375. *Kationoid Reactivity of Aromatic Compounds. Part IV. Hydroxylation of* meso*Benzanthrone.*

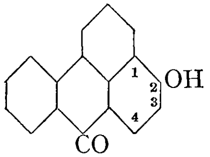
By William Bradley and G. V. Jadhav.

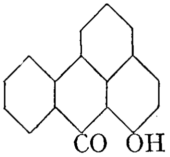
The direct hydroxylation of *meso*benzanthrone by means of potassium hydroxide and an oxidant is shown to yield a mixture of 2- and 4-hydroxy*meso*benzanthrone. These derivatives are formed by replacement of hydrogen situated *para* and *ortho* to a carbonyl group in the respective compounds by hydroxyl.

Many examples are known of the direct replacement of hydrogen, situated either *ortho* or *para* to a nitro- or carbonyl group attached to an aromatic nucleus, by hydroxyl or piperidyl substituents (Bradley and Robinson, J., 1932, 1254; Bradley, this vol., p. 1091). Only in the case of the hydroxylation of nitrobenzene by means of potassium hydroxide (Wohl, *Ber.*, 1899, **32**, 3486. D.R.-P. 116,790) have both *o*- and *p*-derivatives been isolated from the same reaction.

A further instance has now been found in the action of potassium hydroxide on *meso*benzanthrone, which yields both 2- and 4-hydroxy*meso*benzanthrone (I and II respectively). Perkin and Spencer (J., 1922, **121**, 479) observed that 2-hydroxy*meso*benzanthrone was formed when *meso*benzanthrone was fused with potassium hydroxide and potassium chlorate in presence of anthraquinone, and the same compound results when other oxidants are used. The isolation of 4-hydroxy*meso*benzanthrone from the crude hydroxylation product is now described. The yield may reach 8—9% of the *meso*benzanthrone taken or 15—18% of the crude 2-hydroxy*meso*benzanthrone obtained. The 4-hydroxy*meso*benzanthrone was identified by direct comparison with an authentic specimen prepared by dehydrogenating 1-benzoyl-2-naphthol with aluminium chloride (cf. I.G., B.P. 248,791).

(I.)





(II.)

The separation of the isomeric hydroxy*meso*benzanthrones is facilitated by the circumstance that the 2-derivative is a strong acid soluble in sodium hydroxide solution, whereas the 4-derivative forms a salt when fused with potassium hydroxide, but this is almost completely hydrolysed on dilution with water. Further, 4-hydroxy*meso*benzanthrone is readily soluble in hot benzene, whilst the 2-derivative remains practically undissolved. The former affords a characteristic *boroacetate*. Most derivatives of *meso*benzanthrone dissolve in concentrated sulphuric acid to fluorescent orange or red solutions, but 4-hydroxy*meso*benzanthrone gives only a yellow coloration with slight greenish fluorescence, a circumstance which probably indicates the non-occurrence of oxonium salt formation in this instance. Other properties which accord with the formulation of 4-hydroxy*meso*benzanthrone as a chelate structure are the low melting point, 179° (cf. 2-hydroxy*meso*benzanthrone, m. p. 304°; Scholl and Seer, *Annalen*, 1912, **394**, 153), and the resistance of the compound to acetylation. 4-Hydroxy*meso*benzanthrone is remarkably stable to decomposition by fused potassium hydroxide, alone or when mixed with potassium chlorate.

Experimental.

*Boroacetate of 4-Hydroxy*meso*benzanthrone.*—Boroacetic anhydride (5 g.) (Pictet and Geleznoff, *Ber.*, 1903, **36**, 2219) was added to a solution of 4-hydroxy*meso*benzanthrone (2 g., m. p. 179°, prepared by the action of aluminium chloride on 1-benzoyl-2-naphthol) in acetic anhydride (50 c.c.), and the mixture boiled during 15 minutes. On cooling, crystals separated; these were collected, washed with acetic anhydride and with water, and dried. The product was dissolved in chloroform, in which it was easily soluble, and recovered by evaporation of the filtered solution. The residue crystallised from acetic anhydride in yellow needles, decomp. 268° after shrinking at 263° (Found: C, 67·3; H, 4·0. $C_{21}H_{15}O_6B$ requires C, 67·4; H, 4·0%). The *boroacetate* is sparingly soluble in benzene, alcohol or acetic acid.

Action of Potassium Hydroxide and Potassium Chlorate on meso*Benzanthrone in Presence of Anthraquinone.*—A mixture of *meso*benzanthrone (25 g.), potassium chlorate (18 g.), potassium hydroxide (150 g.), and anthraquinone (25 g.) was added to water (37 g.) and slowly heated in an autoclave. When the temperature of the reactants reached 210°, a strongly exothermic reaction occurred and the temperature rose rapidly to 300°. The cold product was extracted with water, then with 5% sodium hydroxide solution until the extracts showed only a faint green fluorescence. Acidification afforded 2-hydroxy*meso*benzanthrone, identified as the acetyl derivative, m. p. 199—200° (Perkin and Spencer, *loc. cit.*). The undissolved portion of the product was dried and extracted with benzene (200 c.c.). A dark brown solid (1·0 g.), m. p. 125—180°, remained when the solvent was evaporated, and this was extracted with acetic anhydride and the filtered solution boiled during 15 minutes with boroacetic anhydride (2 g.). On cooling, yellow needles separated, m. p. 260° (decomp.). Most of the product was easily soluble in chloroform, and evaporation of the filtered solution gave a residue which crystallised from acetic anhydride in yellow needles; these became brown at 255° and melted with decomposition at 263° (Found: C, 67·7; H, 4·1. Calc. for $C_{21}H_{15}O_6B$: C, 67·4; H, 4·0%).

When a modified mode of oxidation was used and the temperature of the reactants was kept at 230—250°, 25 g. of *meso*benzanthrone gave 16 g. of crude 2-hydroxy*meso*benzanthrone (soluble in 7% sodium hydroxide solution), from which 1 g. of 4-hydroxy*meso*benzanthrone could be extracted with benzene. The undissolved residue, further extracted with 0·5% sodium hydroxide solution, gave 0·3 g. of a product (m. p. 160—170°), and this after recrystallisation from glacial acetic acid melted at 176—177° and did not depress the m. p. of authentic 4-hydroxy*meso*benzanthrone (Found: C, 82·7; H, 4·1. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%). When the material which remained undissolved by aqueous alkali was dried and extracted with benzene, 4 g. of crude 4-hydroxy*meso*benzanthrone (m. p. 140—160°) were obtained. The derived boroacetate crystallised from acetic anhydride in yellow needles which became brown at 255° and melted with decomposition at 263° (Found: C, 67·4; H, 4·0%).

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