404. *Phenylpropiolic Acids. Part III.* The Effect of Substituents on the Mode of Cyclisation of Substituted Phenylpropiolic Anhydrides.*

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o-Methoxyphenylpropiolyl chloride and phenylpropiolic acid give a mixture of 1-*o*-methoxyphenyl- and 5-methoxy-1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride. The derived dibasic acids are decarboxylated to 1-*o*-methoxyphenyl- and 5-methoxy-1-phenyl-naphthalene, which are independently synthesised.

Similarly, *o*-methoxyphenylpropiolyl chloride and *p*-nitrophenylpropiolic acid give a mixture of 1-*o*-methoxyphenyl-7-nitro- and 5-methoxy-1-*p*-nitrophenyl-naphthalene-2 : 3-dicarboxylic anhydride. The dibasic acid from the former anhydride is decarboxylated to 2′-methoxy-7-nitro-1-phenylnaphthalene, which on reduction and deamination gives 1-*o*-methoxyphenylnaphthalene.

The cylcisation is believed to be preceded by anhydride formation, for which a mechanism is put forward.

IN Part II * we reported the effect of substituents on the mode of dimerisation of phenylpropiolic acids. It was shown that *p*-nitro- and *p*-methoxy-phenylpropiolic acid were converted by acetic anhydride into 7-nitro-1-*p*-nitrophenyl- and 7-methoxy-1-*p*-methoxyphenyl-naphthalene-2 : 3-dicarboxylic anhydride, and we concluded that the formation of 1-phenylnaphthalene derivatives from unsubstituted and substituted phenylpropiolic acids (see Part I, *J.*, 1947, 224, for references), independently of the nature of the substituent, is explained if dimerisation is preceded by anhydride formation.

In the present investigation we studied the effect of dissimilar substituents.

A mixture of *o*-methoxyphenylpropiolyl chloride and phenylpropiolic acid was refluxed in benzene for 24 hours. The product was a mixture of 1-*o*-methoxyphenyl- and 5-methoxy-1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride in the ratio of about 3 : 1, with traces of 5-methoxy-1-*o*-methoxyphenyl- and 1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride.

The structure of 1-*o*-methoxyphenylnaphthalene-2 : 3-dicarboxylic anhydride (VI; R = H) was determined by decarboxylation of the derived dibasic acid to 1-*o*-methoxyphenylnaphthalene (VIII; R = H), identical with a specimen prepared by dehydrogenation of 3 : 4-dihydro-1-*o*-methoxyphenylnaphthalene, which was prepared from α-tetralone and *o*-methoxyphenylmagnesium bromide (cf. Part II, *loc. cit.*). The structure of 5-methoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (VII; R = H) was similarly determined by conversion into 5-methoxy-1-phenylnaphthalene (IX; R = H), identical with a specimen prepared analogously.

The presence of 1-phenyl- and 5-methoxy-1-*o*-methoxyphenyl-naphthalene-2 : 3-dicarboxylic anhydride in the product may be due to a double decomposition between *o*-methoxyphenylpropiolyl chloride and phenylpropiolic acid to give *o*-methoxyphenylpropiolic acid and phenylpropiolyl chloride.

A mixture of *o*-methoxyphenylpropiolyl chloride and *p*-nitrophenylpropiolic acid, refluxed in benzene for 36 hours, gave a mixture of 1-*o*-methoxyphenyl-7-nitro- (VI; R = NO_2) and 5-methoxy-1-*p*-nitrophenyl-naphthalene-2 : 3-dicarboxylic anhydride (VII; R = NO_2) in nearly equal amounts.

The structure of the former anhydride (VI; R = NO_2) was elucidated by decarboxylation of the dibasic acid to 1-*o*-methoxyphenyl-7-nitronaphthalene (VIII; R = NO_2), which on reduction and deamination gave 1-*o*-methoxyphenylnaphthalene (VIII; R = H).

Attempts to elucidate the structure of the anhydride (VII; R = NO_2) by a similar route were not successful, since the yields are too small and the product of deamination of 1-*p*-aminophenyl-5-methoxynaphthalene (IX; R = NH_2) failed to solidify even after several months. An attempt to synthesise a specimen of 5-methoxy-1-*p*-nitrophenylnaphthalene (IX; R = NO_2) by the Ullmann condensation of 1-iodo-5-methoxynaphthalene (cf. Lockett and Short, *J.*, 1939, 788) with *p*-iodonitrobenzene was also unsuccessful since, contrary to Hodgson and Davey's statement (*J.*, 1939, 348) on the preparation of 1-amino-5-nitronaphthalene, the yield was too small to allow for the carrying on of further steps.

