275. *The Synthesis of 8-Phenyl*meso*benzanthrone.*

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Two syntheses of 8-phenyl*meso*benzanthrone are described.

FEW 8-substituted *meso*benzanthrones have been reported, partly because efforts to synthesise them have been nullified by the attendant isomerisation under the action of aluminium chloride.[1] We have synthesised 8-phenyl*meso*benzanthrone by two methods without using aluminium chloride, but neither method is of preparative value. 1-Oxoperinaphthene-2-carboxylic acid (I) condensed with phenylbutadiene to give a product which is either 8- or 11-phenyl*meso*benzanthrone.[2] It was proved to be the former (II) since it was identical with the substance obtained by heating 1-phenylphenanthraquinone (III) with sulphuric acid, ferrous sulphate, and glycerol.[3] The ultraviolet spectrum of 8-phenyl*meso*benzanthrone closely resembles those of *meso*benzanthrone and 3- and 6-phenyl*meso*benzanthrone,[4] and differs from that of 2-phenyl*meso*benzanthrone (see Figure).

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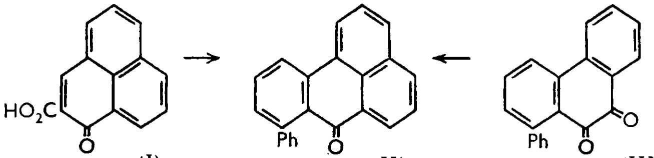
[1] Mayer, Fleckenstein, and Gunther, *Ber.*, 1930, **63**, 1466.

[2] Cf. Fieser and Newton, *J. Amer. Chem. Soc.*, 1942, **64**, 920.

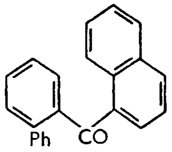
[3] Turski and Pragierowa, *Przemysl Chem.*, 1929, **13**, 33; *Chem. Abs.*, 1929, **23**, 1899.

[4] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235; Hartmann and Lorenz, *Z. Naturforsch.*, 1952, **7a**, 360.

This absence of interaction between the phenyl and the *meso*benzanthrone residues in the 3-, 6-, and 8-phenyl compounds is similar to that encountered in the 1-arylnaphthalenes and in the 1-aryl- and 1 : 5- and 1 : 8-diaryl-anthraquinones and is attributed to steric inhibition of planarity of the aryl groups with the rest of the molecule.[5]



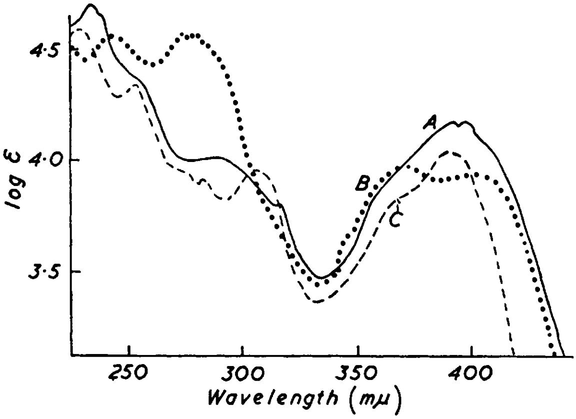
(I) (II) (III)



(IV)

Attempts to convert 1-phenylanthraquinone into phenyl*meso*benzanthrones by heating it with glycerol and sulphuric acid were unsuccessful owing to sulphonation of the phenyl nucleus.

Heating 1-*o*-phenylbenzoylnaphthalene (IV) with aluminium chloride gave a mixture from which only *meso*benzanthrone in very small quantity was isolated. The same method with 1-*p*-phenylbenzoylnaphthalene yielded 10-phenyl*meso*benzanthrone, confirming the results of previous workers,[6] but there was evidence that other products had been formed.



