

**243. 3 : 4-Benzfluorenones. Part II. Further Observations on the Effect of Groups on their Fission with Alkali.**

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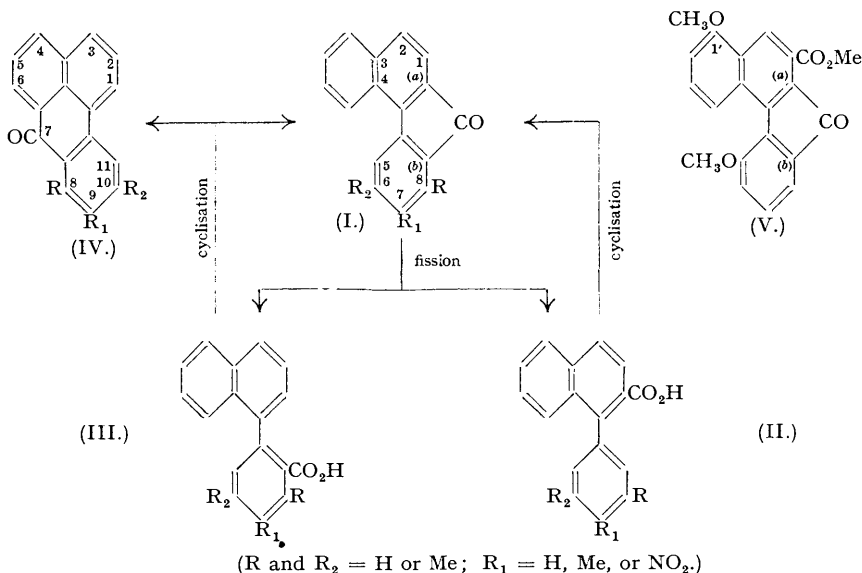
6 : 8-Dimethyl- and 6-methyl-3 : 4-benzfluorenone give, when fused with alkali, mixtures of 1-m-5'-xylylnaphthalene-2- and -4'-carboxylic acid, and 1-m-tolyl-naphthalene-2- and -4'-carboxylic acid respectively. In both cases the 4'-acid is isolated in a greater proportion. 7-Methyl-3 : 4-benzfluorenone, however, gives on fission a mixture of the 2- and 4'-carboxylic acids, in the ratio of about 3 : 2 respectively.

1' : 5-Dimethoxy-3 : 4-benzfluorenone-1-carboxylic acid gives, when similarly treated, 5 : 6'-dimethoxy-1-phenylnaphthalene-2' : 3-dicarboxylic acid only.

These results support the view that the direction of fission of 3 : 4-benzfluorenones by fused potassium hydroxide is influenced by the polar character of the substituent (cf. Part I, *J.*, 1944, 450).

IN Part I (*loc. cit.*) the authors concluded, from a study of the effect of electron-attracting groups (*e.g.*, CO<sub>2</sub>H) on the mode of fission of 3 : 4-benzfluorenones, that the direction of cleavage is governed by the polar character of the group rather than its steric effect.

To prove the validity of this statement, the study has been extended to 3 : 4-benzfluorenones substituted either by electron-repelling groups or by both electron-repelling and electron-attracting groups. The following examples were, therefore, prepared and then cleaved with alkali.



6 : 8-Dimethyl-3 : 4-benzfluorenone (I; R and R<sub>2</sub> = Me, R<sub>1</sub> = H) was prepared by condensation of 5-iodo-*m*-xylene with methyl 1-bromo-2-naphthoate in presence of copper-bronze, and ring closure of the 1-m-5'-xylylnaphthalene-2-carboxylic acid (II; R<sub>1</sub> = H, R and R<sub>2</sub> = Me) so formed.

Methyl 3-bromo-*p*-toluate was condensed with  $\alpha$ -iodonaphthalene in presence of copper-bronze to give 1-m-tolyl-naphthalene-4'-carboxylic acid (III; R and R<sub>1</sub> = H, R<sub>2</sub> = Me). This gave on cyclisation a mixture of 6-methyl-3 : 4-benzfluorenone (I; R and R<sub>1</sub> = H, R<sub>2</sub> = Me) and 10-methylmesobenzanthrone (IV; R and R<sub>1</sub> = H, R<sub>2</sub> = Me).

