NOTE.

2-*Methoxy*meso*benzanthrone*. By FAWZY GHALI BADDAR.

THE synthesis of 2-methoxy*meso*benzanthrone (the important intermediate for Caledon Jade Green) is covered by several patents, but no practical details are given. The author now reports favourable conditions for its preparation. 3-Amino*meso*benzanthrone (cf. Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 285) was acetylated with acetic anhydride to 3-acetamido*meso*benzanthrone which, on nitration with fuming nitric acid in acetic acid solution, gave 2-nitro-3-acetamido*meso*benzanthrone (I), and this was hydrolysed with alcoholic sulphuric acid to the amine (II). This gave on diazotisation with sodium nitrite and sulphuric acid a diazo-oxide, which on being refluxed with alcohol and aluminium powder, was reduced to 2-hydroxy*meso*benzanthrone (III) (cf. I. G. Farbenind. A.-G., D.R.-P. 436,525; *Centr.*, 1927, **98**, *I*, 182). The phenol (III) was then methylated to 2-methoxy*meso*benzanthrone (IV), which gave on fusion with potassium hydroxide, the green dye, Caledon Jade Green.

Experimental.—3-*Acetamido*meso*benzanthrone*. 3-Amino*meso*benzanthrone was acetylated by either of two procedures: (i) The finely powdered base (7 g.) was thoroughly mixed with acetic anhydride (20 c.c.) and heated on the water-bath for 15 minutes; the acetyl derivative was precipitated with ether and crystallised from glacial acetic acid in brown-violet needles, m. p. 279—280°. (ii) The crude base (24 g.) was dissolved in boiling glacial acetic acid (700 c.c.), and the filtered solution treated with acetic anhydride (70 c.c.) and heated on the water-bath for one hour; on cooling, the acetyl derivative crystallised in brown-violet needles, m. p. 279—280° (Found: C, 78·9; H, 4·6; N, 5·0. Calc. for $C_{19}H_{13}O_2N$: C, 79·4; H, 4·6; N, 4·9%); yield, 95%. I.G. Farbenind. A.-G., (*loc. cit.*) and Farbwerke vorm. Meister Lucius and Brüning (E.P. 224,522; *Centr.*, 1926, **97**, I, 1717) give m. p.s 225° and 255° respectively.

2-*Nitro*-3-*acetamido*meso*benzanthrone* (I). The solution of 3-acetamido*meso*benzanthrone (20 g.) in hot glacial acetic acid (1200 c.c.) was heated on the water-bath with stirring. A solution of fuming nitric acid (12 c.c.; *d* 1·486) in glacial acetic acid (80 c.c.) was quickly added, and the stirring continued for 15 minutes. The precipitated nitro-derivative was filtered off while hot, and washed with hot acetic acid. On crystallisation from nitrobenzene, 2-nitro-3-acetamido*meso*benzanthrone was obtained in yellow needles, m. p. above 318° (Found: C, 68·4; H, 3·7; N, 8·7. Calc. for $C_{19}H_{12}O_4N_2$: C, 68·7; H, 3·6; N, 8·4%); yield, 18·5 g. I. G. Farbenind. A.-G. (*loc. cit.*) give m. p. 306°.

2-*Nitro*-3-*amino*meso*benzanthrone*. The acetyl derivative (5 g.) was dissolved in concentrated sulphuric acid (50 c.c.), and ethyl alcohol (250 c.c.) slowly added. The mixture was refluxed for 3—4 hours, and the product precipitated with water and filtered off. On crystallisation from nitrobenzene, 2-nitro-3-amino*meso*benzanthrone was obtained in orange-red crystals, m. p. 316—317°, depressed to 190—200° on admixture with (I) (Found: C, 70·3; H, 3·5; N, 9·4. Calc. for $C_{17}H_{10}O_3N_2$: C, 70·3; H, 3·5; N, 9·7%); yield nearly quantitative.

2-*Hydroxy*meso*benzanthrone* (III). 2-Nitro-3-amino*meso*benzanthrone (3 g.) was dissolved in concentrated sulphuric acid (60 c.c.) and cooled in a freezing mixture. The solution was thoroughly stirred, and finely powdered sodium nitrite (1·2 g.) was added portionwise during one hour. During that time crushed ice (100 g.) was slowly added, so that the temperature was not allowed to rise above 20°, and the stirring was continued for a further hour. The product was then precipitated with a further amount of ice (100 g.), allowed to stand overnight, and the precipitated diazo-oxide was filtered off and dried (yield, 2·3 g.). Its alcoholic solution gave a blue coloration when mixed with resorcinol and treated with a drop of dilute sodium hydroxide solution.

The powdered diazo-oxide (2·3 g.) was suspended in alcohol (100 c.c.) and refluxed with aluminium-bronze for 9 hours (until it ceased to give a blue coloration with resorcinol). The alcohol was evaporated, and the residue extracted with boiling sodium hydroxide solution and filtered. The filtrate (charcoal) on acidification precipitated 2-hydroxy*meso*benzanthrone (yield, 1·1 g.) (cf. Farbwerke vorm. Meister Lucius and Brüning, F.P. 588,035; *Centr.*, 1926, **97**, I, 1051).

2-*Methoxy*meso*benzanthrone*. The phenol (III) was dissolved in sodium hydroxide solution, warmed, and treated with methyl sulphate. The precipitated methoxy-compound crystallised from ethyl alcohol in brownish-yellow crystals, m. p. 174—174·5° (Found: C, 82·6; H, 4·7; OMe, 10·9. Calc. for $C_{18}H_{12}O_2$: C, 83·1; H, 4·7; OMe, 11·9%).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, August* 18*th*, 1947.]