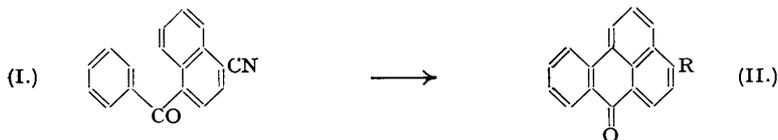


366. 4-Benzoylmesobenzanthrone.

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Oxidative hydrolysis of 4-cyanobenzylmesobenzanthrone, readily obtained by the condensation of mesobenzanthrone with benzyl cyanide, affords an excellent method for the preparation of 4-benzoylmesobenzanthrone. The constitutions of these products have been rigidly established.

IN the presence of alkaline agents mesobenzanthrone condenses with benzyl cyanide to give 4- α -cyanobenzylmesobenzanthrone [II; R = Ph·CH(CN)·]. Many such compounds on hydrolysis with caustic alkali yield the corresponding alkyl- or aryl-mesobenzanthrone. We have found, however, that, although the above cyano-compound with acid hydrolysing agents gives 4-benzylmesobenzanthrone (II; R = Ph·CH₂·), with alkaline reagents in the presence of air it gives 4-benzoylmesobenzanthrone (II; R = Ph·CO). After our work was completed we discovered that the preparation of 4-benzoylmesobenzanthrone by essentially the same method had been outlined in a German patent (G.P. 568,783). The benzoyl compound is also obtained by oxidative hydrolysis of the cyano-compound with acids and an oxidising agent, but the yields are poor. It was previously prepared by the oxidation of the benzyl compound with selenious acid (Kacer, G.P. 557,249).

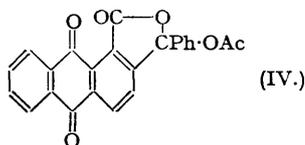
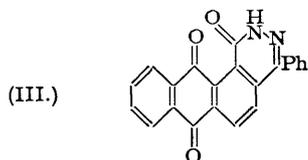


Presumably in such oxidative condensations the intermediate cyano-compound is hydrolysed to the carboxylic acid with simultaneous oxidation by the air. A parallel instance is furnished by sodium fluorene-9-carboxylate which undergoes oxidation and decarboxylation in alkaline solution to yield fluorenone (Wislicenus and Ruthing, *Ber.*, 1913, **46**, 2771).

How far other substances undergo nucleophilic attack by benzyl cyanide in alkaline solution is an interesting speculation but it is noteworthy that the product obtained from benzyl cyanide and *m*-dinitrobenzene (Reissert, *Ber.*, 1904, **37**, 831) may well be 1 : 3-dinitro-2- or -4- α -cyanobenzylbenzene (cf. Lobry de Bruyn, *Rec. Trav. chim.* 1889, **2**, 210). In agreement with this are the analytical figures of what was admittedly an impure product (Found: C, 60.7; H, 4.0; N, 14.8. Calc. for $C_{14}H_9O_4N_3$: C, 59.4; H, 3.2; N, 14.8%).

Evidence that oxidative condensation of mesobenzanthrone in the presence of alkali occurs at the 4-position is to be found in the patent literature. It is, however, difficult to assess the reliability of such evidence, conclusive though it appears. This is due partly to the omission, in the patents, of relevant details such as the constitution or origin of important intermediates as well as lack of methods of identification or analytical figures, and partly to the comparative inaccessibility of the patent literature to academic workers. It was therefore decided to determine unequivocally the structures of the mesobenzanthrone derivatives prepared above. This was done by synthesis and oxidation.