1-*p*-Tolyl-naphthalene-2-carboxylic acid (II; R and R<sub>2</sub> = H, R<sub>1</sub> = Me), prepared by the condensation of *p*-iodotoluene and methyl 1-bromo-2-naphthoate, gave on ring closure 7-methyl-3 : 4-benzfluorenone (I; R and R<sub>2</sub> = H, R<sub>1</sub> = Me).

Methyl 1' : 5-dimethoxy-3 : 4-benzfluorenone-1-carboxylate (V) was prepared by the action of aluminium chloride on 2' : 5-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride in nitrobenzene, followed by esterification with diazomethane in dioxan (cf. Baddar, *J.*, 1947, 224).

$\alpha$ -Iodonaphthalene condensed similarly with methyl 2-iodo-5-nitrobenzoate to give 4'-nitro-1-phenylnaphthalene-2'-carboxylic acid, which was cyclised to a mixture of 7-nitro-3 : 4-benzfluorenone (I; R and R<sub>2</sub> = H, R<sub>1</sub> = NO<sub>2</sub>) and 9-nitromesobenzanthrone (IV; R and R<sub>2</sub> = H, R<sub>1</sub> = NO<sub>2</sub>).

*Alkaline Fission of 3:4-Benzfluorenones.*—6:8-Dimethyl- and 6-methyl-3:4-benzfluorenone gave on fission with alkali mixtures of 1-*m*-5'-xylylnaphthalene-2- and -4' (III; R<sub>1</sub> = H, R and R<sub>2</sub> = Me)-carboxylic acid, and 1-*m*-tolyl-naphthalene-2- (II; R<sub>1</sub> and R<sub>2</sub> = H, R = Me) and 1-*m*-tolyl-naphthalene-4'-carboxylic acid respectively. In both cases the 2- and the 4'-carboxylic acid were obtained in the ratio of about 2:3 respectively. 7-Methyl-3:4-benzfluorenone, however, gave on fission a mixture of 1-*p*-tolyl-naphthalene-2- and -3' (III; R and R<sub>2</sub> = H, R<sub>1</sub> = Me)-carboxylic acid in the ratio of about 3:2 respectively.

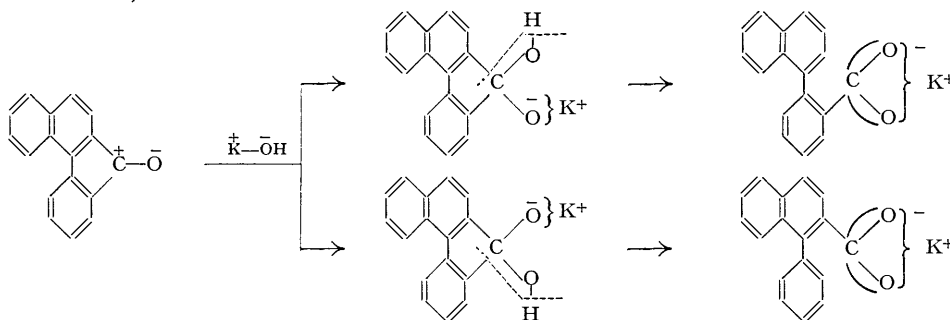
When 1':5-dimethoxy-3:4-benzfluorenone-1-carboxylic acid (or its ester) was similarly treated it gave only 5:6'-dihydroxy-1-phenylnaphthalene-2':3-dicarboxylic acid, owing to demethylation during fission. Its *dimethyl ether* was not identical with 2':5-dimethoxy-1-phenylnaphthalene-2:3-dicarboxylic acid (cf. Baddar, *loc. cit.*); it gave, however, on decarboxylation 2':5-dimethoxy-1-phenylnaphthalene.

Under similar or milder conditions 7-nitro-3:4-benzfluorenone resinified.

These results support the authors' conclusion in Part I (*loc. cit.*), that the factors which operate to determine the point of cleavage of 3:4-benzfluorenones are of polar origin, depending to a great extent on the electron density at carbon atoms (*a*) and (*b*) in (I) and (V). The greater the density of electrons at any of the two carbon atoms (*a*) and (*b*) the more stable is the bond linking this atom with the carbonyl carbon atom (cf. Lea and Robinson, *J.*, 1926, 2351).

