57.—*Benzanthrones. Part IV. The Synthesis of 2- and 4-Methyl-1-phenylnaphthalene-2′-carboxylic Acids. The Conversion of Benzfluorenones into Benzanthrones.*

By Fawzy Ghali Baddar.

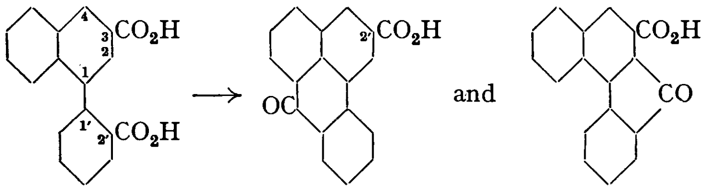
Interaction between diazotised methyl anthranilate and 1- and 2-methylnaphthalene gave a mixture of acids and 1-phenyl-2-methylnaphthalene-2′-carboxylic acid respectively.

Cyclisation of *o*-α-naphthylbenzoic acid, and of 1-*phenyl*-4-*methylnaphthalene*-2′-*carboxylic acid,* gave a mixture of a benzfluorenone and a benzanthrone. Contrary to Schaarschmidt the ring closure of 1-phenylnaphthalene-2′ : 3-dicarboxylic acid led to the formation of a trace of 3 : 4-benzfluorenone-1-carboxylic acid besides the main product, *meso*benzanthrone-2′-carboxylic acid. The latter compound was also obtained by heating 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride with aluminium chloride and sodium chloride. Similar treatment of 3 : 4-benzfluorenone with aluminium chloride gave *meso*benzanthrone.

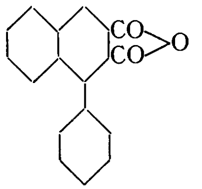
1-PHENYL-2-METHYLNAPHTHALENE-2′-CARBOXYLIC acid was prepared by the condensation of diazotised methyl anthranilate with 2-methylnaphthalene at 45° (cf. Grieve and Hey, J., 1938, 108; Heilbron, Hey, and Wilkinson, *ibid.*, p. 699). 1-*Phenyl*-4-*methylnaphthalene*-2′-*carboxylic acid,* which could not be obtained from 1-methylnaphthalene by this method, was easily prepared from 1-*iodo*-4-*methylnaphthalene* and methyl *o*-iodobenzoate by the Ullmann reaction (cf. Baddar and Warren, Part I, J., 1938, 401).

In Part I (*loc. cit.*) it was stated that, contrary to Schaarschmidt and Georgeacopol (*Ber.*, 1918, **51**, 1082), *o*-α-naphthylbenzoic acid and its 4-ethyl derivative gave on ring closure, both with phosphorus pentachloride, followed by aluminium chloride, and with sulphuric acid, a mixture of a benzfluorenone and a benzanthrone. Grieve and Hey (*loc. cit.*) reported the same results as Schaarschmidt and Georgeacopol (*loc. cit.*), without the isolation of 3 : 4-benzfluorenone. The present author has confirmed the results of Baddar and Warren : the cyclisation of *o*-α-naphthylbenzoic acid with phosphorus pentachloride, followed by aluminium chloride, at 20° or at 60° and with concentrated sulphuric acid at 0°, 20°, or 50° gave a mixture of benzfluorenone and benzanthrone. The same results were obtained when 10% boric acid–sulphuric acid solution or phosphoric oxide was used. Cyclisation of 1-phenyl-4-methylnaphthalene-2′-carboxylic acid by aluminium chloride or sulphuric acid gave a mixture of 2-*methyl*-3 : 4-*benzfluorenone* and 1′-methyl-*meso*benzanthrone, whereas ring closure of 1-phenyl-2-methylnaphthalene-2′-carboxylic acid gives (Baddar and Warren, Part II, J., 1939, 944) only 3′-methyl*meso*benzanthrone owing to the blocking of the 2-position.

Schaarschmidt (*Ber.*, 1917, **50**, 294) isolated only *meso*benzanthrone-2′-carboxylic acid (II) by the ring closure of 1-phenylnaphthalene-2′ : 3-dicarboxylic acid (I) with aluminium chloride or concentrated sulphuric acid : the present author isolated the same product (II) and inferred the formation also of a trace of 3 : 4-benzfluorenone-1-carboxylic acid (III) from the production of 3 : 4-benzfluorenone on decarboxylation.



(I.) (II.) (III.)



(IV.)

