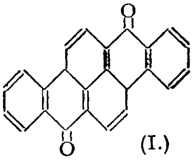
415. *A Synthesis of 3-Acyl- and 3-Aroyl-*meso*benzanthrones.**

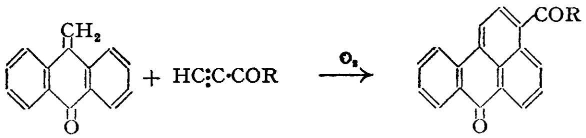
By F. Irving and A. W. Johnson.

3-Acyl- and 3-aroyl-*meso*benzanthrones have been prepared by the reaction of *αβ*-ethynyl ketones and methyleneanthrone.

3-Benzoyl*meso*benzanthrone is an important dye intermediate, for on cyclisation by heating with aluminium chloride–sodium chloride in the presence of oxygen it yields 1 : 2 : 6 : 7-dibenzpyrene-3 : 8-quinone (Indanthrene Golden Yellow GK; I). It is therefore of interest that a simple method has been found for the preparation of 3-aroyl*meso*benzanthrones which are potential sources of dibenzpyrenequinones substituted in one of the terminal rings. The Diels–Alder reaction of methyleneanthrone and αβ-ethynyl ketones proceeds readily in acetic acid solution on warming to give 3-acyl- and 3-aroyl-*meso*benzanthrones in 50—70% yields, the addition being accompanied by oxidation :



(I.)



R = Me, Ph, *o*-$Cl\cdot C_6H_4$, *p*-$Cl\cdot C_6H_4$, *m*-$MeO\cdot C_6H_4$, *p*-$MeO\cdot C_6H_4$, *a*-$C_{10}H_7$.

The αβ-ethynyl ketones required for the Diels–Alder reactions were prepared by chromic acid oxidation of the corresponding carbinols (Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39; Bowden and Jones, *ibid.*, p. 52). The condensation of methyleneanthrone with β-chloropropiophenone (which readily loses hydrogen chloride to give phenyl vinyl ketone) in nitrobenzene solution to give 3-benzoyl*meso*benzanthrone has been described by Allen, Bell, Bell, and van Allan (*J. Amer. Chem. Soc.*, 1940, **62**, 656) although extensions of this method would be restricted by the limited availability of the starting materials.

Experimental.

Preparation of Intermediates.—p-*Methoxyphenylethynylcarbinol.* Purified acetylene was rapidly passed into liquid ammonia (1,000 c.c.) with stirring and cooling, and sodium (23 g.) added in small pieces in such a manner that the blue colour never persisted for more than a few moments. A solution of *p*-methoxybenzaldehyde (redistilled : 136 g.) in ether (100 c.c.) was then added during 1½ hours and the mixture stirred and cooled for a further 3 hours with continued introduction of acetylene. The ammonia was allowed to evaporate overnight, and dilute sulphuric acid (ice) was added to the residue. The product was extracted with ether (3 × 300 c.c.) and the ethereal extracts washed with sodium hydrogen carbonate solution and dried. After removal of the solvent the residue was distilled to yield p-*methoxyphenylethynylcarbinol* (71 g.) as a pale yellow oil, b. p. 146—149°/15 mm. (Found : C, 73·7; H, 6·05. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%). The product readily formed a white insoluble silver derivative.

---

* Patent application pending.

Since the above work was carried out, Rutan and May (*J. Amer. Chem. Soc.*, 1947, **69**, 2017) have described *p*-methoxyphenylethynylcarbinol as a crystalline solid, m. p. 172—173°. This may be a misprint (phenylethynylcarbinol has m. p. 22°). The sample obtained in the above experiment was oxidised directly to the corresponding ketone and no special effort was made to crystallise it.

p-*Methoxyphenyl ethynyl ketone.* To a stirred solution of *p*-methoxyphenylethynylcarbinol (15·6 g.) in acetone (25 c.c.), a solution of chromium trioxide (8·0 g.) in water (30 c.c.) and concentrated sulphuric acid (7 c.c.) was slowly added. The operation, carried out at 5—10° in nitrogen, lasted 1½ hours. After being stirred for a further 30 minutes, the mixture was diluted with water and the product extracted with ether. Evaporation of the ethereal solution gave a yellow solid which was crystallised from aqueous methanol and then petroleum (b. p. 60—80°) to give p-*methoxyphenyl ethynyl ketone* (9·1 g.) as pale yellow needles, m. p. 82—83° (Found : C, 74·7; H, 4·7. $C_{10}H_8O_2$ requires C, 75·0; H, 5·0%). The ketone readily formed a white insoluble silver derivative and a brick-red insoluble copper derivative.