It is concluded, therefore, that in 6:8-dimethyl- and 6-methyl-3:4-benzfluorenone the electron-availability at carbon atom (*b*) is slightly greater than at (*a*), whereas, in 7-methyl-3:4-benzfluorenone it is slightly greater at (*a*) than at (*b*). Although in 1':5-dimethoxy-3:4-benzfluorenone-1-carboxylic acid both the carboxyl group and the methoxyl group decrease the electron density at carbon atoms (*a*) and (*b*) respectively, yet the decrease caused by the carboxyl group greatly surpasses that caused by the methoxyl group.

The mechanism of fission of 3:4-benzfluorenones could, therefore, be put forward according to the following scheme (cf. Schönberg *et al.*, *Annalen*, 1924, 436, 205; Lea and Robinson, *loc. cit.*; Koslow, Fedosjew and Olifsson, *Chem. J., Ser. A., J. Allg. Chem.*, 1936, 6, 259; *Chem. Zentr.*, 1936, II, 1919). The broken lines indicate the fate of electron pairs originally forming the covalent bonds, which are broken.



#### EXPERIMENTAL.

(M. p.s are not corrected. Microanalyses were carried out by Drs. Weiler and Strauss of Oxford.)

*5-Iodo-m-xylene.*—This was obtained from 5-amino-*m*-xylene as a colourless oil, b. p. 92–94°/3 mm.; yield, 65% (cf. Willgerodt and Schmierer, *Ber.*, 1905, 38, 1475).

*1-m-5'-Xylylnaphthalene-2-carboxylic Acid.*—A mixture of methyl 1-bromo-2-naphthoate (13.4 g.; 1 mol.) and 5-iodo-*m*-xylene (11.6 g.; 1 mol.) was stirred at 200°. Copper-bronze (12.6 g.) was then added in the course of 30 minutes, and the temperature quickly raised to 230–235° ( $\alpha$ -methyl-naphthalene bath). The mixture was kept thereat for 3 hours, extracted with acetone, filtered, and the solvent removed (cf. Baddar and Gindy, *loc. cit.*). The residue was dissolved in hot alcohol (100 c.c.), cooled, filtered from the precipitated methyl 1:1'-dinaphthyl-2:2'-dicarboxylate, and hydrolysed with potassium hydroxide (20 g.). The precipitated acids were extracted with benzene, the solution allowed to stand for 2 days, filtered, and the solvent evaporated. The residue (2.9 g.) was then esterified with diazomethane and distilled in a vacuum; b. p. 215–225°/1 mm. The distillate gave on hydrolysis 1-*m*-5'-xylylnaphthalene-2-carboxylic acid, which crystallised from dilute ethyl alcohol in colourless long needles, m. p. 195–196° [Found: C, 82.4; H, 5.8; *M* (Rast), 269. C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> requires C, 82.6; H, 5.8%; *M*, 276]; yield, 20%.

*6:8-Dimethyl-3:4-benzfluorenone.*—1-*m*-5'-Xylylnaphthalene-2-carboxylic acid (5.5 g.) was dissolved in benzene (100 c.c.) and cyclised with phosphoric oxide (11.0 g.) (cf. Baddar and Gindy, *loc. cit.*). On crystallisation from ethyl alcohol 6:8-dimethyl-3:4-benzfluorenone was obtained in silky yellow needles, m. p. 160–161° (shrinking at 145°) (Found: C, 87.9; H, 5.4. C<sub>15</sub>H<sub>14</sub>O requires C, 88.3; H, 5.5%); yield, 95%. It dissolved in concentrated sulphuric acid to a green solution.

*Fusion of 6:8-Dimethyl-3:4-benzfluorenone with Potassium Hydroxide.*—The benzfluorenone (1 part) was added during 10 minutes to fused potassium hydroxide (7 parts) at 230–235° and kept thereat with frequent stirring for a further 15 minutes. The alkaline aqueous extract was filtered and acidified. The dry acids were esterified with ethereal diazomethane and distilled in a vacuum; b. p. 220–230°/3 mm. The ester gave on hydrolysis with alcoholic potassium hydroxide a mixture of acids which melted at 60–70°. The crude acids (0.3 g.) were refluxed with 50% aqueous methyl alcohol (150 c.c.) and filtered hot. This solution precipitated on standing overnight in the ice-chest a crystalline acid (0.1 g.), m. p. 187–191°, raised on recrystallisation to 194–195°, undepressed on admixture with an authentic specimen of 1-*m*-xylylnaphthalene-2-carboxylic acid.