*Ultraviolet absorption spectra of (A) 8-phenyl-*meso*benzanthrone, (B) 2-phenyl*meso*benzanthrone, and (C)* meso*benzanthrone.*

The preparation of 1-*o*-phenylbenzoylnaphthalene (IV) presented some points of interest. Methyl *o*-phenylbenzoate and excess of 1-naphthylmagnesium bromide gave 2-diphenylyl-1-naphthylmethanol (IV; CO replaced by CH·OH) whose spectrum resembled that of α-1-naphthylbenzyl alcohol. Presumably the ketone first formed was reduced by the Grignard reagent since it is known that 1-benzoylnaphthalene is reduced in this way to the alcohol.[7]

o-Phenylbenzoyl chloride and naphthalene in the presence of aluminium chloride yielded fluorenone and indeed the mere distillation of the acid chloride in the absence of catalyst yielded the same product. 1-Naphthonitrile and 2-diphenylylmagnesium iodide, however, afforded 1-*o*-phenylbenzoylnaphthalene (IV), which formed a dinitrophenylhydrazone and whose ultraviolet spectrum resembled that of 1-benzoylnaphthalene. Attempts to reduce the ketone with lithium aluminium hydride and with potassium borohydride were unsuccessful and the Meerwein–Ponndorf method somewhat unexpectedly yielded mainly 1-2′-phenylbenzylnaphthalene (IV; CH_2 for CO) although similar reductions

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[5] Braude, Fawcett, and Webb, *J.*, 1954, 1049; Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

[6] Scholl and Seer, *Annalen*, 1912, **394**, 148; Schmidlin and Garcia-Banus, *Ber.*, 1912, **45**, 3183.

[7] Blicke and Powers, *J. Amer. Chem. Soc.*, 1929, **51**, 3378; Davies, Dixon, and Jones, *J.*, 1930, 1916.

to a methylene group have occasionally been reported.[8] The benzyl compound was also prepared by dehydrogenating 1 : 2-dihydro-4-2′-phenylbenzylnaphthalene, and (along with other products) by the interaction of 2-phenylbenzyl bromide and naphthalene in carbon disulphide in the presence of aluminium chloride.

EXPERIMENTAL

M. p.s were determined on a Kofler block; chromatographic separations were effected on alumina; and fluorescence observations were made under a Hanovia ultraviolet lamp.

Syntheses of 8-*Phenyl*meso*benzanthrone*.—(*a*) 1-Oxoperinaphthene-2-carboxylic acid (1 g.) was boiled (19 hr.) with 1-phenylbuta-1 : 3-diene (6 ml.) in acetic acid (40 ml.). The residue obtained after steam-distillation of the mixture was dissolved in ether–benzene, dried (Na_2SO_4), and evaporated to dryness. The residue in benzene was chromatographed on a column 14″ × ¾″ and was developed with benzene. A yellow zone with a dull yellow fluorescence yielded on elution and evaporation 8-*phenyl*meso*benzanthrone* (22%), yellow needles (from benzene or ethanol–acetic acid), m. p. 201—202° (Found: C, 90·2; H, 4·6. $C_{23}H_{14}O$ requires C, 90·2; H, 4·6%), $\lambda_{max.}$ (log ε in parentheses), 233 (4·64), 288 (3·98), 318 (3·76), 395 mμ (4·12), giving in concentrated sulphuric acid a dark red solution with an orange fluorescence even in daylight.

(*b*) 1 : 2 : 3 : 4-Tetrahydro-1-oxophenanthrene was obtained in 85% yield by the ring-closure of 4-1′-naphthylbutanoic acid with polyphosphoric acid (12 g. of phosphoric oxide and 10 ml. of phosphoric acid per g. of acid) and was converted into 1-phenylphenanthrene. Oxidation with chromic anhydride and acetic acid yielded 1-phenylphenanthraquinone, orange plates (3·8 g.), m. p. 229—230°, after two crystallisations from ethanol, and identical with a sample prepared by another method.[9]