1-Bromo-4-methylnaphthalene (Meyer and Sieglitz, *Ber.*, 1922, **55**, 1839) was converted into 1-bromo-4-benzoylnaphthalene, identical with the product obtained from 1-bromonaphthalene and benzoyl chloride by the Friedel-Crafts reaction. Replacement of the bromine by the cyano-group gave 4-benzoyl-1-naphthonitrile (I) (B.P. 293,768), which was cyclised to 4-cyanomesobenzanthrone (II; R = CN) when heated with aluminium chloride and sodium chloride in a current of oxygen. Hydrolysis gave the 4-carboxylic acid (cf. Copp and Simonsen, *J.*, 1942, 209) which was converted into 4-benzoylmesobenzanthrone (II; R = CPh) identical with our compound prepared above by the oxidative hydrolysis of 4- α -cyanobenzylmesobenzanthrone. Any possibility that rearrangement had occurred during the ring-closure was eliminated by a second proof of the structure of 4-benzoylmesobenzanthrone. Oxidation gave 2-benzoylanthraquinone-1-carboxylic acid previously obtained from 1-chloro-2-benzoylanthraquinone (Scholl *et al.*, *Ber.*, 1936, **69**, 2428). The carboxyl group is in the 1-position and the benzoyl group must be contiguous to it since treatment with hydrazine hydrate or acetic anhydride in pyridine yielded a dihydropyridazine derivative (III) and an acetoxy-lactone (IV) respectively. Control experiments showed that hydrazine hydrate under the same conditions did not react with anthraquinone, and with anthraquinone-1-carboxylic acid gave the hydrazinium salt.



Decarboxylation of 2-benzoylanthraquinone-1-carboxylic acid gave 2-benzoylanthraquinone, previously obtained from 9-benzoylmesobenzanthrone (Moshchinskaya, *Chem. Abstr.*, 1941, **35**, 5488) or anthraquinone-2-carboxylic acid (Waldmann *et al.*, *Ber.*, 1938, **71**, 370). It is of interest that, in contrast to anthraquinone-2-carboxylic acid and 1- and 2-naphthoic acids, 1-nitroanthraquinone-2-carboxylic acid and nitronaphthoic acids (cf. Rule *et al.* *J.*, 1934, 168, 171) are readily decarboxylated by copper in quinoline, thus further demonstrating the influence of negative substituents on decarboxylation.

EXPERIMENTAL.

Compounds denoted by asterisks are mentioned in patents but without analytical data.

Hydrolysis of 4- α -Cyanobenzylmesobenzanthrone.—4- α -Cyanobenzylmesobenzanthrone* was obtained by the method given in G.P. 501,082 (Friedländer, 1932, **17**, 1310) and separated from benzene in orange-yellow plates, m. p. 212° (Found: C, 87.4; H, 4.1; N, 4.1. $C_{25}H_{16}ON$ requires C, 87.0; H, 4.3; N, 4.1%). It (1 g.) was boiled for 7 hours with 75 c.c. of a mixture of glacial acetic acid, concentrated sulphuric acid, and water (4 : 2 : 1). Pouring the mixture into water gave a precipitate (0.9 g.) which after crystallisation first from benzene and then from glacial acetic acid gave 4-benzylmesobenzanthrone as pale yellow needles, m. p. 182° (Found: C, 89.3; H, 5.2. $C_{24}H_{16}O$ requires C, 90.0; H, 5.0%). It gives an orange-red solution with a golden fluorescence when dissolved in concentrated sulphuric acid, but none with methanolic potassium hydroxide.

Oxidative Hydrolysis of 4- α -Cyanobenzylmesobenzanthrone.—Similar treatment of 4-benzylcyano-

mesobenzanthrone in presence of an oxidising agent such as potassium dichromate yielded only 4-benzylmesobenzanthrone. In another experiment 4-cyanobenzylmesobenzanthrone (1.5 g.), powdered sodium dichromate (4.5 g.), and glacial acetic acid (100 c.c.) were refluxed for 2–3 hours and then poured into water. The resulting solid was coagulated by heat and was washed with water, a brown resinous material resulting which was purified by dissolving it in benzene–light petroleum (11 : 9 parts), passing the solution through alumina, and developing the chromatogram first with a similar mixture and then with increasing proportions of benzene. A yellow band developed and passed into the filtrate which on evaporation yielded 4-benzoylmesobenzanthrone,* m. p. 175–177° (Kacer, *loc. cit.*, gives 174–176°) (0.3 g.) (Found : C, 86.3; H, 4.3. $C_{24}H_{14}O_2$ requires C, 86.2; H, 4.2%). It gives no colour with methanolic potassium hydroxide and gives a m. p. depression of 30° when mixed with 4- α -cyanobenzylmesobenzanthrone. It is best prepared, however, by the method given in G.P. 568,783 (Friedländer, 1934, 19, 2127).