a-Naphthyl ethynyl ketone. a-Naphthylethynylcarbinol was prepared from a-naphthaldehyde (35·6 g.; Badger, *J.*, 1941, 536) by the method described above for *p*-methoxyphenylethynylcarbinol. The crude product (34 g.) was not purified but dissolved in acetone (50 c.c.) and oxidised with a solution of chromium trioxide (18 g.) in water (56 c.c.) and concentrated sulphuric acid (15 c.c.) as described for the preparation of *p*-methoxyphenyl ethynyl ketone. The crude ketone (24 g.) was crystallised from petroleum (b. p. 60—80°) to yield *a-naphthyl ethynyl ketone* as pale yellow plates, m. p. 70—71° (Found : C, 86·25; H, 4·7. $C_{13}H_8O$ requires C, 86·65; H, 4·45%).

Preparation of 3-*Acyl- and* 3-*Aroyl-*meso*benzanthrones.*—3-*Benzoyl*meso*benzanthrone.* Methyleneanthrone (1·3 g.; Clar, *Ber.*, 1936, **69**, 1686) and phenyl ethynyl ketone (1 g.; Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39) were dissolved in acetic acid (6 c.c.) and heated under reflux for ¾ hour. The solution at first became dark brown and then lightened until it was finally golden yellow. 3-Benzoyl-*meso*benzanthrone (1·2 g.), m. p. 186—188°, was deposited on cooling and was crystallised from acetic acid, being obtained as bright yellow prisms, m. p. 193—194° (Allen, Bell, Bell, and van Allan, *loc. cit.*, give 192°).

3-*Acetyl*meso*benzanthrone.* Prepared similarly from methyleneanthrone (5 g.) and methyl ethynyl ketone (1·75 g.; Bowden, Heilbron, Jones, and Weedon, *loc. cit.*) in acetic acid (25 c.c.), 3-acetyl*meso*benzanthrone (3·0 g.) formed bright yellow platelets, m. p. 173—175°, from aqueous acetic acid (I.G. Farben., B.P. 440,263, give m. p. 174—175°).

3-p-*Methoxybenzoyl*meso*benzanthrone.* Prepared similarly from methyleneanthrone (3·9 g.) and *p*-methoxyphenyl ethynyl ketone (3·07 g.) in acetic acid (24 c.c.), 3-p-*methoxybenzoyl*meso*benzanthrone* (2·9 g.) formed yellow prisms, m. p. 194—195°, from acetic acid (Found : C, 82·0; H, 4·6. $C_{25}H_{16}O_3$ requires C, 82·4; H, 4·4%).

3-m-*Methoxybenzoyl*meso*benzanthrone.* Prepared similarly from methyleneanthrone (11·1 g.) and *m*-methoxyphenyl ethynyl ketone (8·85 g.; Johnson and Melhuish, *J.*, 1947, 346) in acetic acid (70 c.c.). 3-m-*Methoxybenzoyl*meso*benzanthrone* after crystallisation from acetic acid formed bright yellow prisms (8·85 g.), m. p. 192—193° (Found : C, 82·8; H, 4·7%).

3-o-*Chlorobenzoyl*meso*benzanthrone.* Methyleneanthrone (62·5 g.) and *o*-chlorophenyl ethynyl ketone (50 g., Johnson, *J.*, 1947, 1626) in acetic acid (750 c.c.) were heated on the steam-bath for 1½ hours. The solution at first became dark and then lightened as the dehydrogenation occurred. 3-o-*Chlorobenzoyl*meso*benzanthrone* (49 g.) separated from the solution on cooling and a further quantity (13 g.) was obtained by cautious dilution of the mother liquors. Crystallisation from acetic acid gave the product as yellow prisms, m. p. 206—207° (Found : C, 78·25; H, 3·75. $C_{24}H_{13}O_2Cl$ requires C, 78·2; H, 3·5%).

3-a-*Naphthoyl*meso*benzanthrone.* Prepared similarly from methyleneanthrone (9·1 g.) and a-naphthyl ethynyl ketone (8 g.) in acetic acid (60 c.c.), the product (7·6 g.) was separated and crystallised from chlorobenzene to yield 3-a-naphthoyl*meso*benzanthrone as dark yellow prisms, m. p. 254—255° (I.G. Farben., D.R.-P. 446,187, give m. p. 244—245°) (Found : C, 87·0; H, 4·15. Calc. for $C_{28}H_{16}O_2$: C, 87·5; H, 4·2%). The product dissolved in concentrated sulphuric acid to a cherry-red solution.

IMPERIAL CHEMICAL INDUSTRIES LTD., RESEARCH LABORATORIES,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.

[*Received, February* 16*th*, 1948.]