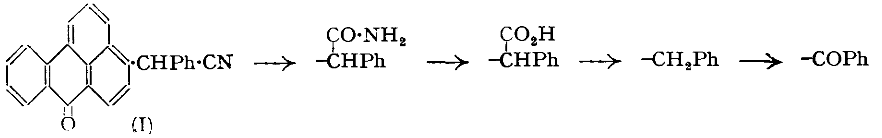
686. *The Oxidative Hydrolysis of* 4-α-*Cyanobenzyl*meso*benzanthrone.*

By Neil Campbell and Anthony A. Woodham.

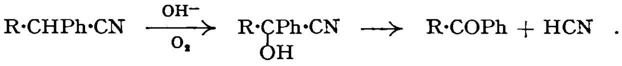
4-α-Cyanobenzyl*meso*benzanthrone in methanolic potassium hydroxide is converted by oxygen at room temperature into 4-benzoyl*meso*benzanthrone. An intermediate in the reaction is probably 4-benzyl*meso*benzanthrone which under these conditions is very rapidly oxidised to give the benzoyl compound in excellent yield. The mechanism of the reaction is discussed.

4-α-CYANOBENZYL*meso*BENZANTHRONE (I) in methanolic potassium hydroxide is converted by a stream of air into pure 4-benzoyl*meso*benzanthrone (G.P. 568,783; Rule, Campbell, McGregor, and Woodham, *J.*, 1950, **1816**). We have now studied the reaction in greater detail with a view to ascertaining its mechanism. A possible course of the reaction is represented by the series (*A*), in which 4-benzyl*meso*benzanthrone, formed from the cyano-compound (I) by successive hydrolysis and decarboxylation, is oxidised to 4-benzoyl*meso*benzanthrone. There is nothing inherently improbable in the first three reactions, especially since we have shown that the amide on hydrolysis with ethanolic potassium hydroxide does in fact give 4-benzyl*meso*benzanthrone. Quite unexpected is the ready oxidation of the benzyl to the benzoyl compound. It is, of course, well known that methylene groups situated between two aromatic rings can be oxidised to the carbonyl group, but strong oxidising reagents are generally required. Kacer (G.P. 557,249), for example, effected the oxidation in question by hot selenious acid under pressure, and Rule *et al.* (*loc. cit.*) used sodium dichromate and boiling acetic acid. Aerial oxidations of hydrocarbons are also known, but except under forcing conditions they do not occur rapidly and the yields are not high. We have found, however, that 3 min. suffice for the practically quantitative oxidation of 4-benzyl- to 4-benzoyl-*meso*benzanthrone by air in the presence of methanolic potassium hydroxide. A similar result was obtained with 4-*p*-methylbenzyl*meso*benzanthrone. A comparable oxidation to which Professor R. D. Haworth, F.R.S., kindly drew our attention is that of certain 1-benzyl-3 : 4-dihydro*iso*quinolines which are oxidised to benzoyl compounds merely by exposure of their solutions to air (Buck, Haworth, and Perkin, *J.*, 1924, **125**, 2176; see also Lindemann, *Helv. Chim. Acta*, 1949, **32**, 69, Buck, *J. Amer. Chem. Soc.*, 1930, **52**, 3610, and Noller and Wunderlich, *ibid.*, 1952, **74**, 3836). It is doubtful however if these oxidations are effected by air (see, *e.g.*, Tsatsas, *Bull. Soc. chim.*, 1949, 884).



(I) (*A*)

A referee has kindly suggested to us an attractive alternative to the series of reactions (*A*), namely, that the cyano-compound under the influence of alkali is oxidised to the cyanohydrin and then loses a molecule of hydrogen cyanide to give the benzoyl*meso*benzanthrone (*B*). We attempted to decide between the schemes *A* and *B* by following



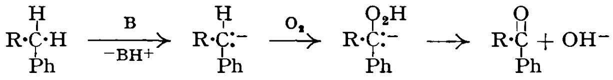
$$\mathrm{R{\cdot}CHPh{\cdot}CN} \xrightarrow[\mathrm{O_2}]{\mathrm{OH^-}} \mathrm{R{\cdot}\underset{OH}{C}Ph{\cdot}CN} \longrightarrow \mathrm{R{\cdot}COPh} + \mathrm{HCN} \quad . \quad . \quad . \quad . \quad (B)$$

(R = *meso*Benzanthrone radical.)

the fate of the cyano-nitrogen. So far, however, we have not been able to detect more than traces of ammonia (as required by scheme *A*) or hydrogen cyanide (scheme *B*), but we hope soon to examine the reaction more thoroughly.

