

**148.** *Oxidative Ring Closure in the Friedel-Crafts Reaction. Part I.*  
*Condensation of  $\beta$ -Naphthoyl Chloride with  $\alpha$ -Methylnaphthalene.*

By GERARD D. BUCKLEY.

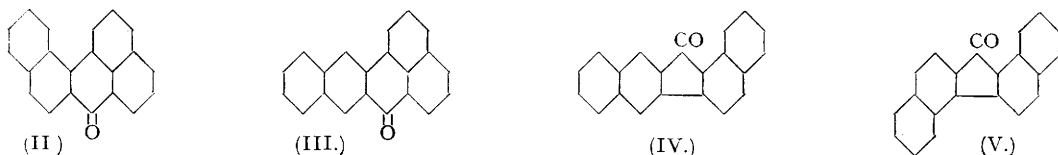
Condensation of  $\beta$ -naphthoyl chloride with  $\alpha$ -methylnaphthalene in carbon disulphide solution in the cold in presence of 1 mol. of aluminium chloride gives the normal product, 4-methyl-1 : 2'-dinaphthyl ketone (I). Use of 2 or more mols. of aluminium chloride under identical conditions results in oxidative cyclisation to give 4-methyl-9' : 10'-benzomesobenzanthrone (VI) in good yield; this ring closure does not occur in solvents other

than carbon disulphide. The *mesobenzanthrone* is also formed in poor yield by treatment of the ketone (I) with aluminium chloride in carbon disulphide solution.

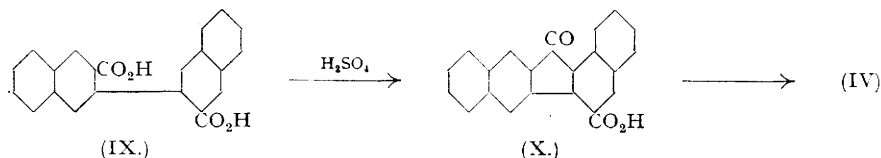
An improved preparation of 1 : 2 : 6 : 7-dibenzfluorenone (IV) from 2-bromo-3-naphthoic acid is described.

In the preparation of 4-methyl-1 : 2'-dinaphthyl ketone (I) by the interaction of  $\beta$ -naphthoyl chloride and  $\alpha$ -methyl-naphthalene in presence of aluminium chloride in carbon disulphide solution, anomalous results were obtained. The ketone (I) was isolated in 40% yield when only 1 mol. of aluminium chloride was used, but the use of 2.5 mols. afforded in 70% yield a yellow crystalline compound,  $C_{22}H_{14}O$ , m. p. 207°, having no ketonic properties.

The structure of the ketone was proved by degradation to 1 : 2'-dinaphthyl ketone, and the compound  $C_{22}H_{14}O$  was shown to be 4-methyl-9' : 10'-benzomesobenzanthrone (VI) by degradation. Oxidation with nitrobenzene and barium oxide, followed by decarboxylation gave a compound,  $C_{21}H_{12}O$ , closely resembling the parent compound in properties. This evidence indicated that the latter was formed by simple cyclisation of (I), and the compound  $C_{21}H_{12}O$  must therefore be represented by one of the structures (II)–(V). It differed

