120. 3 : 4-*Benzfluorenones. Part I. The Effect of Groups on their Formation and their Fission with Alkali.*

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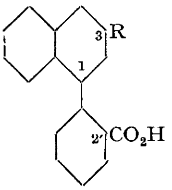
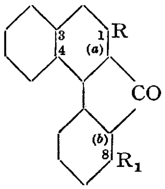
Cyclisation of 1-phenylnaphthalene-2′-carboxylic acids may give 3 : 4-benzfluorenones or *meso*benzanthrones, and it is found that the course of the reaction is greatly influenced by substituents. The direction of fission of 3 : 4-benzfluorenones by fused potassium hydroxide is also influenced by substituents in the molecule. This influence is attributed mainly to the polar character of the substituent.

It has been stated by Baddar (J., 1941, 310) that whereas 1-phenylnaphthalene-2′-carboxylic acid (I, R = H) and its 4-alkyl derivatives give on ring closure a mixture of a 3 : 4-benzfluorenone and a *meso*benzanthrone in the ratio of about 2 : 1 respectively, yet 1-phenylnaphthalene-2′ : 3-dicarboxylic acid gives *meso*benzanthrone-2-carboxylic acid (III; R = CO_2H) as the main product together with traces of 3 : 4-benzfluorenone-1-carboxylic acid (II). Baddar (*loc. cit.*) attributed this to the deactivation of carbon atom in position 2 (I) by the proximity of the carboxyl group. This deactivation is undoubtedly responsible also for the production of 1-phenylnaphthalene-2′ : 3-dicarboxylic acid and 3-benzoyl-1-phenylnaphthalene-2′-carboxylic acid by the alkaline fission of 3 : 4-benzfluorenone-1-carboxylic acid and 1-benzoyl-3 : 4-benzfluorenone respectively. 3 : 4-Benzfluorenone, however, gives on similar treatment, approximately an equimolecular mixture of 1-phenylnaphthalene-2′-carboxylic acid and 1-phenylnaphthalene-2-carboxylic acid (Schaarschmidt and Georgeacopol, *Ber.*, 1918, **51**, 1082).

The authors have now extended the study of the effect of groups on the formation and alkaline fission of differently substituted 3 : 4-benzfluorenones, with a view to elucidate whether this influence is of polar or steric origin.



(I.)



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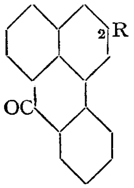

(III.)

1-*Methoxy*-3 : 4-*benzfluorenone and* 2-*Methoxy*meso*benzanthrone.*—4-Iodo-2-naphthyl methyl ether was prepared in poor yield from 4-amino-2-naphthyl methyl ether (cf. Morgan and Evens, J., 1919, **115**, 1126), 2-hydroxy-1 : 4-naphthaquinone being one of many by-products (a better method is that of Hodgson and Birtwell, J., 1943, 468). This ether, on condensation with methyl *o*-iodobenzoate in presence of copper, gave 3-*methoxy*-1-*phenylnaphthalene*-2′-*carboxylic acid*, which afforded on ring closure a mixture of 1-*methoxy*-3 : 4-*benzfluorenone* (II; R = OMe, R_1 = H) and 2-methoxy*meso*benzanthrone (III; R = OMe). Although complete separation of the two constituents could not be effected owing to lack of material, yet the former was proved to be predominant.

3 : 4-*Benzfluorenone*-8-*carboxylic Acid* (II; R = H, R_1 = CO_2H).—1-Phenylnaphthalene-2′ : 3′-dicarboxylic acid, prepared by condensation of 1-iodonaphthalene with ethyl 3-iodophthalate, was converted into its *anhydride*, which gave on cyclisation a mixture of 3 : 4-*benzfluorenone*-8-*carboxylic acid* and *meso*benzanthrone-8-carboxylic acid, the latter predominating.

3 : 4-*Benzfluorenone*-7-*carboxylic Acid.*—1-Phenylnaphthalene-2 : 4′-dicarboxylic acid, prepared by the condensation of methyl 1-bromo-2-naphthoate with ethyl *p*-iodobenzoate, gave on ring closure 3 : 4-*benzfluorenone*-7-*carboxylic acid* only.

3 : 4-Benzfluorenone- and *meso*benzanthrone-carboxylic acids were characterised by decarboxylation to 3 : 4-benzfluorenone and *meso*benzanthrone, respectively.