The aeration of comparable benzyl derivatives in methanolic potassium hydroxide for 10 hr. was studied, but diphenylmethane, fluorene, and dibenzyl gave negative results. We were particularly interested in bis-(*p*-dimethylaminophenyl)methane and 2-benzylpyridine, since the former gives the corresponding benzophenone on mild oxidation with chloranil and 2-benzylpyridine is oxidised merely by exposure to air in ultra-violet light (Muller and Dorfmann, *J. Amer. Chem. Soc.*, 1934, **56**, 2787), but neither compound was oxidised by our method.

Further investigation showed that both aeration and the presence of a base such as potassium hydroxide are essential for the oxidation of the benzyl*meso*benzanthrone, whilst water has an inhibiting effect. These results and the unusual rate of the reaction can be plausibly explained by the formation of a hydroperoxide followed by its base-catalysed decomposition. The formation of a hydroperoxide by the interaction of a reactive methylene group and oxygen in the presence of a base is not surprising, for such reactions are analogous to the well-known carbonyl–methylene condensations (Hock and Lang, *Ber.*, 1944, **77**, 257). Examples of base-catalysed decomposition of peroxides are also known (Kornblum and de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880) and the formation of 4-benzoyl*meso*benzanthrone may well follow a similar course, *viz.*:



$$\mathrm{R{\cdot}\overset{H}{\underset{Ph}{C}}{\cdot}H} \xrightarrow[-\mathrm{BH^+}]{\mathrm{B}} \mathrm{R{\cdot}\overset{H}{\underset{Ph}{C}}{:}^-} \xrightarrow{\mathrm{O_2}} \mathrm{R{\cdot}\overset{O_2H}{\underset{Ph}{C}}{:}^-} \longrightarrow \mathrm{R{\cdot}\overset{O}{\underset{Ph}{C}}} + \mathrm{OH^-}$$

(R = *meso*Benzanthrone radical; B = base.)

Efforts to isolate the hydroperoxide, however, met only with slight success. It was noted that the benzoyl compound separated from a solution which was strongly fluorescent although 4-benzoyl*meso*benzanthrone itself does not fluoresce in methanolic potassium hydroxide and this suggests the presence of another product, possibly a hydroperoxide. Acidification of the solution afforded a yellow solid, which gave a positive test for peroxides with starch iodide, but not with chromic acid. Control experiments, however, showed that the starch–iodide test is more sensitive than the perchromic acid test. Hence it was concluded that the solid isolated was not itself a peroxide but contained a peroxide. By measuring the quantity of oxygen absorbed during the oxidation of 4-α-cyanobenzyl- and 4-benzyl-*meso*benzanthrone it was found that 2 atoms of oxygen per molecule were consumed. Unsuccessful efforts were made to oxidise 4-α-cyanobenzyl*meso*benzanthrone by aeration in benzene in the presence of cobalt naphthenate, a catalyst known to promote hydroperoxide formation and decomposition.

4-Benzoyl*meso*benzanthrone when heated with hydroxylamine in pyridine for 8 hr. gives an oxime (II) in which the 7-carbonyl group remains intact. This structure is in harmony with the facts that under the same conditions *meso*benzanthrone forms no oxime; that the red colour of the oxime with sulphuric acid is similar to that given by *meso*benzanthrone, but different from the yellow colour given by *meso*benzanthrone oxime (Campbell and Woodham, *J.*, 1952, 843); and finally that the oxime undergoes the Beckmann transformation to give the anilide of *meso*benzanthrone-4-carboxylic acid, identical with the anilide obtained by the action of hydrazoic acid on 4-benzoyl*meso*benzanthrone (see below). The last reaction establishes the configuration of the oxime.

$$\mathrm{R{\cdot}\underset{\underset{HO\cdot N}{\|}}{C}{\cdot}Ph}$$

(II)

(R = *meso*Benzanthrone radical.)

