The Relation between Self-condensation and Substitution Processes in the Reactions of meso*Benzanthrone with Anions.*

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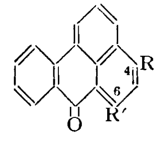
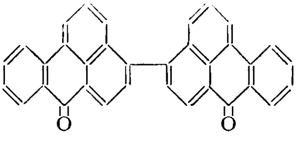
Experiments with *meso*benzanthrone and a series of anions have shown that anions which have the greatest tendency to form covalent links with carbonyl-carbon (*e.g.*, Ph$^-$, NH$_2^-$) react by replacing nuclear hydrogen *ortho* or *para* to the carbonyl group. Anions of higher electron affinity (*e.g.*, OH$^-$, OR$^-$) function mainly as bases and cause the conversion of *meso*benzanthrone into 4 : 4′-di*meso*benzanthronyl.

Previous work has shown that *meso*benzanthrone (I; R = R′ = H) reacts with the anions of weak acids and other bases in one or both of two ways. Nuclear hydrogen situated *ortho* or *para* to the carbonyl group may be replaced by the reagent, or self-coupling of *meso*benzanthrone may occur with the formation of 4 : 4′-di*meso*benzanthronyl (II). The relative importance of the substitution and the self-coupling reaction depends on the reagent employed. Potassium hydroxide in methanol, ethanol, or *iso*propanol at 100—150° gives mainly (II) accompanied by a small amount of 4-hydroxy*meso*benzanthrone (I; R = OH, R′ = H), sodioaniline in aniline at 40° gives 4-anilino*meso*benzanthrone (I; R = Ph·NH, R′ = H) and 50% of (II) (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259), but sodamide gives 6-amino*meso*benzanthrone (I; R = H, R′ = NH$_2$) with no appreciable amount of (II) (Bradley, *J.*, 1948, 1175). From these results it appears that the anions which are most active in forming covalent bonds with carbonyl-carbon, *e.g.*, NH$_2^-$, bring about substitution, whilst those which are less active in this respect, *e.g.*, OH$^-$, function mainly as bases and cause the ionisation of *meso*benzanthrone, so leading to the formation of (II) by the action of the resulting *meso*benzanthrone anion on undissociated *meso*benzanthrone (Bradley and Jadhav, *J.*, 1948, 1622; Bradley and Sutcliffe, *J.*, 1952, 1247). In agreement with this view anions of intermediate activity, *e.g.*, Ph·NH⁻, bring about both substitution and self-condensation simultaneously. These relations have been tested and confirmed in the following experiments, which also indicate the nature of the products that first result from the action of active anions on *meso*benzanthrone. Potassium *tert.*-butoxide in *tert.*-butanol at 90—92° converted (I; R = R′ = H) into (II), only a trace of 4-hydroxy*meso*benzanthrone being formed. Similar results were obtained with potassium *iso*propoxide in *iso*propanol, but potassium phenoxide was without effect. The results with the two alkoxides accord with those of Lüttringhaus and Neresheimer (*loc. cit.*), and it has also been shown that the formation of (II) occurs without evolution of hydrogen, and that when the first reaction is complete the resulting products absorb oxygen. Oxidation implies the intermediate formation of a reduced state of (II), and this could result by the self-addition of two molecules of *meso*benzanthrone to give such structures as (III) and (IV). In this connection reference should be made to the work of Koelsch and Anther (*J. Org. Chem.*, 1941, **6**, 558) who showed that perinaphthenone reacts with phenylmagnesium bromide to give a dihydro-aromatic compound.

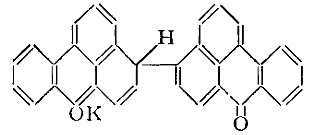
(I)

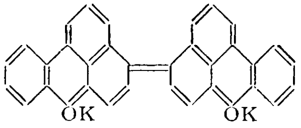




(II)

(III)





(IV)