Alkaline Fission of 3 : 4-*Benzfluorenones.*—3 : 4-Benzfluorenone-8-carboxylic acid gave on fission with alkali 1-*phenylnaphthalene*-2 : 3′-*dicarboxylic acid.* 3 : 4-Benzfluorenone-7-carboxylic acid, however, gave a mixture of acids from which 1-phenylnaphthalene-2 : 4′-dicarboxylic acid was isolated in a pure state. The fact that the remaining mixture of acids gave with warm concentrated sulphuric acid a brownish-red solution with a strong green fluorescence, characteristic of *meso*benzanthrones, indicates that the fission product most probably contains also 1-phenylnaphthalene-2′ : 4′-dicarboxylic acid, as this would be expected to accompany the formation of a *meso*benzanthrone.

From these results it appears that this deactivation effect cannot be attributed to ordinary steric hindrance, as this would necessitate preferential cleavage of the bond linking the carbonyl carbon atom and carbon atoms (*b*) and (*a*) (see II) in 3 : 4-benzfluorenone-1- and -8-carboxylic acids, respectively. Similarly, it would have resulted also in the formation of 2-methoxy*meso*benzanthrone as the main product on ring closure of 3-methoxy-1-phenylnaphthalene-2′-carboxylic acid, which is not the case (cf. the effect of *o*-substituents on the formation and hydrolysis of esters, chlorides, amides, and nitriles of benzoic acids; Lloyd and Sudborough, J., 1899, **75**, 580). The factors, therefore, which operate to determine the point of cleavage of 3 : 4-benzfluorenones, as well as the mode of cyclisation of 1-phenylnaphthalene-2′-carboxylic acids, are of polar origin (cf. Kutz and

Adkins, *J. Amer. Chem. Soc.*, 1930, **52**, 4036), depending to a great extent on the electron density at carbon atoms (*a*) and (*b*) in (II) and 2 and 2′ in (I) (cf. Lea and Robinson, J., 1926, 2351).

EXPERIMENTAL.

(M.p.'s are not corrected. Microanalyses were carried by Dr. G. Weiler and Dr. B. Strauss of Oxford.)

4-*Nitro*-2-*naphthyl Methyl Ether*.—The crude nitro-naphthol (5 g.) was methylated with 10% sodium hydroxide solution (40 c.c.) and methyl sulphate (8 c.c.); the precipitated ether crystallised from alcohol in yellow, lustrous plates, m. p. 102—103° (Morgan and Evens, *loc. cit.*, give m. p. 100—103°); yield, 60—70%.

4-*Amino*-2-*naphthyl Methyl Ether Sulphate*.—The powdered nitro-ether (10 g.) was dissolved in ether (1 l.), aluminium amalgam (8·6 g.) added, and the mixture left for 4 hours with frequent shaking. The fluorescent ethereal filtrate was dried, cooled in ice, and the base sulphate precipitated by addition of the calculated amount of concentrated sulphuric acid; yield about 90%. 4-*Acetamido*-2-*naphthyl methyl ether*, prepared in benzene solution, crystallised from dilute alcohol in silky needles, m. p. 179° (Found: C, 73·0; H, 5·8; N, 6·4. $C_{13}H_{13}O_2N$ requires C, 72·5; H, 6·1; N, 6·5%).

4-*Iodo*-2-*naphthyl Methyl Ether*.—The base sulphate (17 g.) was dissolved in hot 2N-sulphuric acid (240 c.c.), quickly cooled, and a further 40 c.c. of concentrated sulphuric acid added. The mixture was thoroughly cooled to − 5°, and sodium nitrite solution (5·5 g. in 40 c.c. of water) slowly added with stirring. The diazo-solution was stirred for about 15 minutes, treated with powdered urea (2·8 g.), and slowly added to a solution of potassium iodide (23·4 g. in 130 c.c. of 2N-sulphuric acid). The solution was left overnight, then heated on the water-bath for 20 minutes. The precipitated semi-solid was extracted with benzene, washed with alkali to remove phenolic by-products, and then distilled in a vacuum; b. p. 200—210°/3 mm. The solidified yellow distillate gave on crystallisation from light petroleum (b. p. 30—50°) 4-iodo-2-naphthyl methyl ether in colourless plates, m. p. 66—67° (Hodgson and Birtwell, *loc. cit.*, give m. p. 67°) (Found: C, 47·0; H, 3·4; I, 45·7. Calc. for $C_{11}H_9OI$: C, 46·5; H, 3·2; I, 44·7%); yield, 15%. In an attempt to isolate the iodo-compound by steam-distillation, only a small fraction was volatile, and the phenolic residue dissolved in alkali to a red solution and melted after crystallisation from dilute methyl alcohol or benzene at 187—188°. On sublimation in a vacuum it gave orange yellow crystals, m. p. 191—192°, undepressed on admixture with a sample of 2-hydroxy-1 : 4-naphthaquinone (kindly supplied by Dr. Gabra Soliman), prepared by the action of cold alcoholic alkali on 2 : 4-dihydroxynaphthalene. Its formation may be due to the decomposition of the diazonium compound to 2 : 4-dihydroxynaphthalene which was then oxidised on being dissolved in alkali to 2-hydroxy-1 : 4-naphthaquinone.