Synthesis of 4-Benzoylmesobenzanthrone.—1-Bromo-4-methylnaphthalene (Meyer and Sieglitz, *loc. cit.*) gave a 12% yield of 4-bromo-1-naphthoic acid, m. p. 211–212° (lit., 212°) when oxidised by dilute nitric acid. The acid (1 g.) was converted into the chloride by thionyl chloride (2 g.), and a benzene solution of the chloride was treated with aluminium chloride (1 g.), and the solution heated on the water-bath for 3½ hours. The mixture was poured into water, ice, and hydrochloric acid and thoroughly extracted with benzene. The benzene solution was chromatographed on alumina and developed with benzene–light petroleum (b. p. 60–80°). Elution of the dark zone at the top of the column with ethanol gave 4-bromo-1-benzoylnaphthalene,* which after repeated crystallisation from ethanol had m. p. 77° and gave m. p. 81–83° when mixed with the compound prepared as follows. 1-Bromonaphthalene (21 g.) was added to benzoyl chloride (14 g.) and aluminium chloride (14 g.) in carbon disulphide (80 c.c.), and the mixture after 2 hours on the water-bath was poured on ice (250 g.). Ether-extraction followed by evaporation of the dried ($CaCl_2$) extract gave crude 4-bromo-1-benzoylnaphthalene (11 g.) which on crystallisation from ethanol gave prisms, m. p. 87–88° (Found : Br, 25.9. $C_{17}H_{11}OBr$ requires Br, 25.7%).

1-Bromo-4-benzoylnaphthalene (9 g.), cuprous cyanide (5.5 g.), and freshly distilled pyridine (15 c.c.) were boiled for 17 hours in an oil-bath (temp. 210–220°) and poured into concentrated aqueous ammonia (25 ml.) and water (25 ml.). Benzene (25 ml.) and ether (25 ml.) were added and the mixture was filtered. The benzene–ether layer was washed 4 times with dilute aqueous ammonia (25 ml.), twice with 6*N*-hydrochloric acid (25 ml.), twice with water (20 ml.), and finally twice with a saturated solution of sodium chloride. Removal of the solvent gave 4-benzoyl-1-naphthonitrile,* m. p. 67–69° (5 g., 66%) (Found : N, 5.2. $C_{18}H_{11}ON$ requires N, 5.4%). The nitrile (2 g.), aluminium chloride (16.5 g.), and sodium chloride (3.5 g.) were well ground together and heated in an oil-bath (bath-temp. 115–120°) for 24 hours and the product was decomposed with water. The tarry product was dissolved in glacial acetic acid, from which crystals, m. p. 65–70°, separated. These were dissolved in benzene and the solution was chromatographed on alumina and the column developed with benzene–light petroleum. A pale yellow band moved down the column and consisted of unchanged nitrile, m. p. 68–69°, and a thin dark zone at the top of the column on elution with ethanol gave a small quantity of 4-cyanomesobenzanthrone,* m. p. 234°. The nitrile is best prepared by passing oxygen through the above molten mixture maintained at 110–135° for 24 hours and pouring the product into water. Extraction with ether followed by evaporation of the ethereal layer gave the nitrile which, crystallised from glacial acetic acid, had m. p. 234° (0.8 g., 12%) (Found : N, 5.45. $C_{18}H_9ON$ requires N, 5.5%). From the crystallisation liquors 3.0 g. of the original nitrile, m. p. 74°, were obtained.

4-Cyanomesobenzanthrone (0.2 g.), water (2 ml.), concentrated sulphuric acid (2 ml.), and glacial acetic acid (2 ml.) were boiled for 5 hours and then poured into water. Hydrolysis was found to be incomplete and that part of the product which was insoluble in aqueous sodium carbonate was hydrolysed for a further 9 hours. The combined alkaline extracts on acidification yielded mesobenzanthrone-4-carboxylic acid, yellow crystals (from nitrobenzene), m. p. 314–315° (yield, quantitative) (Found : C, 78.5; H, 3.65. Calc. for $C_{18}H_{10}O_3$: C, 78.8; H, 3.65%). The acid chloride [prepared from the acid (0.2 g.) and excess of thionyl chloride], benzene (10 ml.), and aluminium chloride (0.5 g.) were boiled for 4 hours and poured into concentrated hydrochloric acid and ice. The benzene layer was removed and the aqueous layer extracted 3 times with benzene. The combined benzene extracts, after drying (Na_2SO_4), gave on concentration a brown solid, which was dissolved in benzene and passed through a column of alumina (3 × ½ in.). A yellow zone passed quickly down the column and gave a product which after crystallisation first from benzene and then from ethanol yielded yellow crystals of 4-benzoylmesobenzanthrone, m. p. 176°, undepressed when mixed with the benzoyl compound prepared as above (Found : C, 85.7; H, 4.3%).