The quinone (0·47 g.) in concentrated sulphuric acid (15 c.c.) was added to ferrous sulphate heptahydrate (9·0 g.) and glycerol (1·0 g.) in water (10 c.c.) and heated at 100° (1 hr.) and then 150—160° (1 hr.). The mixture was poured into water (100 c.c.) and kept for 3 hr., and the precipitate filtered off and washed with water. The residue was extracted with chloroform (24 hr.), and the solvent evaporated. The residue in benzene was chromatographed on a column 8″ × ½″. Development with benzene yielded a bright yellow zone which on elution with benzene gave 8-phenyl*meso*benzanthrone, yellow needles (20 mg.) (after two crystallisations from ethanol), m. p. 198°, undepressed when mixed with a sample prepared by the first method.

Ring-closure of 1-o-*Phenylbenzoylnaphthalene*.—The ketone (500 mg.), aluminium chloride (2 g.), and sodium chloride (750 mg.) were fused for 1 hr. in an oil-bath at 120—130°. Decomposition of the cooled mass by ice and hydrochloric acid gave a precipitate, which was washed with dilute hydrochloric acid and water, and boiled with acetic acid. The acetic acid on evaporation gave a residue which in benzene was chromatographed on a column 4 × ¼″. The main yellow zone, on elution, yielded an orange solid (15 mg.), which after crystallisation (twice) from methanol gave yellow needles, m. p. 171—173°, undepressed when mixed with *meso*benzanthrone, m. p. 171°, but there was evidence that the compound was not pure.

Ring-closure of 1-p-*Phenylbenzoylnaphthalene*.—Cyclisation was performed as described above, and somewhat impure 10-phenyl*meso*benzanthrone (60 mg.), yellow needles, m. p. 169—171° (lit., 170—171°, 174—175°), was obtained after chromatography and crystallisation from acetic acid and from 80% methanol. A big m. p. depression was obtained when the product was mixed with *meso*benzanthrone.

Preparation of 2-*Diphenylyl*-1-*naphthylmethanol*.—Methyl diphenyl-2-carboxylate (10 g.) in anhydrous benzene was added to the Grignard reagent prepared from 1-bromonaphthalene (37·2 g.), magnesium (4·4 g.), anhydrous ether (100 c.c.), and benzene (25 c.c.). The mixture was distilled until the distillation temperature reached 55°. It was then boiled for 18 hr. and poured into hydrochloric acid and ice. The two layers were separated and the aqueous layer was extracted with benzene. The organic layers were combined and steam-distilled. The residual oil was dissolved in a boiling mixture of acetic acid and ethanol. The cooled solution deposited 2-*diphenylyl*-1-*naphthylmethanol* (70%), pale yellow prisms (after two crystallisations from acetic acid), m. p. 154—155° (Found: C, 89·2; H, 5·5. $C_{23}H_{18}O$ requires C, 89·0; H,

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[8] Campbell and Woodham, *J.*, 1952, 843; Coffey and Boyd, *J.*, 1954, 2468.

[9] Leaver, unpublished results; Fuson and Tomboulian, *J. Amer. Chem. Soc.*, 1957, **79**, 956.

5·9%). The substance in concentrated sulphuric acid gives a violet solution with a blue fluorescence.

Preparation of 1-o-*Phenylbenzoylnaphthalene.*—1-Naphthonitrile (6·5 g.) in anhydrous benzene (75 c.c.) was added to the Grignard reagent made from 2-iododiphenyl (16·5 g.), magnesium (1·65 g.), and anhydrous ether (165 c.c.). Solvent (50 c.c.) was distilled from the solution, and the remaining solution boiled for 14 hr. To the mixture were added dropwise water (20 c.c.) and then concentrated hydrochloric acid (20 c.c.). The solvent were removed in a vacuum, glacial acetic acid (10 ml.) was added, and the mixture heated for 1 hr. on the water-bath. The mixture was steam-distilled until no more oil appeared in the distillate and the residue, which solidified on cooling, was dissolved in hot acetic acid (150 ml.), and the red solution slowly cooled. 1-o-*Phenylbenzoylnaphthalene* (66%) separated; it formed yellow prisms (from ethanol), m. p. 130° (Found: C, 89·5; H, 5·4. $C_{23}H_{16}O$ required C, 89·6; H, 5·2%). The substance gives a red solution showing a yellow fluorescence in sulphuric acid and forms by Brady's method (with the boiling extended to 14 hr.) a dinitrophenylhydrazone, dark red prisms, m. p. 216—220°, which was not obtained pure (Found: N, 10·6. Calc. for $C_{29}H_{20}O_4N_4$: N, 11·5%).