The mother liquor was evaporated under reduced pressure at room temperature until it became turbid. On standing overnight in the ice-chest, 1-*m*-5'-xylylnaphthalene-4'-carboxylic acid (0.14 g.) separated in colourless cubes, m. p. 159–161°, raised on recrystallisation from dilute methyl alcohol to 164–165°, depressed on admixture with authentic 1-*m*-5'-xylylnaphthalene-2-carboxylic acid to 138–155° (Found: C, 82.6; H, 5.9. C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> requires C, 82.6; H, 5.8%). It gave with concentrated sulphuric acid a dirty brown colour with a green fluorescence indicating the formation of a mixture of a mesobenzanthrone and a 3:4-benzfluorenone.

*Ethyl 1-Bromo-2-naphthoate.*—The crude acid (43 g., prepared according to Boyes, Grieve, and Rule, *J.*, 1938, 1833) was refluxed with absolute ethyl alcohol (300 c.c.) and concentrated sulphuric acid (72 c.c.) for 10 hours. The product was crystallised from light petroleum (b. p. 30–50°), from which ethyl 1-bromo-2-naphthoate separated in colourless cubes, m. p. 36–37° (Found: Br, 28.4. C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>Br requires Br, 28.6%; yield, 90%).

*1-*m*-Tolyl-naphthalene-2-carboxylic Acid.*—A mixture of *m*-iodotoluene (13.3 g.; 1 mol.) and ethyl 1-bromo-2-naphthoate (17.0 g.; 1 mol.) was stirred at 200°, treated with copper-bronze (15.3 g.), and worked up as in the case of 1-*m*-5'-xylylnaphthalene-2-carboxylic acid. The product was esterified with diazomethane and distilled in a vacuum. The fraction boiling below 180°/3 mm. was rejected; that boiling at 185–187°/3 mm. was directly hydrolysed with alcoholic potassium hydroxide. The acid was crystallised from dilute alcohol to give 1-*m*-tolyl-naphthalene-2-carboxylic acid in colourless cubes, m. p. 164–165° (Found: C, 82.3; H, 5.3. C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> requires C, 82.4; H, 5.4%); yield, 23.7%.

*Ring Closure of 1-*m*-Tolyl-naphthalene-2-carboxylic Acid.*—The acid was cyclised as usual with phosphoric oxide in benzene. The product was repeatedly crystallised from alcohol to give a eutectic inseparable mixture of 6- and 8-methyl-3:4-benzfluorenone in fine orange needles, m. p. 112–118° (Found: C, 88.0; H, 5.2. Calc. for C<sub>18</sub>H<sub>12</sub>O: C, 88.5; H, 5.0%); yield, quantitative.

*3-Bromo-*p*-toluic Acid*—3-Bromo-*p*-toluidine (46.5 g.) was dissolved in dilute sulphuric acid (25 c.c. acid and 80 c.c. water), and diazotised as usual with sodium nitrite (19 g., in 30 c.c. water). The filtered diazonium salt solution was added portionwise (15 minutes) to a cuprous cyanide solution, obtained by mixing solutions of copper sulphate (124.5 g. of CuSO<sub>4</sub>·5H<sub>2</sub>O in 500 c.c. of water) and sodium cyanide (110 g. in 280 c.c. of water). The mixture was left overnight then steam distilled. 3-Bromo-4-cyanotoluene was obtained in 68% yield as a colourless solid, m. p. 46–47°. This was hydrolysed by refluxing it for 4 hours with 50% v/v sulphuric acid. The product, precipitated on dilution, was filtered off, dissolved in sodium carbonate solution, and the unchanged parent substance (3 g.) extracted with ether. 3-Bromo-*p*-toluic acid crystallised from water or very dilute alcohol in colourless feathery needles, m. p. 143°; yield, 76%. Claus and Kunath (*J. pr. Chem.*, 1889, **39**, 486) give m. p. 140°. The crude acid was esterified with diazomethane, and the methyl ester was distilled in a vacuum, b. p. 167–168°/38 mm., 161–164°/32 mm., to a colourless mobile oil (Found: C, 47.6; H, 4.0; Br, 35.7. C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>Br requires C, 47.2; H, 4.0; Br, 34.9%).