4-Methyl-1-naphthonitrile.—4-Bromo-1-methylnaphthalene (10 g.), cuprous cyanide (6 g.), and pyridine (10 c.c.) were heated for 18 hours in an oil-bath, the temperature of which was 215–225°. The product was worked up as for the nitrile described above and gave 4-methyl-1-naphthonitrile, needles (from light petroleum), b. p. 210–220°/40 mm., m. p. 53–54° (Found : N, 8.1. $C_{12}H_9N$ requires N, 8.4%). In view of the above successful synthesis, conversion of the nitrile into 4-benzoylmesobenzanthrone was not attempted.

Oxidation of 4-Benzoylmesobenzanthrone.—4-Benzoylmesobenzanthrone (0.5 g.), chromic anhydride (AnalaR; 1.5 g.), and glacial acetic acid (15 ml.) were boiled for ½ hour and poured into water (150 ml.). 2-Benzoylanthraquinone-1-carboxylic acid thus obtained was dissolved in sodium hydroxide solution, precipitated from the filtered solution by hydrochloric acid, and crystallised from benzene in needles, m. p. 212–216° (10%). A purer acid was obtained by reducing the volume of the above aqueous liquor, whereupon cooling gave the acid, m. p. 234° (lit., 224°) (33%) (Found : C, 72.9; H, 3.3. Calc. for $C_{22}H_{12}O_5$: C, 74.2; H, 3.3%).

The acid (0.2 g.) and 50% hydrazine hydrate (3.0 ml.) were heated for 30 minutes. The dried product (0.2 g.) was crystallised first from glacial acetic acid and then from ethanol to give yellowish crystals of 3- *keto-6-phenyl-2 : 3-dihydroanthraquinono*(1' : 2'-4 : 5)pyridazine, m. p. 324–327° (Found : C, 73.7; H, 3.6; N, 7.4. $C_{22}H_{12}O_2N_2$ requires C, 74.9; H, 3.4; N, 8.0%). The substance was insoluble in

sodium carbonate solution and its ethanolic solutions had a pronounced olive-green fluorescence. *o*-(*p*-Toluoyle)benzoic acid similarly gave 3-*keto*-6-*phenyl*-2:3-*dihydro*-4:5-*benzpyridazine*, colourless plates (from glacial acetic acid), m. p. 258—259°, insoluble in sodium carbonate solution (Found: N, 11.3. C₁₅H₁₃ON₂ requires N, 11.9%). Under similar conditions anthraquinone was unchanged by hydrazine hydrate and anthraquinone-1-carboxylic acid gave the *hydrazinium* salt, m. p. >360° (Found: N, 10.3. C₁₅H₁₃O₄N₂ requires N, 9.9%), which with hydrochloric acid regenerated the original acid.

2-Benzoylanthraquinone-1-carboxylic acid (0.1 g.), pyridine (0.7 ml.), and acetic anhydride (0.35 ml.) were heated on the steam-bath for 3 hours and poured into water. The *acetoxylactone* [5'-*acetoxyl*-5'-*phenyl*-2':5'-*dihydrofuran*-2'-*ono*(3':4'-1:2)*anthraquinone*] separated and crystallised from glacial acetic acid in pale yellow needles, m. p. 255—256° (Found: C, 71.8; H, 3.8. C₂₄H₁₄O₆ requires C, 72.4; H, 3.5%).

2-Benzoylanthraquinone-1-carboxylic acid on decarboxylation at 170° for $\frac{3}{4}$ hour with quinoline and copper gave 2-benzoylanthraquinone, m. p. 216—217° (Found: C, 80.3; H, 3.6. Calc. for C₂₁H₁₂O₃: C, 80.7; H, 3.8%). Under similar conditions anthraquinone-1-carboxylic acid and 1-nitroanthraquinone-2-carboxylic acid gave anthraquinone and 1-nitroanthraquinone respectively, but anthraquinone-2-carboxylic acid and α - and β -naphthoic acids gave only unchanged acids.

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