1-2'-*Phenylbenzylnaphthalene.*—The above ketone (1·0 g.) was boiled for 1 hr. with aluminium *iso*propoxide prepared from aluminium (0·5 g.) in anhydrous propanol-2-ol. The condenser was replaced by a Hahn partial-reflux condenser with methanol as cooling agent. After 2 hr. no more acetone came over and the mixture was boiled under a full-reflux condenser for 14 hr. Removal of the solvent gave a residue which was decomposed with 4N-sulphuric acid and ice, and the resultant oil was extracted with ether. The dried (Na_2SO_4) ether solution was evaporated in a vacuum, and gave impure 1-2'-phenylbenzylnaphthalene, colourless needles (0·5 g.) (from ethanol), m. p. *ca.* 96° (Found: C, 94·3; H, 5·7. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%).

Ethyl diphenyl-2-carboxylate (6 g.) in ether (100 ml.) was added to lithium aluminium hydride (1 g.) in ether (75 ml.), stirred for ¾ hr., boiled for ½ hr., kept overnight, and after the usual procedure yielded 2-*phenylbenzyl alcohol* (80%), b. p. 179—180°/9 mm., m. p. 41—42° (Found: C, 86·2; H, 6·5. $C_{13}H_{12}O$ requires C, 84·8; H, 6·6%). The alcohol (87%) was also obtained by a similar reduction of *o*-phenylbenzoic acid. 2-Phenylbenzyl bromide (5 g.) (from the alcohol and hydrobromic acid) in ether (100 ml.) was added to magnesium (0·5 g.) in ether (40 ml.) at 0—5°, and to the stirred Grignard reagent 1-tetralone (3 g.) in ether (40 ml.) was added at 0—5°. Decomposition with ice and hydrochloric acid gave an oil, which when cooled in carbon dioxide–acetone afforded crystalline 1 : 2-*dihydro*-4-2'-*phenylbenzylnaphthalene*, needles (from light petroleum), m. p. 112—112·5° (Found: C, 92·5; H, 6·6. $C_{23}H_{20}$ requires C, 93·2; H, 6·8%). It gives an orange colour in sulphuric acid. Dehydrogenation with palladised charcoal in an atmosphere of carbon dioxide yielded 1-2'-*phenylbenzylnaphthalene*, needles (from acetic acid), m. p. 121—122° with sublimation (Found: C, 93·7; H, 6·2. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%). This compound (50 mg.) was also obtained by keeping naphthalene (3·5 g.), 2-phenylbenzyl bromide (3 g.), and stannic chloride (2 g.) in carbon disulphide (18 ml.) for 2 days and boiling (6 hr.), followed by decomposition with ice and hydrochloric acid.

Spectroscopic Measurements.—The ultraviolet spectra of the following substances were measured by means of a Unicam S.P. 500 quartz spectrophotometer. The solvent was 95% ethanol and log ε is given in parentheses. 2-Phenyl*meso*benzanthrone: 243, 275, 370, 403 mμ (4·53, 4·54, 3·95, and 3·92). 3-Phenyl*meso*benzanthrone: 230, 290, 305, 407 mμ (4·58, 4·12, 4·03, 4·15). 6-Phenyl*meso*benzanthrone: 232, 258, 283, 324, 395 mμ (4·56, 4·43, 4·12, 3·79, and 3·94).

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