*1-*m*-Tolyl-naphthalene-4'-carboxylic Acid.*—A mixture of 3-bromo-*p*-toluic ester (11.5 g.; 1 mol.) and *a*-iodonaphthalene (12.7 g.; 1 mol.) was stirred at 180°, and copper-bronze (12.5 g.) was added portionwise during ½ hour. The temperature was then raised to 205–210° (nitrobenzene bath) and the reaction continued for a further 4 hours. The product was worked up as described above, and the precipitated acids were dried and extracted with benzene (to remove the insoluble ditolyldicarboxylic acid). The acid residue was esterified with diazomethane, or with thionyl chloride and methyl alcohol, and fractionally distilled at 40 mm. The fraction of b. p. <200° was rejected; that of b. p. 235–245° gave on hydrolysis 1-*m*-tolyl-naphthalene-4'-carboxylic acid, which crystallised from dilute alcohol in colourless needles, m. p. 176–177° (Found: C, 82.6; H, 5.2. C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> requires C, 82.4; H, 5.4%); yield, 33%. It gave with concentrated sulphuric acid a dark red colour with a green fluorescence.

*6-Methyl-3:4-benzfluorenone and 10-Methylmesobenzanthrone.*—The above acid was cyclised in the usual way to a dark orange product, m. p. 120–130°. This was fractionally crystallised from methyl alcohol, from which 6-methyl-3:4-benzfluorenone separated at first in long feathery orange needles, m. p. 160–161°; it gave with concentrated sulphuric acid a green non-fluorescent solution (Found: C, 87.8; H, 4.6. C<sub>18</sub>H<sub>12</sub>O requires C, 88.5; H, 4.95%); yield, 50%. The mother liquor deposited on further cooling 10-methylmesobenzanthrone in light yellow cubic crystals, m. p. 152–154°, raised after two crystallisations from acetone to 159° (Found: C, 88.3; H, 4.63. Calc. for C<sub>18</sub>H<sub>12</sub>O: C, 88.5; H, 4.95%); yield, 50%. Fieser and Martin (*J. Amer. Chem. Soc.*, 1936, **58**, 1444) give m. p. 158–159°. The pure benzanthrone could be obtained in a 50% yield by heating the cyclisation mixture with 90% v/v sulphuric acid at 100° for 1 hour. Under these conditions the 3:4-benzfluorenone was completely sulphonated.

*Fission of 6-Methyl-3:4-benzfluorenone.*—The ketone (1 g.) was fused with potassium hydroxide as described above, and the resulting acids were purified by esterification and distillation in a vacuum. The fraction, b. p. 230–250°/1 mm., was hydrolysed, and the precipitated acids filtered off (0.3 g.). The separation of the constituents by crystallisation was practically impossible, and the relative amounts of the two acids in the fission product was determined by taking advantage of (a) the fact that 1-*m*-tolyl-naphthalene-2-carboxylic acid gave on ring closure a mixture of 6- and 8-methyl-3:4-benzfluorenone, whereas 1-*m*-tolyl-naphthalene-4'-carboxylic acid gave a mixture of equimolecular amounts of 6-methyl-3:4-benzfluorenone and 10-methylmesobenzanthrone, and (b) that whereas 6- and 8-methyl-3:4-benzfluorenone were completely sulphonated on being heated with 90% v/v sulphuric acid for 1 hour at

100°, 10-methylmesobenzanthrone was recovered totally unchanged. It seemed possible, therefore, that the percentage composition of the fission product could be determined by cyclising it, then heating a known weight with 90% sulphuric acid, and estimating the amount of 10-methylmesobenzanthrone. The cyclised product (0.2 g.) was heated with 90% sulphuric acid (20 c.c.) at 100° for 1 hour, poured into water, and the precipitated solid extracted with pure benzene. The solution was washed, filtered, and the solvent evaporated (constant weight), leaving the unsulphonated 10-methylmesobenzanthrone (0.06 g., 30%). The ratio of 1-*m*-tolyl-naphthalene-4'-carboxylic acid to 1-*m*-tolyl-naphthalene-2-carboxylic acid was then calculated to be:  $2 \times 30 : (100 - 2 \times 30) = 3 : 2$ .

