzanthrone, the preparation of which from *meso*benzanthrone-3-carbonyl chloride and naphthalene is mentioned in G.P. 446,187, on being heated with potassium hydroxide at 180° gives α-naphthoic acid, 4-hydroxy*meso*benzanthrone, and 9 : 10-benzo(4 : 5-1′ : 2′)naphthopyrenequinone. The formation of α-naphthoic acid establishes the constitution of the original naphthoyl*meso*benzanthrone as an α-naphthoyl derivative. The cyclisation reaction (yield 40%) occurred much more readily than with 3-benzoyl*meso*benzanthrone. It was first described in G.P. 446,187, in which alcoholic potassium hydroxide was used. The yield obtained by this process was not stated.

The action of potassium hydroxide and an oxidant on 4 : 5-9 : 10-dibenzopyrene-3 : 8-quinone (II) has been studied also. With manganese dioxide at 220° only a very small amount of a phenolic product was formed, probably because the hydroxylation of the quinone (II) can occur *para* to carbonyl groups only in benzene rings, and these are less readily substituted than naphthalene nuclei, as in *meso*benzanthrone (Bradley, *loc. cit.*), anthanthrone (Bradley and Waller (*loc. cit.*), pyranthrone, and *amphi-iso*pyranthrone (Backhouse and Bradley, *J.*, 1954, 4506).

EXPERIMENTAL

*Action of Potassium Hydroxide on 3-Benzoyl*meso*benzanthrone.*—(*a*) 3-Benzoyl*meso*benzanthrone (2 g.; m. p. 197°) was finely powdered and added during 15 min. to potassium hydroxide (20 g.) and potassium acetate (2 g.) at 150°. The reactants were stirred for 1 hr. at 180°, then cooled and added to water (500 c.c.), and the resulting suspension was filtered. The residue was extracted with 1% aqueous sodium hydroxide and the yellow alkaline solutions, which showed an intense green fluorescence, were combined and acidified. A precipitate (0·25 g.) formed and this gave a single yellow band; the product isolated therefrom had m. p. 302—304°, not depressed by 4-hydroxy*meso*benzanthrone, on sublimation *in vacuo* from a bath at 250°.

The alkali-insoluble part of the residue was heated for 1 hr. at 60—70° with a solution of sodium hydroxide (4 g.) and sodium dithionite (4 g.) in water (200 c.c.). The resulting deep cherry-red solution was filtered from undissolved solid, and on aeration for 4 hr. 4 : 5-9 : 10-dibenzopyrene-3 : 8-quinone (0·17 g.) separated. After purification by chromatography from chlorobenzene on alumina the quinone was obtained as golden-orange crystals which showed the same light absorption in 95% alcohol as the authentic compound.

The material which was insoluble in aqueous sodium hydroxide and sodium hydroxide–sodium dithionite was extracted with chlorobenzene, and the solution was chromatographed on alumina. Several bands were formed, and elution afforded (*a*) *meso*benzanthrone (0·11 g.; m. p. 172—173°); (*b*) 3-benzoyl*meso*benzanthrone (0·13 g.; m. p. 196—197°); (*c*) 4 : 5-9 : 10-dibenzopyrenequinone (0·03 g.). The chlorobenzene-insoluble solid (0·16 g.) was blue-black and showed the reactions of violanthrone.

(*b*) In a repetition of the above experiment the original alkaline filtrates were steam-distilled after acidification. Ether-extraction of the distillate gave benzoic acid (0·32 g.).

(*c*) In a further modification manganese dioxide (2 g.) was intimately mixed with the 3-benzoyl*meso*benzanthrone before the heating with the potassium hydroxide. Under these conditions the yields were: 4-hydroxy*meso*benzanthrone, 0·32 g., and 4 : 5-9 : 10-dibenzopyrenequinone, 0·05 g.

The 3-benzoyl*meso*benzanthrone used in these experiments was prepared by heating benzoyl chloride, *meso*benzanthrone, and aluminium chloride at 125° for 5 hr. (cf. Moschinskaya, *Chem. Abs.*, 1940, **34**, 1653) and chromatography of the product on alumina.

4 : 5-9 : 10-Dibenzopyrene-3 : 8-quinone was very stable to alkaline oxidants. An intimate mixture of the quinone (5 g.), manganese dioxide (5 g.), potassium hydroxide (50 g.), and potassium acetate (5 g.), stirred and heated for 1 hr. at 240°, afforded only 0·4 g. of acidic products.

3-m-*Nitrobenzoyl*meso*benzanthrone*.—*m*-Nitrobenzoyl chloride (12 g.) and an intimate mixture of *meso*benzanthrone (15 g.) and anhydrous aluminium chloride (100 g.) were stirred together and heated for 5 hr. in an oil-bath at 110°. The resulting viscous mass was cooled, crushed, and added to ice-water (1 l.), and the resulting yellow precipitate was collected, and then washed with dilute sodium hydroxide solution. The insoluble portion, dissolved in chlorobenzene and chromatographed on alumina, gave a mobile band of unchanged *meso*benzanthrone and a second band which was more strongly absorbed. This was eluted with chlorobenzene, crystallised by concentration of the eluate, and then recrystallised six times from this solvent, to give yellow crystals, m. p. 261—262·5° (Found: C, 75·8; H, 3·4; N, 3·7. $C_{24}H_{13}O_4N$ requires C, 76·0; H, 3·7; N, 3·9%), of (probably) 9-m-*nitrobenzoyl*meso*benzanthrone*. The mother-liquors from the initial chlorobenzene eluate gave a second crop of crystals on further concentration and these (0·5 g.) gave 3-m-*nitrobenzoyl*meso*benzanthrone* as yellow crystals, m. p. 223° (Found: C, 76·0; H, 3·4; N, 3·9%) after further crystallisation.