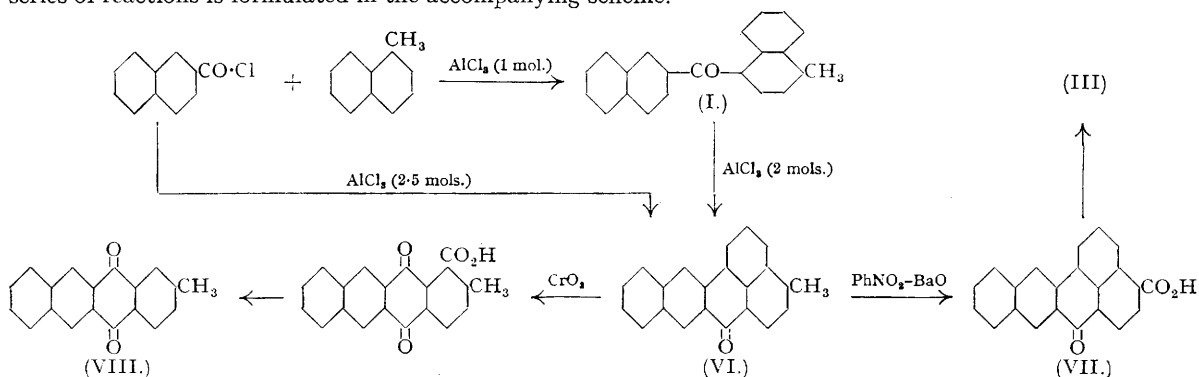


markedly from 10 : 11-benzomesobenzanthrone (II) (Martin, J., 1941, 682) and 1 : 2 : 5 : 6-dibenzfluorenone (V) (Swain and Todd, J., 1941, 674) in m. p. and properties. 1 : 2 : 6 : 7-Dibenzfluorenone (IV), first described by Martin (*loc. cit.*), seemed more likely and it was therefore synthesised by a simplified route, *viz.*, (IX)  $\rightarrow$  (X)  $\rightarrow$  (IV). The product appeared to be the same as that described by Martin, but was not identical with



the compound  $C_{21}H_{12}O$ , for which a fluorenone structure was further rendered improbable by its failure to undergo reduction to a hydrocarbon by heating at 200–220° with hydrazine, or fission to a dinaphthylcarboxylic acid by fusion with potassium hydroxide.

It was therefore concluded that it was 9 : 10-benzomesobenzanthrone (III), and that the compound  $C_{22}H_{14}O$  was 4-methyl-9' : 10'-benzomesobenzanthrone (VI). This was confirmed by oxidation of the latter with chromic acid; the product, after decarboxylation, was 2-methylnaphthacene-5 : 12-quinone (VIII), identified by comparison with an authentic specimen (Waldmann and Mathiowetz, *Ber.*, 1931, 64, 1717). The complete series of reactions is formulated in the accompanying scheme.



Interaction of  $\beta$ -naphthoyl chloride and  $\alpha$ -methyl-naphthalene in presence of 2.5 mols. of aluminium chloride, excess of  $\alpha$ -methyl-naphthalene being used as solvent, yielded 4-methyl-1 : 2'-dinaphthyl ketone as the sole product; in nitrobenzene the product was a tar containing none of the *mesobenzanthrone*, and in light petroleum (b. p. 60–80°) only traces of the *mesobenzanthrone* were formed. Similarly, attempts to cyclise 4-methyl-1 : 2'-dinaphthyl ketone by treatment with aluminium chloride in nitrobenzene, benzene, and light petroleum failed.

It has long been known that 1-arylnaphthalenes may be cyclised to *mesobenzanthrones* by fusion with a large amount of aluminium chloride at relatively high temperatures (cf. Scholl and Seer, *Annalen*, 1912, 394, 143), but there seems to be no recorded instance of the formation of a *mesobenzanthrone* directly from an acid chloride and a naphthalene derivative in the cold. It has, however, been shown (Ruzicka and Hösl, *Helv.*

*Chim. Acta*, 1934, 17, 470; Ruzicka and Morgeli, *ibid.*, 1936, 19, 377) that 1 : 2-diarylethanes are cyclised to phenanthrene, chrysene, and picene derivatives by aluminium chloride in boiling carbon disulphide, but not in light petroleum. The fact that 4-methyl-1 : 2'-dinaphthyl ketone is cyclised only very slowly by aluminium chloride in cold carbon disulphide indicates that, although 4-methyl-9' : 10'-benzomesobenzanthrone is formally a cyclisation product of this ketone, the ketone is not formed as an intermediate in the one-stage preparation of the benzanthrone. The evidence suggests that  $\beta$ -naphthoyl chloride and  $\alpha$ -methyl-naphthalene combine with 1 mol. of aluminium chloride to form a complex which on treatment with water gives 4-methyl-1 : 2'-dinaphthyl ketone, but which may under anhydrous conditions combine with carbon disulphide and a further 1 mol. of aluminium chloride to form a new complex which on treatment with water breaks down to 4-methyl-9' : 10'-benzomesobenzanthrone. This hypothesis is in harmony with the results of experiments carried out in a closed system to determine the fate of the hydrogen which must be eliminated on cyclisation. These made it clear that, whereas no gas was evolved during the formation of the complex, hydrogen was liberated on treatment of the complex with water.

## EXPERIMENTAL.

(Microanalyses by Mr. E. S. Morton. M. p.'s are uncorrected.)