3-*Methoxy*-1-*phenylnaphthalene*-2′-*carboxylic Acid*.—A mixture of 4-iodo-2-naphthyl methyl ether (0·5 g.) and methyl *o*-iodobenzoate (1·0 g.) was stirred at 180—190°. Copper bronze (0·5 g.) was then added during 30 minutes, the temperature being slowly raised to 200—210°, and the mixture was kept at this temperature for a further 4—5 hours, then worked up as usual (cf. Baddar and Warren, J., 1938, 401); the sticky solid obtained from the benzene extract was esterified with diazomethane and distilled in a vacuum, b. p. 200—210°/3 mm. The yellowish-brown distillate gave on hydrolysis 3-*methoxy*-1-*phenylnaphthalene*-2′-*carboxylic acid*, which crystallised from methyl alcohol in long cubic rods, m. p. 191—192° (Found: C, 78·1; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1%); yield, 26%.

1-*Methoxy*-3 : 4-*benzfluorenone and* 2-*Methoxy*meso*benzanthrone*.—3-Methoxy-1-phenylnaphthalene-2′-carboxylic acid was dissolved in benzene and cyclised with phosphoric oxide (cf. Baddar, *loc. cit.*). On crystallisation from methyl alcohol, two types of crystals were obtained (yellow and orange), which were incompletely separated by mechanical means. Attempts to purify them by fractional crystallisation or chromatography failed. The yellow crystals were, however, proved to be 2-methoxy*meso*benzanthrone as they gave with concentrated sulphuric acid a yellowish-red solution with a green fluorescence, and on fusion with potassium hydroxide followed by reduction with sodium hyposulphite a blue-green vat was produced, which dyed cotton green, identical with that of Caledon jade-green, *i.e.*, 2 : 2′-dimethoxydibenzanthrone. The orange crystals were the major product and melted after several crystallisations from methyl alcohol at 148—150° (Found: C, 82·5; H, 4·5. $C_{18}H_{12}O_2$ requires C, 83·0; H, 4·7%). These were proved to be 1-*methoxy*-3 : 4-*benzfluorenone*, probably contaminated with traces of 2-methoxy*meso*benzanthrone, by the following tests: (1) they gave with concentrated sulphuric acid a brownish-green solution; (2) when heated at 100° with concentrated sulphuric acid, they were easily sulphonated (*meso*benzanthrones, in general, are much more resistant to sulphonation than are 3 : 4-benzfluorenones); (3) on fusion with potassium hydroxide followed by reduction with sodium hyposulphite, only very little green vat was obtained.

Ethyl 3-*Nitrophthalate*.—This ester, prepared by refluxing a mixture of 3-nitrophthalic acid (60 g.), absolute alcohol (240 c.c.), and concentrated sulphuric acid (80 c.c.) for 8 hours on the water-bath, crystallised from light petroleum in long, colourless needles, m. p. 45—46°. Miller (*Annalen*, 1881, **208**, 243) and Curtius and Semper (*Ber.*, 1913, **46**, 1168) give m. p. 45° and 46° respectively.

Ethyl 3-p-*Toluenesulphonamidophthalate*.—This was prepared in the usual manner and crystallised from benzene–light petroleum (70—80°) in colourless needles, m. p. 147—148° (Found: N, 4·0; S, 8·8. $C_{19}H_{21}O_6NS$ requires N, 3·6; S, 8·2%). It is soluble in benzene, moderately soluble in water, and sparingly soluble in light petroleum.