Action of potassium hydroxide. 3-*m*-Nitrobenzoyl*meso*benzanthrone (0·4 g., m. p. 223°) was stirred at 180° for 1 hr. with potassium hydroxide (10 g.) and potassium acetate (1 g.). After being cooled the melt was added to water (100 c.c.); a yellow solution having a green fluorescence was formed, from which 4-hydroxy*meso*benzanthrone (0·025 g.), m. p. 302—304°, was obtained by acidification, separation of the precipitate, and sublimation of this *in vacuo* from a bath at 250—300°. The alkali-insoluble portion of the product afforded a deep bluish-red solution on being heated at 60—70° for 1 hr. with dilute alkaline sodium dithionite. Aeration of the filtered solution gave a brown solid (0·10 g.) which was very sparingly soluble in the common solvents, gave a purple solution in concentrated sulphuric acid, and again dissolved in alkaline sodium dithionite with a bluish-red colour.

Similar treatment of the isomer, m. p. 262°, gave 0·04 g. of material which dissolved in aqueous alkali with a yellow colour and a green fluorescence, but there was no indication of the formation of a quinone reducible by alkaline sodium dithionite.

meso*Benzanthrone*-3-*carbonyl Chloride*.—*meso*Benzanthrone-3-carboxylic acid was prepared by hydrolysis of 3-cyano*meso*benzanthrone according to G.P. 420,412, except that the conditions used were refluxing 3-cyano*meso*benzanthrone (50 g.) with concentrated sulphuric acid (200 g.), glacial acetic acid (200 g.), and water (200 g.) for 72 hr. The yield of the 3-carboxylic acid was 15 g., m. p. 352—355°, after recrystallisation from nitrobenzene. It decomposed readily with formation of *meso*benzanthrone on being refluxed with quinoline and a small amount of copper powder.

The 3-carboxylic acid (5 g.) was refluxed for 4 hr. with chlorobenzene (100 c.c.) and thionyl chloride (10 c.c.). The resulting solution was concentrated, and the crystals formed were collected, washed with a small volume of benzene, then dried *in vacuo* (yield 4 g.). meso*Benzanthrone*-3-*carbonyl chloride* had m. p. 285—290° (Found: C, 73·8; H, 3·15; Cl, 12·3. $C_{18}H_9O_2Cl$ requires C, 73·5; H, 3·1; Cl, 12·0%).

Ethyl meso*Benzanthrone*-3-*carboxylate*.—Prepared from the chloride and dry alcohol, or by heating the silver salt of the 3-carboxylic acid with ethyl iodide, this *ester* crystallised from alcohol in slender, dark yellow prisms, m. p. 154° (Found: C, 79·1; H, 4·8. $C_{20}H_{14}O_3$ requires C, 79·45; H, 4·7%). It dissolved in concentrated sulphuric acid with a golden-yellow colour and a green fluorescence.

3-α-*Naphthoyl*meso*benzanthrone*.—The preparation of this diketone (m. p. 244—245°; no analysis) is mentioned, but not described, in G.P. 446,187. *meso*Benzanthrone-3-carbonyl chloride (4 g.), aluminium chloride (5 g.), and naphthalene (5 g.) refluxed in carbon disulphide (200 c.c.) during 10 hr. gave, after steam-distillation followed by heating with dilute sodium hydroxide solution, a solid which was then chromatographed from chlorobenzene on alumina. The crude *ketone* obtained by this means had m. p. 244—246° (Found : C, 87·1; H, 4·3. $C_{28}H_{16}O_2$ requires C, 87·5; H, 4·2%) after crystallisation from pyridine.

Action of fused potassium hydroxide. The ketone (0·5 g.) was finely ground, then stirred for 1 hr. at 180° with potassium hydroxide (5 g.) and potassium acetate (0·5 g.). The cooled melt was added to water, and the alkaline solution separated, acidified, and then extracted with ether. Evaporation of the extract gave a solid (0·1 g.) which, after recrystallisation from water, had m. p. 150—154°, not depressed by α-naphthoic acid, but depressed by β-naphthoic acid. The acidified aqueous solution contained a precipitate (0·1 g.), which, after collection, washing, and drying was sublimed *in vacuo* from a bath at 250—300°. The bright yellow sublimate had m. p. 300—304°, not depressed by 4-hydroxy*meso*benzanthrone.

The material which remained undissolved when the original melt was added to water was collected, washed, and heated at 60—70° for 1 hr. with a solution of sodium hydroxide (1 g.) and sodium dithionite (1 g.) in water (50 c.c.). The resulting carmine-red solution was filtered and then aerated. The precipitate of 9 : 10-benzo(4 : 5-1′ : 2′)naphthopyrene-3 : 8-quinone (0·2 g.) which formed was collected and chromatographed from chlorobenzene on alumina. The main orange band on elution with chlorobenzene gave crystals, m. p. 356—368° (Found : C, 87·5; H, 3·7. Calc. for $C_{28}H_{14}O_2$: C, 87·9; H, 3·7%). These dissolved in concentrated sulphuric acid with a dark blue colour similar to that reported for the product (no analysis recorded) obtained by the action of potassium hydroxide in alcohol at 100—230° (G.P. 446,187).

We thank Imperial Chemical Industries Limited, Dyestuffs Division, for a maintenance grant to one of us (A. J. B.) and for gifts of *meso*benzanthrone.

CLOTHWORKERS' RESEARCH LABORATORY,
UNIVERSITY OF LEEDS.

[*Received, November* 10*th*, 1954.]