**1-*p*-Tolyl-naphthalene-2-carboxylic Acid.**—A mixture of *p*-iodotoluene (21 g.; 1 mol.) and methyl 1-bromo-2-naphthoate (25.5 g.; 1 mol.) was stirred at 200°, and copper-bronze (21 g.) added portionwise during  $\frac{1}{2}$  hour. The temperature was then quickly raised to 230—235°, and the reaction continued for a further 3 hours. The product was worked up as usual, and the dry acids extracted with benzene. The benzene solution was left for 2 days, and then filtered from the precipitated dinaphthyl-dicarboxylic acid. The acid was purified through its ester (b. p. 194—196°/1 mm.), and then crystallised from benzene-light petroleum (b. p. 40—70°), from which 1-*p*-tolyl-naphthalene-2-carboxylic acid separated in monoclinic crystals, m. p. 183—184° (Found: C, 82.7; H, 5.3.  $C_{18}H_{14}O_2$  requires C, 82.4; H, 5.4%); yield, 33%. It was soluble in alcohol, ether, and benzene, sparingly so in light petroleum. It gave with concentrated sulphuric acid a green non-fluorescent solution.

**7-Methyl-3 : 4-benzfluorenone.**—The above acid was cyclised quantitatively with phosphoric oxide in benzene. The product was repeatedly crystallised from alcohol, from which 7-methyl-3 : 4-benzfluorenone was obtained in orange needles, m. p. 127—128°, soluble in ether and benzene, sparingly soluble in light petroleum. It gave with concentrated sulphuric acid a green non-fluorescent solution. When the ketone was distilled at 230—240°/5 mm., and the distillate crystallised from alcohol, it gave light yellow needles with the same m. p. which turned orange on heating (100—110°) (Found: C, 88.4; H, 5.0.  $C_{18}H_{12}O$  requires C, 88.5; H, 4.95%).

**Fusion of 7-Methyl-3 : 4-benzfluorenone with Alkali.**—7-Methyl-3 : 4-benzfluorenone (1 g.) was fused with potassium hydroxide, and worked up as above. The resulting acids were esterified, distilled (b. p. 230—240°/1 mm.), and hydrolysed. The dry acids (0.4 g., m. p. 65—75°) were dissolved in the least amount of 75% v/v aqueous methyl alcohol, left for 1 hour at room temperature (30—35°), and the crystals filtered off; these were proved to be 1-*p*-tolyl-naphthalene-2-carboxylic acid. The mother liquor was evaporated to dryness, the residue crystallised from the least amount of 70% methyl alcohol, and the product filtered off after 1—2 hours. Recrystallisation from dilute methyl alcohol gave 1-*p*-tolyl-naphthalene-3'-carboxylic acid in colourless needles, m. p. 161—162°, depressed to 135—145° on admixture with 1-*p*-tolyl-naphthalene-2-carboxylic acid (Found: C, 82.1; H, 5.4.  $C_{18}H_{14}O_2$  requires C, 82.4; H, 5.4%). It gave with concentrated sulphuric acid a dirty red solution with a green fluorescence. The -2- and the -3'-carboxylic acid were obtained in the ratio of about 3 : 2 respectively.

**Methyl 1' : 5-Dimethoxy-3 : 4-benzfluorenone-1-carboxylate.**—The cold suspension of the acid (20 g.) (cf. Baddar, *loc. cit.*) in dioxan (200 c.c.) was treated with an ethereal solution of diazomethane, and the mixture kept at room temperature (15—20°) for 24 hours. The precipitated ester was washed with hot ammonia solution, then crystallised from dioxan-alcohol, from which methyl 1' : 5-dimethoxy-3 : 4-benzfluorenone-1-carboxylate separated in red prismatic needles, m. p. 190.5—191.5° (cf. Baddar, *loc. cit.*); yield, 63.9%.

**Alkaline Fission of Methyl 1' : 5-Dimethoxy-3 : 4-benzfluorenone-1-carboxylate.**—The above ester (2 g.) was similarly fused with potassium hydroxide; a copious evolution of gas was observed which subsided after about 15 minutes. The precipitated acid (1.7 g.) was crystallised from water, from which 5 : 6'-dihydroxy-1-phenyl-naphthalene-2' : 3-dicarboxylic acid separated in brownish-yellow clusters, m. p. 283—285° (Found: C, 60.7; H, 4.56.  $C_{18}H_{12}O_6, 2H_2O$  requires C, 60.0; H, 4.48%). On dehydration, by heating at 200—210° in a vacuum, the m. p. was raised to 294—296° (Found: C, 66.4; H, 4.0.  $C_{18}H_{12}O_6$  requires C, 66.6; H, 3.7%).