The product (VII; R = NO_2) cannot be, however, a *cyclo*butadiene derivative (cf. Manthey, *Ber.*, 1900, **33**, 3081), for the solution of the derived acid in sodium hydrogen carbonate failed

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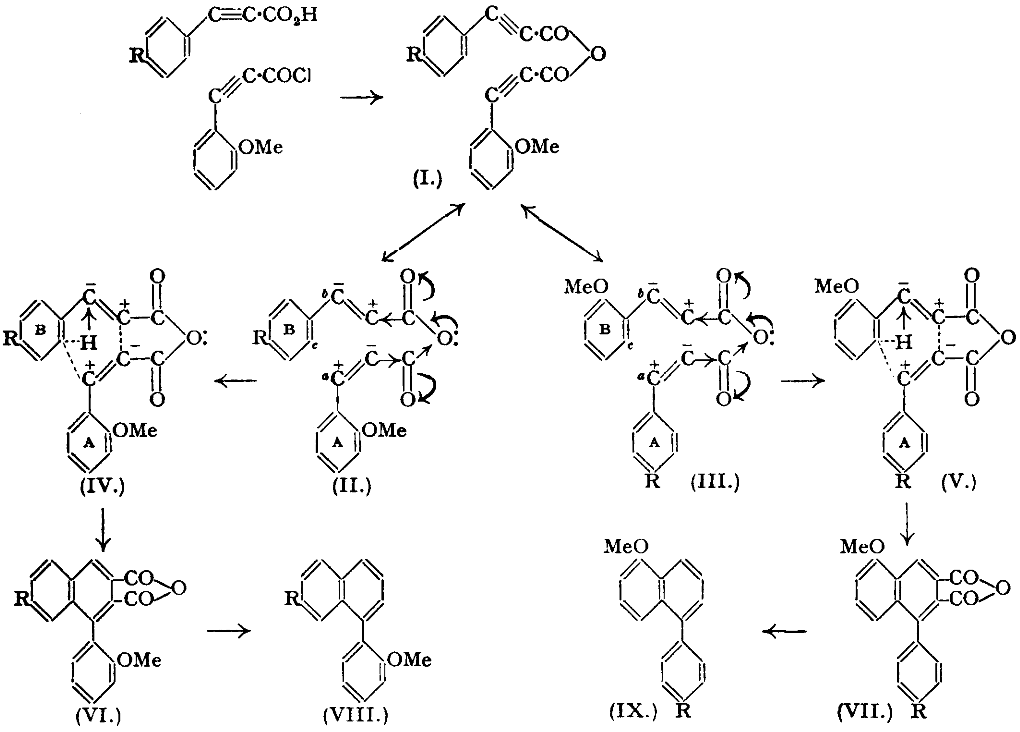
* Part II, *J.*, 1948, 1267.

to discharge the colour of potassium permanganate solution (cf. Bucher, *J. Amer. Chem. Soc.*, 1908, **30**, 1244; Baddar, *loc. cit.*). It cannot be a 2-phenylnaphthalene derivative, since it is insoluble in boiling sodium carbonate solution and dissolves only in hot sodium hydroxide solution to give a dibasic acid, which recyclises to the anhydride on mere boiling with acetic anhydride. Furthermore it gave an imide when heated with ammonium carbonate or when its ammonium salt was strongly heated (cf. Baddar, *loc. cit.*). These facts showed that the product can only be 5-methoxy-1-*p*-nitrophenylnaphthalene-2 : 3-dicarboxylic anhydride (VII; R = NO_2).



The above results can be interpreted electronically. Thus, the interaction between *o*-methoxyphenylpropiolyl chloride and phenylpropiolic acid leads to the formation of the anhydride (I; R = H). The actual state of the molecule is a resonance hybrid of the three possible contributing structure (I, II, and III; R = H). However, as the methoxyl group is electron-repelling, the contribution of (II) to the actual state of the molecule is more important than that of (III). On cyclisation (II) and (III) give rise to 1-*o*-methoxyphenyl- and 5-methoxy-1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride respectively. This explains the formation of (VI; R = H) in a greater proportion.