4-Methyl-1 : 2'-dinaphthyl Ketone (I).—Anhydrous aluminium chloride (7.5 g.) was added to a stirred mixture of  $\beta$ -naphthoyl chloride (9.5 g.),  $\alpha$ -methyl-naphthalene (8 g.), and carbon disulphide (40 c.c.) at 0—10°. The mixture was stirred at 0—10° for 4 hours, poured into ice and dilute hydrochloric acid, and the solvent removed by steam-distillation. The residue was cooled and extracted with ether, and the extract washed with sodium carbonate solution, dried over potassium carbonate, and the solvent evaporated. Crystallisation of the residue from glacial acetic acid gave colourless needles (5.8 g.), m. p. 83—84°, soluble in concentrated sulphuric acid to give an orange-red solution (Found : C, 88.9; H, 5.4.  $C_{22}H_{16}O$  requires C, 89.2; H, 5.4%).

Degradation of 4-methyl-1 : 2'-dinaphthyl ketone. The ketone (5 g.), selenium dioxide (5 g.), and nitrobenzene (50 c.c.) were stirred and refluxed together for 12 hours. The solution was filtered from selenium, and the nitrobenzene removed by steam-distillation. The residual solid was collected and extracted thoroughly with boiling dilute sodium carbonate solution, the extract was acidified, and the precipitated carboxylic acid collected and dried (1.9 g.). The crude acid was boiled under reflux with quinoline (20 c.c.) and copper bronze (0.2 g.) for 6 hours. The mixture was poured into excess of dilute hydrochloric acid, and the precipitate collected, dried, and purified by sublimation at 110°/0.05 mm. and crystallisation from acetic acid. This gave colourless needles, m. p. 135° (Found : C, 88.9; H, 4.9. Calc. for  $C_{21}H_{14}O$  : C, 89.3; H, 4.95%). Tschitschibabin and Korjagin (*Chem. Zentr.*, 1914, I, 1658) describe 1 : 2'-dinaphthyl ketone as colourless needles, m. p. 136—137°.

4-Methyl-9' : 10'-benzomesobenzanthrone (VI).—(a) From  $\beta$ -naphthoyl chloride and  $\alpha$ -methyl-naphthalene.  $\beta$ -Naphthoyl chloride (60 g.) was added slowly to a stirred mixture of  $\alpha$ -methyl-naphthalene (55 g.), anhydrous aluminium chloride (92 g.), and carbon disulphide (250 c.c.) at 0—10°. The mixture was stirred overnight at 20°, poured into ice and dilute hydrochloric acid, and left until the complex was completely decomposed. The solvent was removed by steam-distillation and, after cooling, the residual solid was collected and crystallised from acetic acid, giving 64 g. of yellow crystals, m. p. 198—200°, soluble in concentrated sulphuric acid to give a brilliant blue-green solution. Recrystallisation from chlorobenzene gave golden-yellow needles, m. p. 207° (Found : C, 88.9; H, 4.6.  $C_{22}H_{14}O$  requires C, 89.75; H, 4.75%).

(b) From 4-methyl-1 : 2'-dinaphthyl ketone. The ketone (1 g.), anhydrous aluminium chloride (1 g.), and carbon disulphide (10 c.c.) were stirred together at 20° overnight, and the mixture was then worked up as before. The ketone appeared to be largely unchanged, but after repeated recrystallisation from acetic acid there was isolated a crystalline product (0.1 g.), m. p. 201—203°, identical in properties with the 4-methyl-9' : 10'-benzomesobenzanthrone described above.

(c) Examination of gaseous products.  $\alpha$ -Methyl-naphthalene (0.012 g.-mol.) was mixed with aluminium chloride (0.025 g.-mol.) and carbon disulphide (10 c.c.) in a flask fitted with a mercury-sealed stirrer and a reflux condenser and connected to a system for collecting evolved gases over water.  $\beta$ -Naphthoyl chloride (0.01 g.-mol.) was added, and the mixture stirred for 18 hours at 20°. The volume of gas in the system remained unchanged. The product was then poured into a large volume of ice and dilute hydrochloric acid, and the evolved gases were collected over water. The volume of gas in the system increased by 110 c.c. (ca. 0.005 g.-mol.), but some of the complex remained unaltered owing to the formation of waxy lumps, and it was impossible to overcome this difficulty in quantitative experiments. The evolved gas, which was inflammable and formed an explosive mixture with air, appeared to be hydrogen.

A second experiment was carried out exactly as above, but the complex was decomposed by dropwise addition of *n*-hydrochloric acid (80 c.c.). The volume of gas in the system decreased initially by 25 c.c. and then increased by 50 c.c. as the addition proceeded, suggesting that the hydrogen formed was being partly removed by reaction with atmospheric oxygen.