Using sodioaniline in aniline at the room temperature we obtained the same result as Lüttringhaus and Neresheimer (*loc. cit.*) at 40°. With sodiodiphenylamine in benzene at 80° self-coupling and substitution occurred, 4-diphenylamino*meso*benzanthrone (I; R = Ph_2N, R′ = H) and (II) resulting. Self-coupling was the more important reaction and the yield of (II) accorded with the smaller basic strength of diphenylamine in relation to aniline and the corresponding smaller tendency of its anion to form a covalent link—Conant and Wheland (*J. Amer. Chem. Soc.*, 1932, **54**, 1212) and McEwen (*ibid.*, 1936, **58**, 1124) have recorded the following values of p*K* on an arbitrary scale; phenol, 10; methanol, 16; ethanol, 18; *tert.*-butanol, 19; diphenylamine, 23; aniline, 27; triphenylmethane, 33. There was no evolution of hydrogen when either sodioaniline or sodiodiphenylamine was used, thus confirming the additive character of the self-condensation and the substitution process under the conditions employed. The reaction with sodiodiphenylamine did not take place in ether.

In accord with the feeble acid strength (Brönsted) of benzene and the relation referred to, phenylsodium gave 6-phenyl*meso*benzanthrone (I; R = H, R′ = Ph) (Allen and Overbaugh, *J. Amer. Chem. Soc.*, 1935, **57**, 740), but there was no indication of the formation of (II); nor was there a reaction between *meso*benzanthrone and triphenylmethylsodium, possibly on account of steric factors.

EXPERIMENTAL

meso*Benzanthrone and Potassium* tert.*-Butoxide.*—*meso*Benzanthrone (10 g.) was heated and stirred for an hour at 92° (internal temperature), in an atmosphere of nitrogen, with a solution of potassium *tert.*-butoxide prepared from potassium (15·6 g.) and *tert.*-butanol (250 c.c.). Water was then added, the nitrogen was replaced by oxygen, and stirring was continued. Absorption of oxygen occurred and when it was complete more water was added. A solid separated and this was collected, washed, dried (yield, 7·1 g.), and identified as 4 : 4′-di*meso*benzanthronyl, m. p. 315°.

In a similar experiment in which *meso*benzanthrone (10 g.) was stirred for an hour at 90—

92° with potassium *iso*propoxide prepared from potassium (15·6 g.) and *iso*propanol (122 c.c.), it was shown that no evolution of gas occurred during the reaction, and that on the further addition of water, admission of oxygen, filtration, and purification of the alkali-insoluble product, the yield of 4 : 4'-di*meso*benzanthronyl, m. p. 313°, was 5·0 g. In this experiment the alkaline filtrate yielded 0·1 g. of 4-hydroxy*meso*benzanthrone.

*meso*Benzanthrone (1 g.) was recovered unaltered after 1·5 hours' heating with potassium hydroxide (3 g.) in phenol (10 g.).

meso*Benzanthrone and Sodioaniline.*—As directed by Lüttringhaus and Neresheimer (*loc. cit.*) *meso*benzanthrone (7·5 g.) was added at the room temperature to a solution prepared by refluxing sodium (2·5 g.) with " AnalaR " aniline (50 c.c.) in nitrogen for 2·5 hr. The reactants were stirred for 4 hr.; there was no rise in temperature or evolution of hydrogen. Alcohol (50 c.c.) and then water (200 c.c.) were added, and again no evolution of gas occurred. When the nitrogen was replaced by oxygen, however, absorption occurred. When the reaction was complete the products were 4 : 4'-di*meso*benzanthronyl (2·9 g.; m. p. 315°) and 4-anilino*meso*benzanthrone (3·2 g.; m. p. 214—215°, after recrystallisation from xylene).