Similarly, the interaction between *o*-methoxyphenylpropiolyl chloride and *p*-nitrophenylpropiolic acid leads to the formation of the anhydride (I; R = NO_2), which exists as a resonance hybrid of (I), (II), and (III) (R = NO_2). Since the nitro-group is electron-attracting, it is expected that (II) should be more important than structure (III). However, the formation of (VI) and (VII) (R = NO_2) in nearly equal amounts could be explained by assuming that this cyclisation is similar to an electrophilic substitution which is known to be retarded by electron-attracting groups. The positively charged carbon atom (*a*) (see II and III) approaches the benzene molecule (B) at (*c*), leading to a transition state (IV and V); this is followed by the liberation of a proton which combines with the negatively charged carbon atom (*b*) giving rise to the anhydrides (VI) and (VII). Thus, although owing to the presence of the nitro-group in the benzene nucleus structure (II; R = NO_2) affords a greater contribution to the actual state of the molecule than does (III), it retards the cyclisation by decreasing the electron density at carbon atom (*c*), and at the same time absorbs, by its strong $-M$ effect, the negative charge on carbon atom (*b*).

EXPERIMENTAL.

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

1-*Phenylnaphthalene*-2 : 3-*dicarboxylic Anhydride.*—A mixture of phenylpropiolic acid (0·4 g., 1 mol.) (Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510), phenylpropiolyl chloride (0·45 g., 1 mol.), and dry benzene (30 c.c.) was refluxed for 24 hours. Removal of the benzene left a solid residue which was washed with ether and crystallised from acetic acid, to give 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride, m. p. and mixed m. p. 252—253° (*ca.* 82%).

o-*Methoxyphenylpropiolyl Chloride.*—A mixture of *o*-methoxyphenylpropiolic acid (3·5 g.) (cf. Baddar, *loc. cit.*) and thionyl chloride (4 c.c.) was left overnight at 15—20°. Light petroleum (b. p. 30—50°) was added, and the excess thionyl chloride and the solvent were removed on the water-bath under reduced pressure. The product was distilled in a vacuum, to give a reddish-yellow mobile liquid, b. p. 140—145°/3 mm., which soon solidified. On crystallisation from light petroleum (b. p. 40—60°) o-*methoxyphenylpropiolyl chloride* was obtained in lemon-yellow needles, m. p. 93—94° (3·2 g., 82%) (Found : Cl, 19·9. $C_{10}H_7O_2Cl$ requires Cl, 18·3%).

5-*Methoxy*-1-*phenyl- and* 1-*o*-*Methoxyphenyl-naphthalene*-2 : 3-*dicarboxylic Anhydride.*—A mixture of freshly prepared *o*-methoxyphenylpropiolyl chloride (uncrystallised product) (5·4 g., 1 mol.) and phenylpropiolic acid (4·3 g., 1 mol.) was refluxed in dry thiophen-free benzene (60 c.c.) for 24 hours. Removal of the solvent gave a highly viscous residue which was treated with dry ether and left overnight. The precipitated product (4·8 g.), filtered off and washed with ether, had m. p. 180—190°. On crystallisation from benzene (40—50 c.c.) it gave a lemon-yellow crystalline product (after 3 hours), m. p. 257—258° (0·5 g.), which was recrystallised from the same solvent to give 5-*methoxy*-1-*phenylnaphthalene*-3 : 2-*dicarboxylic anhydride* in lemon-yellow plates, m. p. 267—268° [Found : C, 75·0; H, 3·8; OMe, 10·1%; *M* (Rast), 328. $C_{19}H_{12}O_4$ requires C, 75·0; H, 4·0; OMe, 10·2%; *M*, 304].

The benzene mother-liquor from the first crystallisation was concentrated and left overnight. The colourless product which crystallised was filtered off and washed with ether; it had m. p. 196—204° (1·5 g.). On crystallisation from the same solvent 1-o-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* was obtained in colourless crystals, m. p. 212—213° (Found : C, 74·9; H, 3·9; OMe, 9·4%; *M*, 300).

Evaporation of the first mother-liquor to dryness left a product which contained 5-methoxy-1-*o*-methoxyphenyl- and 1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride. The mixture was boiled with 10% sodium hydroxide solution and the insoluble fraction was proved to be the former anhydride by m. p. and mixed m. p. (cf. Baddar, *loc. cit.*). The acid which was precipitated on acidification was decarboxylated with copper and quinoline at 200—210°, then refluxed with acetic acid (8 c.c.)–hydriodic acid (5 c.c.; *d* 1·9) for 5 hours; the product was extracted with ether and washed with sodium hydroxide solution to remove phenolic substances (*ca.* 0·08 g.). Removal of the ether left an oily residue (*ca.* 0·5 g.) which gave on nitration 4-nitro-1-phenylnaphthalene, m. p. and mixed m. p. 129—130°.