The acid (1.6 g.), which was proved to contain no methoxyl groups (demethylation during fusion), was methylated by refluxing its suspension in dry acetone (60 c.c.) with methyl iodide (6 c.c.) and potassium carbonate (7 g.) for 3 hours; then a further quantity of methyl iodide (4 c.c.) was added, and the refluxing continued for a further 8 hours. The acetone was removed, and the residue extracted with benzene and washed with sodium hydroxide solution. The solvent was evaporated, and the residue hydrolysed to the free acid, which was refluxed with acetic anhydride for 10 minutes. The product was precipitated with water, filtered off, and extracted with dilute cold sodium hydroxide solution (all dissolved), which indicated that the fission product was free from 2' : 5-dimethoxy-1-phenyl-naphthalene-2 : 3-dicarboxylic acid. The alkaline solution (charcoal) was acidified, and the precipitated acid was crystallised from glacial acetic acid, from which 5 : 6'-dimethoxy-1-phenyl-naphthalene-2' : 3-dicarboxylic acid separated in colourless small cubes, m. p. above 340°. It was best identified as its dimethyl ester, which was prepared by treating a dioxan solution of the acid with an ethereal solution of diazomethane. On crystallisation from ether, followed by benzene-light petroleum (b. p. 60—70°), the methyl ester was obtained in colourless rods, m. p. 170—171°, depressed on admixture with a specimen of methyl 2' : 5-dimethoxy-1-phenyl-naphthalene-2 : 3-dicarboxylate to 125—140° (cf. Baddar, *loc. cit.*) (Found: C, 69.0; H, 5.0.  $C_{22}H_{20}O_6$  requires C, 69.4; H, 5.3%). It gave with concentrated sulphuric acid a clear red solution with a brown fluorescence.

**2' : 5-Dimethoxy-1-phenyl-naphthalene.**—A mixture of the above acid (0.5 g.), quinoline (3 c.c.), and copper-bronze (0.1 g.) was stirred at 200—210° for 3 hours. The product was worked up as usual (cf. Baddar, *loc. cit.*), distilled in a vacuum, and then crystallised from methyl alcohol to give 2' : 5-dimethoxy-1-phenyl-naphthalene in monoclinic crystals, m. p. 95—96°, undepressed on admixture with an authentic specimen.

**4'-Nitro-1-phenyl-naphthalene-2'-carboxylic Acid.**—A mixture of methyl 2-iodo-5-nitrobenzoate (5 g.; 1 mol.) and  $\alpha$ -iodonaphthalene (5 g.; 1.2 mol.) was stirred and heated at 180°, and copper-bronze (4 g.) added slowly during  $\frac{1}{2}$  hour. The temperature was then raised to 200—210°, and the reaction continued

for a further 2 hours. The product was extracted in the usual way, and hydrolysed by being boiled with a mixture of 80% acetic acid (65 c.c.) and concentrated sulphuric acid (5 c.c.) for 2 hours. The acids were precipitated with ice, filtered off, and extracted with sodium hydrogen carbonate solution (charcoal). The precipitated acids were extracted with benzene and filtered from the insoluble dinitrodiphenic acid. On crystallisation from alcohol *4'-nitro-1-phenylnaphthalene-2'-carboxylic acid* separated in yellow needles, m. p. 195—196° (Found: C, 69.8; H, 3.7; N, 5.0.  $C_{17}H_{11}O_4N$  requires C, 69.6; H, 3.8; N, 4.8%). It gave with concentrated sulphuric acid a brown colour with a green fluorescence.

2-Iodo-5-nitrobenzoic acid was prepared according to Goldstein and Grampoloff (*Helv. Chim. Acta*, 1930, **13**, 310) with only half the amount of the nitrating mixture, and heating for  $1\frac{1}{2}$ —2 hours at 140—150°.

*Ring-closure of 4'-Nitro-1-phenylnaphthalene-2'-carboxylic Acid.*—The above acid was ring-closed with phosphoric oxide in benzene to a mixture of a 3 : 4-benzfluorenone and a mesobenzanthrone. On crystallisation from glacial acetic acid, *7-nitro-3 : 4-benzfluorenone* was obtained in red needles, m. p. 265—266° (Found: N, 5.2.  $C_{17}H_9O_3N$  requires N, 5.1%).

The 9-nitromesobenzanthrone was present in a very small proportion and did not crystallise out from the acetic acid.

FOUAD I UNIVERSITY, CAIRO, EGYPT.

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