

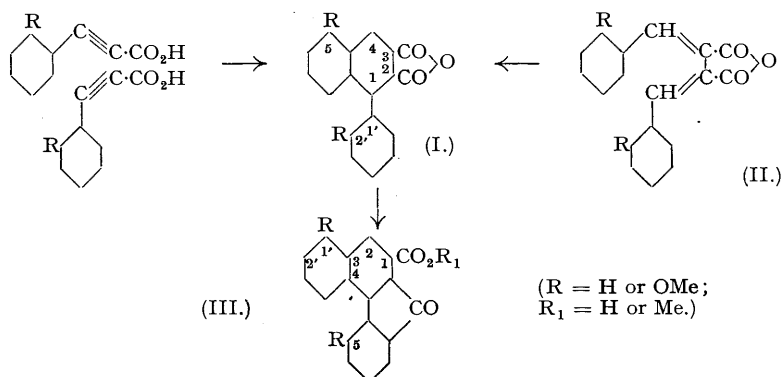
52. *Phenylpropionic Acids. Part I. The Dimerisation of o-Methoxyphenylpropionic Acid.*

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o-Methoxyphenylpropionic acid dimerises when heated with acetic anhydride or acetyl chloride to 2':5-dimethoxy-1-phenylnaphthalene-2:3-dicarboxylic anhydride (I; R = OMe). This is converted by aluminium chloride in nitrobenzene into 1':5-dimethoxy-3:4-benzfluorenone-1-carboxylic acid (III; R = OMe, R₁ = H), which is decarboxylated to 1':5-dimethoxy-3:4-benzfluorenone. The acid from (I; R = OMe) gives on decarboxylation 2':5-dimethoxy-1-phenylnaphthalene which is demethylated to 2':5-dihydroxy-1-phenylnaphthalene.

PHENYLPROPIOLIC acid is converted by acetic anhydride or phosphorus oxychloride into 1-phenylnaphthalene-2:3-dicarboxylic anhydride (I; R = H), the structure of which was established by Stobbe (*Ber.*, 1907, **40**, 3372) and Bucher (*J. Amer. Chem. Soc.*, 1908, **30**, 1244). The latter author has obtained similar products from substituted phenylpropionic acids (cf. Haworth and Sheldrick, *J.*, 1935, 636; Haworth and Kelly, *J.*, 1936, 745) and has claimed that

2-phenylnaphthalene derivatives can also be formed under other conditions, but no experimental details have been recorded.



In the present investigation *o*-methoxyphenylpropionic acid, prepared by refluxing 1:2-dibromo-2-(*o*-methoxyphenyl)propionic acid with alcoholic potassium hydroxide (cf. Perkin, *J.*, 1881, **39**, 409; Reimer and Howard, *J. Amer. Chem. Soc.*, 1928, **50**, 196), was refluxed with acetic anhydride or acetyl chloride to give a product which was proved, by molecular-weight determination, to be a dimer of the phenylpropionic acid. Furthermore, it was shown to be the anhydride of an *o*-dibasic acid from the following facts: (1) When fused with potassium hydroxide it gave a dibasic acid which recycled completely to the anhydride on melting or on mere boiling with acetic anhydride. (2) When heated with ammonium carbonate it was converted into the corresponding imide (cf. Schaarschmidt and Korten, *Ber.*, 1918, **51**, 1081). This excludes the possibility that the dimer is a 2-phenylnaphthalene derivative. It cannot be, however, a cyclobutadiene derivative (cf. Manthey, *Ber.*, 1900, **33**, 3081), for the solution of its acid in sodium hydrogen carbonate failed to discharge the colour of potassium permanganate solution (cf. Bucher, *loc. cit.*).

It appears, therefore, that the dimer must be 2':5-dimethoxy-1-phenylnaphthalene-2:3-dicarboxylic anhydride (I; R = OMe). This is rigidly established by the fact that the same anhydride is obtained by the action of light or heat on di-(*o*-methoxybenzylidene)succinic anhydride (II; R = OMe) (unpublished work by F. G. Baddar and Munir Gindy; cf. Stobbe, *loc. cit.*; Bucher, *loc. cit.*).

