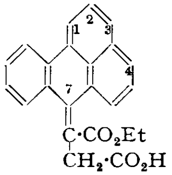
313 *The Stobbe Condensation between* meso*Benzanthrone and Ethyl Succinate.*

By G. R. Clemo, L. Munday, and G. A. Swan.

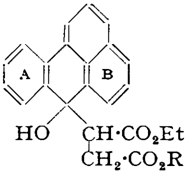
*meso*Benzanthrone and ethyl succinate give an aldol-type condensation product. The low yield and the difficult purification of the product reduce the value of the reaction as a possible synthetic route to higher polycyclic hydrocarbons.

If *meso*benzanthrone reacted in the Stobbe condensation to give (I) and ultimately the corresponding propionic acid derivative, subsequent cyclisation would lead to a polycyclic derivative.

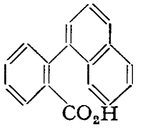
Johnson, Goldman, and Schneider's method (*J. Amer. Chem. Soc.*, 1945, **67**, 1357), in which the reaction is carried out in *tert.*-butanol, gives only very low yields of an impure product because of the low solubility of *meso*benzanthrone in the boiling solvent. However, reaction in boiling toluene, with finely divided potassium *tert.*-butoxide, affords a 16% yield of an acid. Analyses of this acid and of its methyl ester suggest that it is β-carbethoxy-β-(7-hydroxybenzanthren-7-yl)propionic acid (II), the methyl ester being (III). It is known that, in the Stobbe reaction, benzophenone and fluorenone yield substituted itaconic acids (cf. I) (Stobbe, *Annalen*, 1899, **308**, 89; Stobbe and Gollücke, *Ber.*, 1906, **39**, 1066), although an aldol (cf. II) is presumably an intermediate. For elimination of the hydroxyl group and the hydrogen atom of the α-CH group to form the ethylenic bond, the attached groups must become coplanar. A model suggests that this is improbable in the present case as the carbethoxy-group and the hydrogen atoms at positions 6 and 8 come into too close proximity. In the case of benzophenone, the two phenyl groups are free to rotate and so do not interfere.



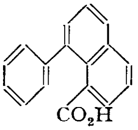
(I.)



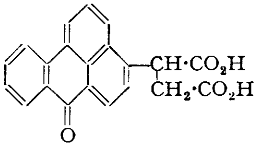
(II; R = H.)
(III; R = Me.)



(IV.)



(V.)



(VI.)

In G.P. 499,320 and 501,282 (*Chem. Zentr.*, 1930, II, 2697, 2696) it is claimed that *meso*benzanthrone can be condensed in position 4 with compounds containing a reactive methylene group. This does not seem to have been proved, however, and under the very mild reaction conditions used therein it would appear unlikely that two hydrogen atoms would be eliminated to give compounds such as (VI).

A possible, but less likely, interpretation of the analytical figures is that the action of potassium *tert.*-butoxide splits *meso*benzanthrone to (IV) or (V), as it is known that non-enolisable ketones may undergo such fission (Swan, *J.*, 1948, 1408), and that reaction with the succinic ester then ensues. However, when *meso*benzanthrone in toluene was treated with potassium *tert.*-butoxide, only a trace of acidic product was obtained: in addition to unchanged *meso*benzanthrone, 4 : 4′-dibenzanthronyl was isolated (the latter was also produced during the Stobbe condensation).

EXPERIMENTAL.

β-Carbethoxy-β-(7-hydroxybenzanthren-7-yl)propionic Acid (II).—To potassium (1·2 g., 0·03 mol.), powdered under toluene (70 c.c.), *tert.*-butanol (2·8 c.c., 0·03 mol.) was added slowly, agitation being continued for 4 hours and the mixture kept overnight at room temperature. *meso*Benzanthrone (6·0 g., 0·026 mol.) and ethyl succinate (7·8 g., 0·045 mol.) were added, and the mixture was stirred and heated under reflux for 6 hours in a current of nitrogen. The solution darkened rapidly. It was then cooled and washed with water (3 × 50 c.c.). The deep-brown aqueous layer was washed with toluene, filtered, and acidified. The resulting pale brown solid (1·55 g.) was dried in a vacuum-desiccator and recrystallised from benzene–light petroleum, giving the *acid* (II) as a fawn-coloured, micro-crystalline solid, m. p. 151—152° (decomp.) after sintering and darkening at 100° (Found: C, 73·55; H, 5·1. $C_{23}H_{20}O_5$ requires C, 73·4; H, 5·3%).

A solution of the acid (0·2 g.) in ethyl acetate (20 c.c.) was treated with one of diazomethane (0·12 g.) in ether (10 c.c.), and the mixture was set aside overnight. The solvents were removed (reduced pressure). The black, tarry residue was extracted with boiling benzene and the solution diluted with light petroleum (b. p. 60—80°). The resulting light-brown solid recrystallised from benzene–light petroleum (charcoal), affording the *methyl* ester (III) as a buff-coloured powder, m. p. 142—146° (decomp.) (Found: C, 74·0; H, 5·2. $C_{24}H_{22}O_5$ requires C, 73·85; H, 5·6%).

Action of Potassium tert.*-Butoxide on* meso*Benzanthrone.*—*meso*Benzanthrone (3 g.) in dry toluene (38 c.c.) was heated under reflux for 8 hours with potassium *tert.*-butoxide (4·4 g.), with the addition of water (0·23 g.), cooled, washed with sodium hydroxide solution and water, dried, and concentrated. On cooling, a yellowish-brown powder separated; this was recrystallised from toluene, giving 4 : 4′-dibenzanthronyl, m. p. 310—315° (lit., 320—321°).

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