The inference that only a trace of 3 : 4-benzfluorenone-1-carboxylic acid (III) is formed suggests that the reactivity of the carbon atom in position 2 is diminished by the proximity of the carboxyl group. Such a deactivating effect appears to be responsible for the production of 1-phenylnaphthalene-2′ : 3-dicarboxylic acid (I), by the fusion of 3 : 4-

benzfluorenone-1-carboxylic acid (III) with potash (Schaarschmidt, *loc. cit.*), and not a mixture of two acids as in the case of benzfluorenone itself (Schaarschmidt and Georgeacopol, *loc. cit.*).

Stobbe (*Ber.*, 1907, **40**, 3383) stated that when 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (IV) was treated with cold concentrated sulphuric acid, 3 : 4-benzfluorenone-1-carboxylic acid (III) was obtained. Schaarschmidt and Korten (*Ber.*, 1918, **51**, 1074), on trying to hasten this reaction by using hot 91% sulphuric acid, obtained *meso*benzanthrone-2′-carboxylic acid (II) in poor yield. The latter authors stated also that, although benzfluorenone was sulphonated on similar treatment, yet the development of fluorescence could be considered as an indication of its partial transformation into *meso*benzanthrone.

The best reagent for converting a benzfluorenone into a benzanthrone is a melt of aluminium chloride and sodium chloride. The old method of Schaarschmidt (*loc. cit.*) for converting (IV) quantitatively into (II) was carried out in three steps. It is possible, however, under the influence of aluminium chloride to effect a direct conversion in good yield. The transformation undoubtedly includes the formation of 3 : 4-benzfluorenone-1-carboxylic acid (III) as an intermediate product, which is then converted into *meso*-benzanthrone-2′-carboxylic acid (II). The mechanism of the reaction is not known, but it involves the fission of the five-membered ring, followed by formation of the six-membered one.

EXPERIMENTAL.

1-*Phenyl-2-methylnaphthalene-2′-carboxylic Acid.*—A mixture of diazotised methyl anthranilate (25 g.; 1 mol.) and 2-methylnaphthalene (50 g.; 2·1 mols.) in 200 c.c. of carbon tetrachloride was stirred at 0—5° while sodium hydroxide solution (31·5 g., 2 mols., in 50 c.c. of water) was added during 1 hour. The temperature was kept at 0—10° for 1½ hours, raised to 45° during 3½ hours, and maintained for 5 hours. The carbon tetrachloride layer was separated, washed with sodium hydroxide solution and with water, and distilled at the ordinary pressure to remove unchanged 2-methylnaphthalene and the by-products, b. p. 230—250°; the remainder was distilled under reduced pressure, and the fraction, b. p. 195—215°/7 mm., hydrolysed. The acid obtained was twice crystallised from methyl alcohol to give 1-phenyl-2-methylnaphthalene-2′-carboxylic acid (1·1 g.), m. p. 188° (Found: C, 82·3; H, 5·3. Calc. for $C_{18}H_{14}O_2$: C, 82·4; H, 5·4%).

1-*Iodo-4-methylnaphthalene* was obtained from 4-methyl-α-naphthylamine as an orange-yellow mobile liquid, b. p. 159°/6 mm., in 51% yield (Found: I, 47·3. $C_{11}H_9I$ requires I, 47·4%).

1-Iodo-4-methylnaphthalene (3·8 g.; 1 mol.), methyl *o*-iodobenzoate (8 g.; 2·1 mols.), and copper bronze (4 g.; 4·5 mols.) were heated at 180—190° for 5 hours. The resulting 1-*phenyl-4-methylnaphthalene-2′-carboxylic acid* crystallised from methyl alcohol in colourless rods (0·6 g.), m. p. 200—201° (Found: C, 82·4; H, 5·4. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%). The yield of diphenic acid was 2·1 g. (for details, see Part I, *loc. cit.*).

Ring closure of the acid chloride of the above acid with aluminium chloride, and fractional crystallisation of the product from methyl alcohol and then from acetic acid, gave 2-*methyl-3 : 4-benzfluorenone* in orange-red crystals, m. p. 148—149° (Found: C, 88·6; H, 5·3. $C_{18}H_{12}O$ requires C, 88·5; H, 5·0%), and 1′-methyl*meso*benzanthrone in yellow silky needles, m. p. 162—163° (F.P. 631,995; *Centr.*, 1928, I, 2210, gives m. p. 164°) (Found: C, 88·3; H, 5·0. Calc. for $C_{18}H_{12}O$: C, 88·5; H, 5·0%).