We have found that the carbonyl group of *meso*benzanthrone is inert towards hydrazoic acid (Campbell and Woodham, *loc. cit.*), but 4-benzoyl*meso*benzanthrone gives mainly the anilide of *meso*benzanthrone-4-carboxylic acid (96% yield), whose structure follows from its hydrolysis to *meso*benzanthrone-4-carboxylic acid and aniline. The side-product is *N*-benzoyl-4-*meso*benzanthronylamine.

These results afford another example of an unsymmetrical ketone yielding the same main products by the Beckmann and the Schmidt reaction. It is also noteworthy that the oxime, and presumably the intermediate in the Schmidt reaction (Smith *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 320; 1950, **72**, 2503, 3718; Newman and Gilderhorn, *ibid.*, 1948, **70**, 317), possess the *cis*-configuration, *i.e.*, the hydroxyl and the bulky *meso*benzanthrone group are *cis* to one another.

EXPERIMENTAL

*4-α-Carbamylbenzyl*meso*benzanthrone.*—4-α-Cyanobenzyl*meso*benzanthrone was obtained by the method given in G.P. 501,082 (for details see Woodham, Thesis, Edinburgh, 1951, p. 20). The method is highly capricious. Of twenty-one condensations, seven were reasonably successful, giving yields ranging from 25 to 40%; five yielded traces of the cyanobenzyl-product; two gave a red product; and eight were entirely unsuccessful and afforded only unchanged *meso*benzanthrone. In spite of many experiments we have not succeeded in finding the factor required to give reproducible results, but the temperature seems to be critical, for all the successful condensations were effected at 20° whereas below 18° no condensation occurred.

4-α-Cyanobenzyl*meso*benzanthrone (0·5 g.), in concentrated sulphuric acid (10 ml.) was kept at room temperature for 4 days and then poured into water. The yellow amide was washed free from acid, and crystallised from glacial acetic acid in pale yellow elongated prisms, m. p. 277—280°, which were shown by analysis to be not quite pure (Found: C, 81·5; H, 4·7; N, 4·5. Calc. for $C_{25}H_{17}O_2N$: C, 82·6; H, 4·7; N, 3·9%). The presence of the amido-group was shown by the liberation of ammonia by warm alkali.

The amide (0·1 g.) in 10% ethanolic potassium hydroxide (10 ml.) was boiled until the initial deep green fluorescence disappeared and the evolution of ammonia had practically ceased. The mixture was poured into water (50 ml.) and extracted with ether. Evaporation of the ether gave 4-benzyl*meso*benzanthrone, m. p. and mixed m. p. 177—178°. The same product was obtained by hydrolysis with ethanolic hydrogen chloride.

Attempts to convert the carbamyl group into the carboxyl group by heating the substance with ethanol, sodium nitrite, and concentrated hydrochloric acid gave only 4-benzyl*meso*benzanthrone and some unchanged amide.

Oxidative Hydrolysis Experiments.—4-Benzyl*meso*benzanthrone (0·025 g.) was boiled for 3 min. with methanolic 2N-potassium hydroxide (10·0 ml.) in a current of air. 4-Benzoyl*meso*benzanthrone (yield >90%) separated and, crystallised from benzene, had m. p. and mixed m. p. 175—176°. Similar experiments without alkali gave only unchanged benzyl*meso*benzanthrone.

To a solution of 4-benzyl*meso*benzanthrone (0·02 g.) in methanol (10 ml.) and methanolic 2N-potassium hydroxide (5 ml.) water (3 ml.) was added. A slight separation of the benzyl compound resulted. The solution was boiled and aerated for 35 min. and gave a product which was chiefly unchanged material with a small quantity of 4-benzoyl*meso*benzanthrone.

4-Benzyl*meso*benzanthrone (0·03 g.) was boiled and aerated in methanol (10 ml.) and piperidine (4 ml.) for 10 hr. A pronounced green fluorescence occurred after 30 min. The product was a mixture of unchanged material and 4-benzoyl*meso*benzanthrone.