3 : 4-*Dihydro*-5-*methoxy*-1-*phenylnaphthalene.*—A solution of 5-methoxy-α-tetralone (cf. Lockett and Short, *loc. cit.*) (3·5 g., 1 mol.) [prepared by the cyclisation of γ-*o*-methoxyphenylbutyric acid (cf. Baddar and El-Assal, *J.*, 1950, 3606)] in a mixture of thiophen-free benzene (15 c.c.) and dry ether (20 c.c.) was gradually added to an ice-cold stirred solution of phenylmagnesium bromide in ether [from freshly distilled bromobenzene (3·1 g., 1·1 mols.) and magnesium (0·5 g., 1·2 atoms)]. The reaction mixture was worked up as described for 3 : 4-dihydro-7-methoxy-1-*p*-methoxyphenylnaphthalene (Part II, *loc. cit.*), and purified by distillation in a vacuum; it had b. p. 185—190°/4 mm. On crystallisation from methyl alcohol 3 : 4-*dihydro*-5-*methoxy*-1-*phenylnaphthalene* was obtained in colourless crystals (2·2 g., 47%), m. p. 47—48° (Found : C, 86·2; H, 6·8; OMe, 13·6%; *M*, 218. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; OMe, 13·1%; *M*, 236).

5-*Methoxy*-1-*phenylnaphthalene* (IX; R = H).—3 : 4-Dihydro-5-methoxy-1-phenylnaphthalene (0·8 g.) was heated with selenium (0·6 g.) at 270—280° for 16—18 hours. The product was extracted with ether and crystallised from methyl alcohol, from which 5-*methoxy*-1-*phenylnaphthalene* was obtained in colourless crystals (*ca.* 0·3 g.), m. p. 84—85° (Found : C, 86·9; H, 5·8; OMe, 13·1%, *M*, 250. $C_{17}H_{14}O$ requires C, 86·8; H, 6·0; OMe, 13·2%; *M*, 234).

Decarboxylation of 5-*Methoxy*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic Acid.*—5-Methoxy-1-phenylnaphthalene-2 : 3-dicarboxylic acid (0·5 g.), prepared by refluxing the anhydride with 20% sodium hydroxide solution, was dissolved in quinoline (5 c.c.) and gradually heated in a nitrobenzene bath at 200—210°. Copper bronze (0·4 g.) was gradually added while stirring during 2 hours; the stirring and heating was continued for a further hour. The reaction mixture was worked up as usual, and the product extracted with ether or benzene. It was then purified by vacuum distillation, having b. p. 165—170°/2 mm., to give a light yellowish-brown oil which solidified after 3 months. On crystallisation from methyl alcohol 5-methoxy-1-phenylnaphthalene was obtained in colourless crystals (0·25 g., 70%), m. p. 84—85°, undepressed on admixture with an authentic specimen (Found : C, 87·0; H, 5·9; OMe, 13·1%; *M*, 217).

3 : 4-*Dihydro*-1-o-*methoxyphenylnaphthalene.*—Ice-cold *o*-methoxyphenylmagnesium bromide, prepared from freshly distilled *o*-bromoanisole (12·8 g., 1 mol.) and magnesium metal (1·68 g., 1·1 atoms) in dry ether (30 c.c.), was treated dropwise with a solution of α-tetralone (10·8 g., 1·2 mols.) in dry ether (20 c.c.). The mixture was worked up as above and the product was purified by vacuum-distillation to give 3 : 4-*dihydro*-1-o-*methoxyphenylnaphthalene* in colourless crystals (6·5 g., 68%), m. p. 74—75° (Found : C, 86·2; H, 6·7; OMe, 13·0%; *M*, 232. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; OMe 13·1%; *M*, 236).