The acid from (I; R = OMe) gave on decarboxylation 2':5-dimethoxy-1-phenylnaphthalene, which was demethylated to 2':5-dihydroxy-1-phenylnaphthalene. The latter on being distilled with zinc dust gave a viscous oil from which no pure nitro-derivative of 1-phenylnaphthalene could be obtained (cf. Haworth and Sheldrick, *loc. cit.*). This may be due to the contamination of the product with fluoranthene resulting from 2':5-dihydroxy-1-phenylnaphthalene during zinc dust distillation. The anhydride (I; R = OMe) was converted by aluminium chloride in nitrobenzene into 1':5-dimethoxy-3:4-benzfluorenone-1-carboxylic acid (III; R = OMe, R₁ = H). The reaction was incomplete if carried out in cold or hot carbon disulphide or benzene instead of nitrobenzene (cf. Schaarschmidt, *loc. cit.*). This acid was decarboxylated to 1':5-dimethoxy-3:4-benzfluorenone. Similarly, *p*-nitro- and *p*-methoxy-phenylpropionic acids dimerised when refluxed with acetic anhydride; the product from the former was proved to be a 1-phenylnaphthalene derivative, that from the latter is under investigation (unpublished work by F. G. Baddar and Lanson Salib El-Assal).

EXPERIMENTAL.

(M. p.'s are not corrected. Microanalyses were carried out by Drs. Weiler and Strauss of Oxford.)
cis-*o*-Methoxycinnamic Acid.—This was prepared according to Stoermer and Friemel (*Ber.*, 1911, **44**, 1843) but by using 50 g. of sodium hydroxide instead of 30 g., and hydrolysing the ether ester directly by refluxing for 30–45 minutes. The alkaline solution was extracted with ether, and the aqueous layer (charcoal) filtered and acidified. The acid was freed from unchanged coumarin by dissolving it in sodium carbonate solution. On crystallisation from dilute alcohol, *cis*-*o*-methoxycinnamic acid was obtained in colourless cubes, m. p. 94–95° (Stoermer and Friemel, and Reimer and Howard, *loc. cit.*, give m. p.'s 88–89° and 92–93° respectively; yield about 90%).

1:2-Dibromo-2-(*o*-methoxyphenyl)propionic Acid.—A cold solution of pure *cis*-*o*-methoxycinnamic acid (120 g.; 1 mol.) in carbon tetrachloride (600 c.c.) was brominated with bromine (36 c.c., 1 mol.) in 120 c.c. of carbon tetrachloride (cf. *Org. Synth.*, XII, 36). The precipitated bromination product was

filtered off and washed with carbon tetrachloride. The crude product (ca. 200—220 g.) shrank at about 130° and had m. p. 160—165°. This was purified by crystallisation from benzene; the first crop melted at 165—170° (ca. 120 g.) and a further crop, precipitated on concentration, melted indefinitely between 130° and 160° (ca. 50—60 g.). This was probably a mixture of the two dibromo-acids isolated by Reimer and Howard (*loc. cit.*). The two crops, however, were mixed together and subjected to the following treatment.

o-Methoxyphenylpropionic Acid.—A powdered mixture of the above crystallised acids (180 g.) was added to cold 20% alcoholic potassium hydroxide (700 c.c.), and the mixture heated under reflux for 6 hours and worked up as usual (cf. *Org. Synth.*, XII, 60). The acid was best purified by dissolving it in ether and re-extracting it from the solution by sodium carbonate. On crystallisation from benzene *o*-methoxyphenylpropionic acid separated in colourless crystals, m. p. 128—129° (yield about 50%). When twice crystallised from benzene, it was obtained in aggregates of monoclinic crystals, m. p. 120—130° (Found: C, 68.1; H, 4.6. Calc. for C₁₀H₈O₃: C, 68.2; H, 4.6%); Perkin (*loc. cit.*) and Reimer and Howard (*loc. cit.*) give m. p.'s 124—126° and 125°, respectively.

2': 5-Dimethoxy-1-phenyl-naphthalene-2: 3-dicarboxylic Anhydride (I; R = OMe).—*o*-Methoxyphenylpropionic acid (20 g.) was refluxed with acetic anhydride (60 c.c.) for 3 hours, and the precipitated pure anhydride filtered off and washed with ether (yield 85%). It melted at 244—245° and was pure enough for the following steps. On crystallisation from glacial acetic acid the anhydride separated in straw-yellow, tabular, prismatic crystals, m. p. 245—246° [Found: C, 71.8; H, 4.2; OCH₃, 18.5; *M* (Rast), 346. C₂₀H₁₄O₅ requires C, 71.8; H, 4.2; OCH₃, 18.6%; *M*, 334].