Ring closure of the acid with 90% sulphuric acid resulted mainly in the benzfluorenone. The isolation of pure 1′-methyl*meso*benzanthrone, which was rather tedious by the ordinary method of fractional crystallisation, was easily accomplished by heating the mixture with concentrated sulphuric acid at 100° for 2 hours, whereby the benzfluorenone was sulphonated.

meso*Benzanthrone-2′-carboxylic Acid.*—1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride (2 g.) was added to a melt of aluminium chloride (20 g.) and sodium chloride (4 g.) at 100°. The temperature was raised to 150° during ½ hour and kept at 140—150° for 2½ hours. The hot brown mixture was poured on ice and digested with dilute hydrochloric acid. After filtration the product was dissolved in hot sodium carbonate solution, boiled (charcoal), filtered, and acidified with hydrochloric acid. The precipitated jelly-like acid was filtered off, dried, and crystallised from nitrobenzene, from which *meso*benzanthrone-2′-carboxylic acid was obtained in 85% yield in silky yellow needles, m. p. 347—348°, undepressed by an authentic specimen (Schaarschmidt, *loc. cit.*, and Schaarschmidt and Korten, *loc. cit.*, give m. p. 347°).

meso*Benzanthrone.*—The preceding acid (0·35 g.; 1 mol.) and copper-bronze (0·08 g.; 1 mol.) were refluxed in quinoline (5 c.c.) for 1 hour, benzene added, and the filtered solution repeatedly extracted with dilute hydrochloric acid. The product was crystallised from methyl alcohol, giving *meso*benzanthrone in yellow needles, m. p. and mixed m. p. 170°, in nearly quantitative yield.

3 : 4-*Benzfluorenone.*—3 : 4-Benzfluorenone-1-carboxylic acid was treated with copper-bronze as described above. The product was crystallised from alcohol, from which 3 : 4-benzfluorenone separated in orange crystals, m. p. 160°, identical with an authentic specimen. This method gave a better yield (71%) than that of Schaarschmidt and Georgeacopol (*loc. cit.*) and Schaarschmidt (*Ber.*, 1916, **49**, 1540).

Conversion of 3 : 4-*Benzfluorenone into* meso*Benzanthrone.*—Benzfluorenone (1·2 g.) was added to a melt of aluminium chloride and sodium chloride (15 g. and 3 g. respectively) at 100°, and the temperature raised to 145° during ½ hour and maintained for 1½ hours. The product was poured on ice, and the precipitated sticky solid extracted with benzene, decolourised with animal charcoal, and crystallised from methyl alcohol to give *meso*benzanthrone, m. p. 160—165°, in 62% yield. After two crystallisations from alcohol the m. p. was 169—170°, not depressed by an authentic specimen.

Ring Closure of o-α-*Naphthylbenzoic Acid.*—(1) The acid was mixed with concentrated sulphuric acid and left either (*a*) in the ice chest for 3 days or (*b*) at room temperature (20°) for 24 hours. (2) The acid chloride, prepared by means of phosphorus pentachloride, was cooled in ice, treated with aluminium chloride, and left overnight at room temperature. (3) The acid (0·2 g.) was dissolved in benzene (4 c.c.) and treated with phosphoric oxide (2 g.). The mixture was heated for 4 hours at 60° and poured on ice, and the product worked up in the usual way. In all three cases the product was a mixture of benzanthrone and benzfluorenone.

Ring Closure of 1-*Phenylnaphthalene*-2′ : 3-*dicarboxylic Acid.*—The crystallised acid was refluxed for 4 hours with acetic anhydride (5 parts) to convert any trace of the isomeric 1-phenylnaphthalene-2 : 3-dicarboxylic acid into its anhydride (IV). The acetic anhydride solution was decomposed with warm aqueous sodium carbonate, filtered from any insoluble anhydride (IV), and acidified. The precipitated acid was crystallised from acetic acid and cyclised with concentrated sulphuric acid. The product (0·85 g.) was separated into its constituents by two methods : (*a*) Crystallisation from nitrobenzene gave pure *meso*benzanthrone-2′-carboxylic acid. The mother-liquor was steam-distilled; the residue (0·1 g.) gave pure benzfluorenone on decarboxylation. (*b*) The product was decarboxylated; fractional crystallisation from methyl alcohol then gave *meso*benzanthrone and a trace of benzfluorenone.

FOUAD I UNIVERSITY, ABBASSIA, CAIRO.

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