1-o-*Methoxyphenylnaphthalene* (VIII; R = H).—This was prepared by the dehydrogenation of 3 : 4-dihydro-1-*o*-methoxyphenylnaphthalene (0·5 g.) with selenium (0·4 g.) at 270—275° for 16—17 hours. By crystallisation from methyl alcohol, 1-o-*methoxyphenylnaphthalene* was obtained in colourless crystals (0·35 g., 69%), m. p. 97—98° (Found: C, 86·9; H, 5·9; OMe, 12·2%; *M*, 219. $C_{17}H_{14}O$ requires C, 86·8; H, 6·0; OMe, 13·2%; *M*, 234).

Decarboxylation of 1-o-*Methoxyphenylnaphthalene*-2 : 3-*dicarboxylic Acid*.—This was carried out as described for 5-methoxy-1-phenylnaphthalene-2 : 3-dicarboxylic acid. The product, distilled in a vacuum, had b. p. 190—195°/4 mm., then crystallised from methyl alcohol, from which 1-*o*-methoxyphenylnaphthalene separated in colourless crystals (0·27 g., 70%), m. p. 97—98°, undepressed on admixture with an authentic specimen (Found: C, 86·9; H, 5·8; OMe, 13·5%; *M*, 222).

1-o-*Methoxyphenyl*-7-*nitro- and* 5-*Methoxy*-1-p-*nitrophenyl-naphthalene*-2 : 3-*dicarboxylic Anhydride*.—A solution of *o*-methoxyphenylpropiolyl chloride (9·4 g., 1 mol.) and *p*-nitrophenylpropiolic acid (9·2 g., 1 mol.) in dry thiophen-free benzene (200 c.c.) was refluxed for 36 hours. The product, m. p. 304—308°, precipitated on cooling, was filtered off and thoroughly washed with ether. On crystallisation from glacial acetic acid 5-*methoxy*-1-p-*nitrophenylnaphthalene*-2 : 3-*dicarboxylic anhydride* was obtained in fine yellow crystals (*ca.* 3·2 g.), m. p. 312—313° (Found: C, 64·9; H, 3·4; N, 4·0; OMe, 9·7%; *M*, 350. $C_{19}H_{11}O_6N$ requires C, 65·3; H, 3·2; N, 4·0; OMe, 8·9%; *M*, 349). It is soluble in hot sodium hydroxide solution and insoluble in boiling sodium carbonate solution. The *dimethyl* ester prepared (74%) in dioxan by means of diazomethane in ether, crystallised from methyl alcohol in pale yellow needles, m. p. 195—196° (Found: C, 63·9; H, 4·6; N, 3·7; OMe, 23·3%; *M*, 407. $C_{21}H_{17}O_7N$ requires C, 63·8; H, 4·6; N, 3·5; OMe, 23·5%; *M*, 395).

The benzene mother-liquor was distilled and the dark-brown viscous oil treated with ether and left overnight. The precipitated product was filtered off and crystallised from dilute acetic acid, from which 1-o-*methoxyphenyl*-7-*nitronaphthalene*-2 : 3-*dicarboxylic anhydride* separated in orange-yellow crystalline flakes (*ca.* 3·0 g.), m. p. 233—234° (Found: N, 3·8; OMe, 8·4. $C_{19}H_{11}O_6N$ requires N, 4·0; OMe, 8·9%). The *dimethyl* ester, prepared as above, crystallised from methyl alcohol in pale lustrous fine yellow crystals, m. p. 219—220° (Found: C, 63·6; H, 4·5; N, 3·7; OMe, 23·1%; *M*, 400. $C_{21}H_{17}O_7N$ requires C, 63·8; H, 4·6; N, 3·5; OMe, 23·5%; *M*, 395).

1-o-*Methoxyphenyl*-7-*nitronaphthalene* (VIII; R = NO_2).—A solution of 1-*o*-methoxyphenyl-7-nitronaphthalene-2 : 3-dicarboxylic acid (0·6 g.) in quinoline (5 c.c.) was stirred with copper-bronze (0·2 g.) while gradually heated to 230—235° during 15 minutes. The temperature was kept thereat for 30 minutes during which a further amount of copper-bronze (0·2 g.) was added portionwise; the heating was continued for a further 30 minutes. The reaction mixture was worked up as usual, and the product was crystallised from methyl alcohol or benzene–light petroleum (b. p. 40—60°), from which 1-o-*methoxyphenyl*-7-*nitronaphthalene* (0·3 g., 66%) was obtained in yellow crystalline flakes, m. p. 133—134° (Found: C, 73·2; H, 4·8; N, 5·0; OMe, 11·3%; *M*, 285. $C_{17}H_{13}O_3N$ requires C, 73·5; H, 4·7; N, 5·0; OMe, 11·1%; *M*, 279).