meso*Benzanthrone and Sodiodiphenylamine.*—(*a*) Sodamide (8 g.), diphenylamine (150 g.), and benzene (75 c.c.) were stirred and heated under reflux until evolution of ammonia ceased (2 hr.). The product was cooled, *meso*benzanthrone (10 g.) was added, and stirring was continued at the room temperature for 24 hr. There was no evolution of gas at this stage. Alcohol (100 c.c.) was added, and steam was admitted until all unchanged diphenylamine had been removed. The residue was collected, washed, and dried. On extraction with acetone an insoluble portion (4·75 g.) remained which was identified as 4 : 4'-di*meso*benzanthronyl, m. p. 313°. The soluble fraction was isolated and passed in benzene down an alumina column (50 × 2·5 cm.). The adsorbed band was developed by means of benzene and the main, reddish-brown portion was separated and eluted with acetone. The extract gave 3·5 g. of an orange-brown solid, m. p. 147—170°. This was separated by chromatography from benzene on alumina into two orange-brown bands. The more strongly retained afforded *meso*benzanthrone (1 g.), m. p. 170—172°. The lower band was a product which, eluted and crystallised from benzene, formed small, orange-yellow needles (1·6 g.), m. p. 200—202° (Found: C, 87·2; H, 4·8; N, 3·8. $C_{29}H_{19}ON$ requires C, 87·7; H, 4·9; N, 3·6%), identical with 4-*diphenylamino*meso*benzanthrone* prepared from 4-iodo*meso*benzanthrone and diphenylamine. It showed light absorption maxima in " AnalaR " pyridine at 3980 (ε 7400) and 4680 Å (ε 15,400).

(*b*) Sodamide (8 g.), diphenylamine (33·8 g.), and dry ether (200 c.c.) were stirred at the room temperature and then refluxed. When the evolution of ammonia ceased (2 hr.), *meso*benzanthrone (10 g.) and ether (50 c.c.) were added, and the stirring and heating were resumed for 3 hr. There was no evidence of reaction; 8·5 g. of *meso*benzanthrone, m. p. 171—172°, were recovered.

4-*Diphenylamino*meso*benzanthrone.*—Diphenylamine (2 g.), 4-iodo*meso*benzanthrone (0·5 g.), copper bronze (0·01 g.), and nitrobenzene (5 c.c.) were heated under reflux for 5 hr. and then distilled in steam. The residual dark tar was extracted with benzene, the solution was chromatographed on alumina, and the adsorbed band was developed with benzene. An orange band passed through the column and from this was obtained 4-diphenylamino*meso*benzanthrone, m. p. 198—200°, identical with the same compound described under (*a*).

meso*Benzanthrone and Phenylsodium.*—As instructed by Gilman (*J. Amer. Chem. Soc.*, 1940, **62**, 1514) phenylsodium was prepared under nitrogen, below 40°, by adding bromobenzene (31·4 g.) to powdered sodium (9·2 g.) in dry benzene (100 c.c.). *meso*Benzanthrone (10 g.) was added and the reactants were stirred at the room temperature for 3 hr. No evolution of gas or rise in temperature was noted. Alcohol (50 c.c.) and water (200 c.c.) were added, the nitrogen was replaced by oxygen, and the products were vigorously stirred. The benzene layer was separated, washed with water, and distilled in steam, finally in superheated steam. The residue was a green, resinous mass and this was dissolved in benzene and chromatographed on a column of alumina (30 × 2·5 cm.). On treatment with benzene first a green, then a brown, band passed through the column, leaving behind a main brown band; this was eluted with benzene containing 5% by volume of methanol. The solutes were isolated from the three eluates and each was stirred with ether and yielded a quantity of brownish-yellow crystals. These were collected, combined (1·5 g.), and recrystallised from benzene (m. p. 186—188°). The ether-soluble materials were similarly isolated, combined, and heated in a molecular still at approx. 200—230°/10^{-5} mm. The orange, resinous distillate (4 g.), when stirred with ether, gave a solid, and this after purification from benzene afforded an additional 1·3 g. of crystals, m. p. 182—185°. The two crops of crystals were united and then recrystallised from benzene (charcoal). 6-Phenyl*meso*benzanthrone, m. p. 187—187·5°, was obtained, identical with the compound prepared from *meso*benzanthrone and phenylmagnesium bromide (Allen and Overbaugh, *loc. cit.*). In solution in " AnalaR " pyridine the 6-phenyl*meso*benzanthrone showed maximum light absorption at 3640 (ε 8100) and 3900 Å (ε 9300).

There was no reaction when triphenylmethylsodium, prepared from triphenylmethyl chloride (27·8 g.) according to *Org. Synth.*, Coll. Vol. II, p. 607, was added to a suspension of *meso*benzanthrone (10 g.) in benzene (50 c.c.), or when benzene (100 c.c.) was added subsequently, the ether being removed by distillation, and the reactants were heated for a further 4 hr.

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