9 : 10-Benzomesobenzanthrone (III).—4-Methyl-9' : 10'-benzomesobenzanthrone (5 g.), barium oxide (12 g.), and dry nitrobenzene (50 c.c.) were stirred together in an oil-bath at 190—200° for 3 hours. The mixture was cooled, poured into excess of dilute hydrochloric acid, and freed from nitrobenzene and azobenzene by steam-distillation. After cooling, the solid was collected, washed free from acid, and extracted thoroughly with boiling dilute sodium hydroxide solution. After treatment with kieselguhr, the extract was acidified, and the precipitate collected, washed with water, and dried (5.25 g.). A specimen was further purified by dissolving it in 0.5% sodium hydroxide solution (200 c.c.). The solution was allowed to cool slowly, and the crystalline sodium salt was collected, washed with 2% brine, and converted into the free 9' : 10'-benzomesobenzanthrone-4-carboxylic acid (VII), which was isolated as an orange powder, m. p. above 340°, soluble in concentrated sulphuric acid to give a green solution (Found : C, 80.5; H, 4.05.  $C_{22}H_{12}O_3$  requires C, 81.4; H, 3.7%).

The crude acid (2 g.) was mixed with copper-bronze (0.2 g.) and quinoline (20 c.c.) and stirred and refluxed for 6 hours. After cooling, the mixture was poured into excess of dilute hydrochloric acid, and the precipitate was collected, dried, and crystallised from toluene. Sublimation at 200—210°/0.002 mm. and recrystallisation from toluene gave golden-yellow needles, m. p. 199—200°, soluble in concentrated sulphuric acid to give a brilliant blue-green solution (Found : C, 89.9; H, 4.0.  $C_{21}H_{12}O$  requires C, 90.0; H, 4.3%).

Oxidation of 4-Methyl-9' : 10'-benzomesobenzanthrone with Chromic Acid.—4-Methyl-9' : 10'-benzomesobenzanthrone (2.5 g.) was dissolved in 98% sulphuric acid (25 c.c.) at 10—20° and poured into water (200 c.c.). The suspension was stirred at the boil, and crystalline sodium dichromate (15 g.) slowly added. The mixture was stirred and refluxed overnight, cooled, and the precipitate collected and extracted thoroughly with boiling dilute sodium hydroxide. The extract was acidified, and the carboxylic acid isolated as a dark brown powder (0.8 g.).

The crude acid was decarboxylated by refluxing with quinoline (8 c.c.) and copper-bronze (0.1 g.). The product, after sublimation at  $170^{\circ}/0.06$  mm., consisted of pale yellow needles, m. p.  $243^{\circ}$  (Found: C, 83.75; H, 4.55. Calc. for  $C_{19}H_{12}O_2$ : C, 83.8; H, 4.45%). It dissolved in alkaline sodium hyposulphite (hydrosulphite) solution to form a green vat, and in concentrated sulphuric acid to give a red-violet solution, and did not depress the m. p. of an authentic specimen of 2-methylnaphthacene-5:12-quinone, prepared by the method of Waldmann and Mathiowetz (*Ber.*, 1931, **64**, 1717).

1:2:6:7-Dibenzfluorenone (IV).—2:2'-Dinaphthyl-3:3'-dicarboxylic acid (5.4 g.), prepared as described by Martin (*loc. cit.*), was dissolved in cold 98% sulphuric acid (55 c.c.), heated on the steam-bath for 5 minutes, and poured into ice water. The precipitate was collected, washed with water, stirred with cold methyl alcohol, collected, and washed with methyl alcohol until free from mineral acid. The resulting yellow powder (3 g.) was sparingly soluble in dilute sodium hydroxide solution and, after crystallisation from acetic acid, had m. p.  $304-305^{\circ}$ . This 1':2':6':7'-dibenzfluorenone-4-carboxylic acid (X) was decarboxylated in the usual way, and the crude product purified by crystallisation from  $\beta$ -ethoxyethyl alcohol, sublimation at  $190-200^{\circ}/0.04$  mm., and recrystallisation from xylene, which gave orange-yellow plates, m. p.  $214^{\circ}$ , soluble in concentrated sulphuric acid to give a bluish-red solution. Martin (*loc. cit.*) describes 1:2:6:7-dibenzfluorenone as orange plates, m. p.  $211^{\circ}$ , giving a carmine-red solution in concentrated sulphuric acid (Found: C, 89.6; H, 4.55. Calc. for  $C_{21}H_{12}O$ : C, 90.0; H, 4.3%).

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

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