1-*Phenylnaphthalene*-2′ : 3′-*dicarboxylic Acid*.—Ethyl 3-iodophthalate (2 g.) and 1-iodonaphthalene (1·6 g.) were heated together with stirring in a boiling nitrobenzene bath; copper bronze (2·0 g.) was slowly added during ½ hour, and the heating continued for 4 hours. The product was hydrolysed with alcoholic sodium hydroxide and the sodium salt of the acids dissolved in water (80—90 c.c.) and extracted with benzene to remove neutral substances. The alkaline solution (charcoal) gave on acidification a white amorphous precipitate which crystallised from alcohol–benzene to give 1-phenylnaphthalene-2′ : 3′-dicarboxylic acid in colourless cubic crystals (yield, 36%), m. p. 192—193° (quick heating); when slowly heated it melted at 178—179°, probably owing to anhydride formation (see below). The acid was, therefore, best identified as its *methyl* ester, which crystallised from alcohol in colourless crystals, m. p. 133—134° (Found: C, 74·8; H, 5·3. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

1-*Phenylnaphthalene*-2′ : 3′-*dicarboxylic Anhydride*.—The acid (1 part) was refluxed with acetic anhydride (3 parts) for ½ hour. The *anhydride* was then precipitated by addition of ether, and crystallised from benzene–light petroleum (b. p. 60—80°) in colourless leaflets, m. p. 179—180° (Found: C, 79·0; H, 3·6. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%); yield, 85%.

3 : 4-*Benzfluorenone*-8-*carboxylic Acid and* meso*Benzanthrone*-8-*carboxylic Acid*.—1-Phenylnaphthalene-2′ : 3′-dicarboxylic anhydride (2 g.), carbon disulphide (15 c.c.), and finely powdered aluminium chloride (3 g.) were refluxed on the water-bath for 4 hours with occasional shaking. Carbon disulphide was evaporated off, and the product decomposed with dilute hydrochloric acid. The acids were filtered off, dissolved in hot ammonium hydroxide, the solution filtered, and the acids reprecipitated. The dry product was washed with a little ether, then crystallised from glacial acetic acid; the silky brown-red needles precipitated at once were proved to be 3 : 4-*benzfluorenone*-8-*carboxylic acid* (0·4 g.), m. p. 276—276·5°, as they gave 3 : 4-benzfluorenone on decarboxylation with copper bronze and quinoline (Found: C, 78·8; H, 3·6. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%). The yellow needles (0·8 g.) precipitated on standing were proved to be *meso*benzanthrone-8-carboxylic acid, m. p. 262—263°, as they gave on decarboxylation *meso*benzanthrone (Found:

C, 78·6; H, 3·7. Calc. for $C_{18}H_{10}O_3$: C, 78·8; H, 3·7%); Copp and Simonsen (J., 1942, 212) give m. p. 254—255°. The acetic acid mother-liquor gave on concentration a mixture of the two acids, *meso*benzanthrone-8-carboxylic acid predominating. Methyl *meso*benzanthrone-8-carboxylate was prepared by means of diazomethane in dioxan as brilliant yellow needles, m. p. 173·5—174·5°, undepressed on admixture with an authentic specimen (kindly supplied by Prof. J. L. Simonsen). The acid prepared by hydrolysing the ester with acetic–hydrochloric acids melted at 257—258°. This may account for the low m. p. of the acid prepared by Copp and Simonsen (*loc. cit.*), which they obtained by hydrolysis of its methyl ester.

Fusion of 3 : 4-*Benzfluorenone*-8-*carboxylic Acid with Potassium Hydroxide.*—The benzfluorenone (1 part) was added during 10 minutes to fused potassium hydroxide (7 parts) at 200—210°, the temperature being slowly raised to 225—230° and kept thereat with frequent stirring for a further ½ hour. The alkaline fluorescent solution was filtered and acidified. The dry acid, which was soluble in benzene, became insoluble on being digested with successive small amounts of benzene, probably owing to dehydration. This process was repeated until no more acid was precipitated. On crystallisation from alcohol–benzene, then from dilute alcohol, 1-*phenylnaphthalene*-2 : 3′-*dicarboxylic acid* was obtained in colourless crystals, m. p. 255—256°, mixed m. p. with 1-phenylnaphthalene-2′ : 3′-dicarboxylic acid 180—210° (Found : C, 74·0; H, 4·2. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%). When warmed with concentrated sulphuric acid it gave a green non-fluorescent solution.