Methyl 1': 5-Dimethoxy-3: 4-benzfluorenone-1-carboxylate (III; R = OMe, R₁ = Me).—Nitrobenzene (180 c.c.) was cooled with stirring to -5° and a finely powdered mixture of the anhydride (I; R = OMe) (15 g.) and aluminium chloride (75 g.) was slowly added during an hour. The whole was kept at 0° for 2—3 hours, then allowed to stand at room temperature (20—30°) for 3 days with occasional stirring. The brownish-green product was poured on ice, acidified, and the nitrobenzene removed by steam-distillation. The product was dissolved in hot ammonium hydroxide, filtered, and precipitated. The dry crude acid (yield, 12 g.), being difficultly soluble in most organic solvents, was directly esterified by refluxing it with a mixture of methyl iodide (60 g.), acetone (500 c.c.), and dry potassium carbonate (40 g.) for 4 hours. The acetone was removed, and the solution of the ester in benzene was washed with sodium hydroxide solution. The methyl ester was best purified by crystallisation from dioxan and then from alcohol-dioxan or alcohol, giving red prismatic needles, m. p. 190.5—191.5° [Found: C, 72.5; H, 4.6; *M* (Rast), 348. C₂₁H₁₆O₅ requires C, 72.4; H, 4.6%; *M*, 348]; yield, 7 g. (ca. 54%). The free acid (III; R = OMe, R₁ = H) was obtained by hydrolysing the ester with alcoholic potassium hydroxide; it crystallised with difficulty from benzene or toluene in reddish-brown needles, m. p. 258—259°.

1': 5-Dimethoxy-3: 4-benzfluorenone.—1': 5-Dimethoxy-3: 4-benzfluorenone-1-carboxylic acid (1 g.) and copper bronze (0.12 g.) were refluxed in quinoline (10 c.c.) for ½ hour. The benzene solution was repeatedly extracted with hydrochloric acid, then washed with sodium hydroxide solution. On crystallisation from dilute acetic acid and then dioxan-alcohol, 1': 5-dimethoxy-3: 4-benzfluorenone was obtained in red prismatic needles, m. p. 176° (Found: C, 78.5; H, 4.88; OCH₃, 19.2; *M*, 282. C₁₉H₁₄O₃ requires C, 78.6; H, 4.86; OCH₃, 21.4%; *M*, 290).

2': 5-Dimethoxy-1-phenyl-naphthalene-2: 3-dicarboxylic Acid.—The powdered anhydride (I; R = OMe) (5 g.) was added to molten potassium hydroxide (15 g.) and stirred at 200—210° for about 20 minutes. The ice-cold aqueous extract gave on acidification 2': 5-dimethoxy-1-phenyl-naphthalene-2: 3-dicarboxylic acid; yield, ca. 80%. On crystallisation from acetic acid it was partly converted into the anhydride. It melted at 245—246° being transformed into the anhydride. It was easily converted into the anhydride on being boiled with acetic anhydride for 1—2 minutes. The acid was best identified as its methyl ester which was prepared by treating a dioxan solution of the acid with diazomethane in ether. On crystallisation from benzene-light petroleum (b. p. 60—70°), this ester separated in colourless crystals, m. p. 133—134° (Found: C, 69.5; H, 5.3; OCH₃, 30.7; *M*, 368. C₂₂H₂₀O₆ requires C, 69.5; H, 5.3; OCH₃, 32.6%; *M*, 380).

