Phenylpropiolic Acids. Part V. Self-condensation of* m-*Alkoxy- and* 3 : 4-*Dialkoxy-phenylpropiolic Acids.*

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m-Alkoxyphenylpropiolic acids are converted by acetic anhydride into a mixture of colourless 6- and yellow 8-alkoxy-1-*m*-alkoxyphenylnaphthalene-2 : 3-dicarboxylic anhydride in equal amounts. The dibasic acids derived from the 3′ : 6-dialkoxy-anhydrides (II; R = Me or Et, R′ = H) are decarboxylated to 6-alkoxy-1-*m*-alkoxyphenylnaphthalenes.

The structure of the yellow anhydrides (III; R = Me and Et, R′ = H) follows from the fact that they give acid imides, and their alkaline solutions do not discharge the colour of potassium permanganate solution.

3 : 4-Diethoxyphenylpropiolic acid gives under the same conditions 6 : 7-diethoxy-1-(3′ : 4′-diethoxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride together with a small amount of the 7 : 8-diethoxy-isomer. 3 : 4-Dimethoxyphenylpropiolic acid gives a mixture from which 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride is the only isomer isolated in a pure state.

Cyclisation of *m*-substituted phenylpropiolic acids *via* the anhydrides (I) to 1-phenylnaphthalene derivatives could take place in either of two positions to give two isomeric compounds. We set out to test this assumption since Haworth and Sheldrick (*J.*, 1935, 636) and Haworth and Kelly (*J.*, 1936, 745) reported that they isolated from the action of acetic anhydride on 3 : 4-dimethoxy- and 3 : 4-methylenedioxy-phenylpropiolic acid only one 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride.

m-Methoxyphenylpropiolic acid and acetic anhydride gave a mixture from which (II) and (III), colourless and yellow, respectively, were isolated in nearly equal proportion. The structure of the former anhydride was elucidated by decarboxylation of the derived dibasic acid to 6-methoxy-1-*m*-methoxyphenylnaphthalene (IV; R = Me, R′ = H),

* Part IV, preceding paper.

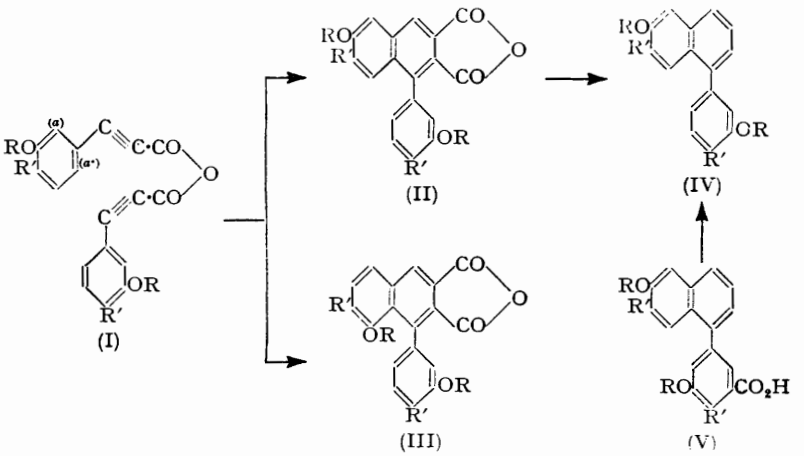
whose nitro-derivative was identical with one prepared by nitration of the product of decarboxylation of 3-methoxy-5-(6-methoxy-1-naphthyl)benzoic acid (V; R = Me, R′ = H).

m-Ethoxy- and *m-iso*propoxy-phenylpropiolic acid behaved analogously when similarly treated. The structure of the colourless anhydride (II; R = Et, R′ = H) was proved by decarboxylation of the derived dibasic acid to 6-ethoxy-1-*m*-ethoxyphenylnaphthalene (IV; R = Et, R′ = H), which was de-ethylated and then methylated to 6-methoxy-1-*m*-methoxyphenylnaphthalene. This gave a nitro-derivative identical with the authentic specimen. Attempted nitration of the product of decarboxylation of 6-ethoxy-1-*m*-ethoxyphenylnaphthalene-2 : 3-dicarboxylic or 3-ethoxy-5-(6-ethoxy-1-naphthyl)benzoic acid gave an inseparable mixture of nitro-derivatives.

The yellow anhydrides (III; R = Me or Et, R′ = H) cannot be *cyclo*butadiene derivatives (cf. Manthey, *Ber.*, 1900, **33**, 3081), for the solution of the derived acids in sodium hydrogen carbonate failed to discharge the colour of potassium permanganate solution (cf. Bucher, *J. Amer. Chem. Soc.*, 1908, **30**, 1244; Baddar, *J.*, 1947, 224; 1948, 1267). Moreover, they cannot be 2-phenylnaphthalene derivatives, since they were insoluble in boiling sodium carbonate solution and dissolved only in hot sodium hydroxide solution to give dibasic acids, which were converted back into the corresponding anhydrides on mere boiling with acetic anhydride. Furthermore, they gave imides when fused with solid ammonium carbonate (cf. Baddar, *loc. cit.*). The anhydrides must therefore be the isomers (III; R′ = H, R = Me and Et, respectively).

The structures of the two *iso*propoxy-anhydrides were assumed by analogy.