1-*Phenylnaphthalene*-2 : 4′-*dicarboxylic Acid.*—A mixture of methyl *p*-iodobenzoate (2 g.) and methyl 1-bromo-2-naphthoate (2 g.) was thoroughly dried and stirred in an ethyl cinnamate bath at 200—210°. Copper bronze (2 g.) was added during 30 minutes, and the mixture slowly (½ hour) heated to 240—250°, kept thereat for 2 hours, again slowly (½ hour) heated to 260—265°, and stirring continued for a further 3—4 hours. The product was extracted with acetone, and removal of the solvent gave a viscous brown oil, which was twice extracted with hot alcohol (total 120—150 c.c.). The cold alcoholic extract was filtered from the tarry residue (about 0·1 g.), concentrated to about 30 c.c., then hydrolysed with alcoholic sodium hydroxide, filtered off, and worked up as usual. The dry acids were extracted with hot benzene (residue *ca.* 0·15—0·2 g.), the extract concentrated to about 20 c.c., then kept for two days and filtered from the precipitated acids (0·15—0·2 g.), probably 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid mixed with traces of 1-phenylnaphthalene-2 : 4′-dicarboxylic acid. Removal of the benzene gave a sticky solid which was heated at 160° and the crystalline white sublimate, m. p. 220—225°, rejected. The dark brown acid residue was then esterified with diazomethane in ether and fractionally distilled at 3 mm. The first fraction, b. p. 150—180°, crystallised from light petroleum in colourless crystals, m. p. 70—72°, and was not investigated. The second fraction, b. p. 200—240°, failed to crystallise and was therefore directly hydrolysed. The precipitated acids were filtered off, dried, and extracted with benzene, the benzene evaporated, and the process repeated until the acids became insoluble in benzene. The crude product was fractionally crystallised from dilute acetic acid (*ca.* 30%). The first crop, m. p. 255—260°, was recrystallised from dilute acetic acid to give 1-*phenylnaphthalene*-2 : 4′-*dicarboxylic acid* in colourless rods, m. p. 265—266° (Found : C, 73·7; H, 4·2. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%). The second crop melted at 220—235° and was proved to be an inseparable mixture of 1-phenylnaphthalene-2 : 4′- and 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acids, for it gave on cyclisation a mixture of 3 : 4-benzfluorenone-7-carboxylic acid and an anthanthrone; yield, *ca.* 7%.

3 : 4-*Benzfluorenone*-7-*carboxylic Acid.*—1-Phenylnaphthalene-2 : 4′-dicarboxylic acid chloride was treated with aluminium chloride in carbon disulphide and worked up as usual (cf. Schaarschmidt, *Ber.*, 1917, **50**, 294). The resulting acid chloride was refluxed with 15% potassium hydroxide solution for ½ hour, the solution filtered and acidified, and the crystals filtered off. On crystallisation from nitrobenzene, 3 : 4-*benzfluorenone*-7-*carboxylic acid* separated in lustrous, orange-red crystals, m. p. 323—324° (Found : C, 78·7; H, 3·8. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%). It gave on decarboxylation 3 : 4-benzfluorenone.

Fusion of 3 : 4-*Benzfluorenone*-7-*carboxylic Acid with Potassium Hydroxide.*—The acid (0·1 g.) was fused with potassium hydroxide as for the 8-carboxylic acid. The product obtained after refluxing with benzene (0·05—0·06 g.) was a mixture, m. p. 225—235°; it was extracted with dilute alcohol (20 c.c., 12%) and filtered hot. The insoluble fraction melted at 250—255° and gave on crystallisation from dilute acetic acid 1-phenylnaphthalene-2 : 4′-dicarboxylic acid in cubic rods, m. p. 263—264° (0·02 g.; *ca.* 40%), undepressed on admixture with an authentic specimen. The alcoholic mother-liquor was evaporated to dryness, and the residue (0·03—0·04 g.), m. p. 220—230°, was most probably a mixture of 1-phenylnaphthalene-2 : 4′- and -2′ : 4′-dicarboxylic acids. Their separation could not be effected either by fractional crystallisation or by refluxing with acetic anhydride followed by differential decomposition of their mixed anhydrides with sodium carbonate or hydroxide solution (cf. Huntress and Seikel, *J. Amer. Chem. Soc.*, 1939, **61**, 1358).

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