2': 5-Dimethoxy-1-phenyl-naphthalene.—A stirred mixture of 2': 5-dimethoxy-1-phenyl-naphthalene-2: 3-dicarboxylic acid (13 g.), quinoline (40 c.c.), and copper bronze (2.6 g.) was slowly heated during ½ hour to 200°. The temperature was kept at 200—210° and a further amount of copper bronze (2.6 g.) was added during 2 hours, and stirring and heating continued for a further hour. The reaction mixture was poured into dilute hydrochloric acid, and the precipitated solid was filtered off, dried, and thoroughly extracted with ether or benzene. The solution was washed with sodium hydroxide and the viscous yellow-brown oil obtained on vacuum distillation, b. p. 190—200°/5 mm. (yield, 40%), gave on repeated crystallisation from methyl or ethyl alcohol 2': 5-dimethoxy-1-phenyl-naphthalene in colourless aggregates of monoclinic crystals, m. p. 95—96° [Found: C, 81.3; H, 6.1; OCH₃, 19.0; *M* (Rast), 250. C₁₈H₁₆O₂ requires C, 81.8; H, 6.1; OCH₃, 23.5%; *M*, 264]. The dilute alcoholic solution showed a strong blue fluorescence. The sodium hydroxide extract, on acidification, precipitated a mono-carboxylic acid which gave on crystallisation from benzene-light petroleum (b. p. 60—70°) 2': 5-dimethoxy-1-phenyl-naphthalene-2 (or 3)-carboxylic acid in pale yellow prisms, m. p. 229.5—230.5° (Found: C, 74.4; H, 5.2; *M*, 308. C₁₉H₁₆O₄ requires C, 74.0; H, 5.3%; *M*, 308). Its methyl ester, prepared by diazomethane, crystallised from alcohol in yellow flakes, m. p. 165.5—166.5° [Found: C, 74.5; H, 5.7; *M* (Rast), 326. C₂₀H₁₈O₄ requires C, 74.5; H, 5.6%; *M*, 322].

2': 5-Dihydroxy-1-phenyl-naphthalene.—The dimethyl ether (4 g.) was refluxed with a mixture of glacial acetic acid (60 c.c.) and hydriodic acid (30 c.c.) for 5 hours. The reaction mixture was diluted with sodium sulphite solution, the acetic acid neutralised with sodium carbonate, and the product extracted with ether. The ethereal solution was extracted with alkali and the precipitated phenol re-extracted with ether (yield, 2.7 g.). On crystallisation from benzene 2': 5-dihydroxy-1-phenyl-naphthalene was obtained in very pale yellow crystals, m. p. 187—188° (Found: C, 81.1; H, 5.2; active H, 0.88; *M*, 224. C₁₆H₁₂O₂ requires C, 81.4; H, 5.1; active H, 0.85%; *M*, 236). It gave with alcoholic ferric chloride a green solution.

1-Phenylnaphthalene-2:3-dicarboxyimide.—1-Phenylnaphthalene-2:3-dicarboxylic anhydride (4 g.) was thoroughly powdered with ammonium carbonate (7 g.), and the mixture heated on the direct flame with frequent shaking until it melted. The gentle heating was continued, the mass being kept just molten until no more ammonia was evolved. The product was washed with sodium carbonate solution, and the insoluble residue extracted with sodium hydroxide, filtered and reprecipitated with acid. On crystallisation from alcohol, the imide was obtained in colourless, silky needles, m. p. 249° (yield, 85%) (cf. Schaaarschmidt and Korten, *loc. cit.*) (Found: C, 79.2; H, 4.25; N, 5.45. Calc. for $C_{18}H_{11}O_2N$: C, 79.1; H, 4.06; N, 5.1%).

2':5-Dimethoxy-1-phenylnaphthalene-2:3-dicarboxyimide.—The anhydride (I; R = OMe) (1 g.) was powdered with ammonium carbonate (8 g.) and treated as above. The product (0.2 g.) crystallised from acetic acid or dioxan-alcohol to give the *imide* in colourless leaflets, m. p. 273—274° (Found: C, 71.4; H, 4.6; N, 4.55. $C_{20}H_{15}O_4N$ requires C, 72.1; H, 4.5; N, 4.2%).

3:4-Benzfluorene.—3:4-Benzfluorenone-1-carboxylic acid (0.5 g.) was distilled with zinc dust (10 g.), and the distillate was extracted with alcohol (charcoal), and then twice crystallised from methyl alcohol to give 3:4-benzfluorene in colourless leaflets, m. p. 126—127° (Found: C, 94.4; H, 5.6. Calc. for $C_{17}H_{12}$: C, 94.4; H, 5.6%); Cook *et al.* (*J.*, 1935, 1323) give m. p. 124—125°.

1':5-Dimethoxy-3:4-benzfluorenone-1-carboxylic acid was prepared by Munir Gindy for studying its fission with alkali. The results will be published soon.

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