7-*Amino*-1-o-*methoxyphenylnaphthalene* (VIII; R = NH_2).—Zinc dust (7 g.) was added portionwise during 30 minutes to a boiling mixture of 1-*o*-methoxyphenyl-7-nitronaphthalene (0·45 g.), ethyl alcohol (40 c.c.), and concentrated hydrochloride acid (30 c.c.). The mixture was refluxed for a further hour, with occasional shaking, and worked up as described for 7-amino-1-*p*-aminophenylnaphthalene (Baddar and El-Assal, Part II, *loc. cit.*). The base (0·35 g.) was converted (Schotten–Baumann) into its *benzoyl* derivative, which crystallised from benzene–light petroleum (b. p. 40—60°) in pinkish-yellow crystalline aggregates, m. p. 116—117° (Found: C, 82·0; H, 5·6; N, 3·7; OMe, 8·7. $C_{24}H_{19}O_2N$ requires C, 81·6; H, 5·4; N, 4·0; OMe, 8·8%).

Deamination of 7-*Amino*-1-o-*methoxyphenylnaphthalene*.—A mixture of the base (0·5 g.), glacial acetic acid (6 c.c.), and concentrated sulphuric acid (6 c.c.) was cooled in ice, with stirring. Finely powdered sodium nitrite (0·8 g.) was added portionwise during 30 minutes. The stirring was continued for a further hour, and then the diazonium solution was added to a vigorously stirred suspension of finely powdered, freshly prepared cuprous oxide (0·8 g.) in ethyl alcohol (60 c.c.). Stirring was continued for 4 hours and the product was extracted as described for 7-amino-1-*p*-aminophenylnaphthalene (Baddar and El-Assal, *loc. cit.*). Purified by vacuum-distillation, this had b. p. 180—185°/1 mm. Repeated crystallisation from methyl alcohol gave 1-*o*-methoxyphenylnaphthalene in light brown crystals, m. p. 94—95°, undepressed on admixture with an authentic specimen.

5-*Methoxy*-1-p-*nitrophenylnaphthalene* (IX; R = NO_2).—5-Methoxy-1-*p*-nitrophenylnaphthalene-2 : 3-dicarboxylic acid (1·2 g.) was decarboxylated with copper-bronze (0·5 g.) and quinoline (10 c.c.) as described for 1-*o*-methoxyphenyl-7-nitronaphthalene-2 : 3-dicarboxylic acid. The product was crystallised from acetone (small volume) from which 5-*methoxy*-1-p-*nitrophenylnaphthalene* was obtained in yellow shining flakes (0·6 g., 66%), m. p. 159—160° (Found: C, 73·2; H, 4·6; N, 4·8; OMe, 10·9%; *M*, 250. $C_{17}H_{13}O_3N$ requires C, 73·5; H, 4·7; N, 5·0; OMe, 11·1%; *M*, 279).

1-p-*Aminophenyl*-5-*methoxynaphthalene*.—5-Methoxy-1-*p*-nitrophenylnaphthalene (0·6 g.) was reduced with zinc dust (8 g.) and concentrated hydrochloric acid (40 c.c.) as described for 7-amino-1-*o*-methoxyphenylnaphthalene. The base (0·45 g.) was converted (Schotten–Baumann) into its *benzoyl* derivative, which crystallised from benzene in fine light pink crystals (70%), m. p. 193—194° (Found: C, 81·6; H, 5·6; N, 4·0; OMe, 8·4%; *M*, 342. $C_{24}H_{19}O_2N$ requires C, 81·6; H, 5·4; N, 4·0; OMe, 8·8%; *M*, 353).

5-*Methoxy*-1-p-*nitrophenylnaphthalene*-2 : 3-*dicarboxyimide*.—This was prepared either by heating 5-methoxy-1-*p*-nitrophenylnaphthalene-2 : 3-dicarboxylic anhydride with excess of ammonium carbonate (cf. Baddar, *loc. cit.*) at 320—330° for 10—15 minutes, or by strongly heating the ammonium salt till no more ammonia was evolved. The product was crystallised from acetic acid, from which the *imide* was obtained in reddish-brown crystals, m. p. 327—328°, depressed on admixture with the anhydride to 280—290° (Found: N, 8·1. $C_{19}H_{12}O_5N_2$ requires N, 8·1%).

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