To measure the quantity of oxygen consumed, experiments were carried out in a 50-ml. gas burette (for details see Woodham, Thesis, Edinburgh, 1951) containing methanolic 2N-potassium hydroxide previously saturated with oxygen. Control experiments showed that 9·9 and 18·6 ml. of oxygen were absorbed after 1 and 2 weeks respectively. Since the burette was sealed at both ends by methanolic potassium hydroxide traps this result must be due to loss of oxygen at the outer surface of the methanol followed by absorption of oxygen at the surface in the reaction bulb. After the necessary corrections had been made the following results were obtained: 4-α-cyanobenzyl*meso*benzanthrone (0·345 g., 1/1000 mol.) after 1 week absorbed 25 ml. of oxygen at N.T.P., and 4-benzyl*meso*benzanthrone (0·320 g., 1/1000 mol.) after 2 weeks absorbed 22 ml. of oxygen. In both cases therefore the benzanthrone compound absorbs approximately 1 mol. of oxygen.

*Oximation of 4-Benzoyl*meso*benzanthrone.*—4-Benzoyl*meso*benzanthrone (1 g.), hydroxylamine hydrochloride (5 g.), and pyridine (50 c.c.) were heated for 8 hr., and the pyridine then removed by vacuum-distillation. The residue was poured into water and extracted with ether, evaporation of which gave the oxime which, crystallised from ethanol, had m. p. 234—235° (yield 0·83 g.). The oxime was dissolved in benzene and passed down a column of alumina (B.D.H. chromatographic). Development with benzene gave two zones, the lower of which on extraction with ethanol gave the *oxime*, m. p. 245—246° (from ether) (Found: N, 4·0. $C_{24}H_{15}O_2N$ requires N, 4·0%). The above experiment was repeated, but with the heating continued for 50 hr. The crude product on trituration with ether yielded the *dioxime*, yellow crystals, m. p. 246—247° (decomp.) (Found: C, 78·5; H, 4·2; N, 7·8. $C_{24}H_{16}O_2N_2$ requires C, 79·1; H, 4·4; N, 7·7%).

*Beckmann Rearrangement of 4-Benzoyl*meso*benzanthrone Oxime.*—The oxime (0·1 g.) in dry ether (10 ml.) was boiled with phosphorus pentachloride (0·15 g.) for 10 min. Removal of the ether left a brown oil which was triturated with water. Unchanged oxime was removed from the resulting orange solid, and the insoluble portion was extracted with benzene which on evaporation yielded *meso*benzanthrone-4-carboxyanilide, m. p. 268°, undepressed when mixed with a sample prepared as below.

*Schmidt Reaction of 4-Benzoyl*meso*benzanthrone.*—Sodium azide (0·5 g.) was added to 4-benzoyl*meso*benzanthrone (0·5 g.) dissolved in concentrated sulphuric acid (10 ml.). After 3 hr. the solution was poured into water (80 ml.). *meso*Benzanthrone-4-carboxyanilide separated and after being well washed with water to remove sulphate was dried in the oven (yield 0·43 g., 85%; m. p. 265—270°). The *anilide* separated from glacial acetic acid in yellow prisms, m. p. 268—270°, not depressed when mixed with the product of the Beckmann transformation (see above) (Found: C, 81·5; H, 4·6; N, 4·7. $C_{24}H_{15}O_2N$ requires C, 82·5; H, 4·3; N, 4·0%). The anilide (0·3 g.) was boiled for 50 hr. with 60 ml. of a mixture containing equal weights of glacial acetic acid, concentrated sulphuric acid, and water and was then poured into water (450 ml.). The precipitate was extracted with aqueous sodium carbonate in which it was completely soluble and on acidification gave *meso*benzanthrone-4-carboxylic acid (96·5%), m. p. 310—315°, not depressed when admixed with an authentic sample.

The original aqueous acidic liquors were made alkaline with sodium hydroxide and thoroughly shaken with ether. The dried extract on evaporation gave red prisms of 4-amino-*meso*benzanthrone (1%), m. p. 220—222° (lit., 223—224°).

Thanks are expressed to the Anglo-Iranian Oil Company Limited for a grant.

UNIVERSITY OF EDINBURGH.

[*Received, April 25th,* 1953.]