3 : 4-Diethoxyphenylpropiolic acid, when heated with acetic anhydride, gave yellow 6 : 7-diethoxy-1-(3′ : 4′-diethoxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride (II; R = Et, R′ = OEt) together with a small amount of the colourless 7 : 8-diethoxy-isomer (III; R = Et, R′ = OEt). The isolation of (III; R = Et, R′ = OEt) threw some doubt on the results of Haworth and Sheldrick (*loc. cit.*) and Haworth and Kelly (*loc. cit.*). 3 : 4-Dimethoxyphenylpropiolic acid was therefore treated under the same conditions as those used by Haworth and Sheldrick (*loc. cit.*); the product had m. p. 305—309°, raised to 316—317° by repeated crystallisation from nitrobenzene or *o*-dichlorobenzene, so it was assumed to be a mixture of the two possible isomers, and the same would apply to



Haworth and Sheldrick's product (m. p. 305—306°). However, from 3 : 4-methylenedioxyphenylpropiolic acid both 6 : 7-methylenedioxy- and 7 : 8-methylenedioxy-1-(3′ : 4′-methylenedioxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride were isolated. The latter, m. p. 280—282°, was obtained in very small amount (unpublished work by Baddar, Fahim, and Fleifel), and depressed the m. p. of the former; Haworth and Kelly (*loc. cit.*) reported the isolation of the former only.

m-Nitrophenylpropiolic acid gave under the same conditions a resinous, uncrystallisable material.

The structure of these anhydrides was supported by the fact that each coloured isomer of type (III) shows three maxima : R = Me, λ 342, 360, 378; R = Et, λ 343·5, 362, 381; and R = Pr^{i}, λ 346·5, 364, 384 mμ. The colourless isomers (II) possess inflexions at 320 mμ (unpublished work by Baddar and Sawires).

These results can be interpreted according to the annexed scheme (cf. Baddar and El-Assal, *J.*, 1951, 1844). The isolation of (II; R′ = H) and (III; R′ = H) in nearly equal proportions indicates that both carbon atoms (*a*) and (*a*′) are similarly activated, and that the group OR exerts an insignificant steric effect. However, the introduction of another alkoxyl group (R′) in position 4 enormously reduces the amount of the isomer (III; R = Et, R′ = OEt). Since that cannot be due to electronic factors, as both position (*a*) and (*a*′) are similarly affected by this group, it is most probably due to steric factors. The group R′ has apparently forced the group OR out of its position, and thus increased the steric influence of the OR group. As the methylenedioxy-group exhibits the same phenomenon, the effect of the group R′ on OR is more probably repulsive in origin (cf. Wheland, "Advanced Organic Chemistry," J. Wiley and Sons, New York, 1949, p. 207).

Experimental

m-iso*Propoxybenzaldehyde*.—A solution of *m*-hydroxybenzaldehyde (18·3 g.; 1 mol.) in 7·5% (w/w) alcoholic sodium ethoxide (60 ml.) was refluxed with *iso*propyl iodide (38·3 g.; 1·5 mol.) for 4 hr. The alcohol was evaporated, and the residue diluted with water and extracted with ether. The product was distilled to give *m-iso*propoxybenzaldehyde (61%), b. p. 121°/10 mm., 134°/28 mm. Morris (*J.*, 1950, 1915) gave b. p. 110—113°/2 mm. Its 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in red plates, m. p. 181—182° (Found : N, 15·9. $C_{16}H_{16}O_5N_4$ requires N, 16·3%).

Preparation of the Cinnamic Acids.—A mixture of the benzaldehyde (0·1 mole), malonic acid (0·15 mole), ethyl alcohol (20 ml.), and pyridine (2·5 ml.) was heated on a boiling-water bath for 7—8 hr. The mixture was cooled in ice, and the solid triturated with ethyl alcohol (*ca.* 10 ml.) and filtered off. It was washed with dilute hydrochloric acid, then crystallised from alcohol (cf. Walling and Wolfstirn, *J. Amer. Chem. Soc.*, 1947, **69**, 852). *m*-Methoxycinnamic acid had m. p. 117° (84%) (Jones and James, *J.*, 1935, 1600, recorded the same m. p.), *m*-ethoxycinnamic acid, m. p. 133° (93%) (Werner, *Ber.*, 1895, **28**, 2001, gave m. p. 122°), m-iso*propoxycinnamic acid*, m. p. 100—101° (98%) (Found : C, 69·6; H, 6·5. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%), and 3 : 4-diethoxycinnamic acid, m. p. 156° (70%) (Ide and Buck, *J. Amer. Chem. Soc.*, 1937, **59**, 726, gave the same m. p.). *m*-Nitrocinnamic acid, m. p. 196—197°, was obtained in 90% yield after 4 hours' heating (Tiemann and Oppermann, *Ber.*, 1880, **13**, 2060, gave the same m. p.).

αβ-*Dibromo*-m-*ethoxy- and* -m-iso*propoxy-cinnamic Acid*.—A carbon tetrachloride solution of bromine (1 mol.) was added dropwise to a boiling solution of the cinnamic acid (1 mol.) in dry carbon tetrachloride, exposed to direct sunlight. When bromination was complete (0·5—1 hr.), the precipitate was filtered off and the mother-liquor was evaporated at room temperature. αβ-*Dibromo*-m-*ethoxycinnamic acid* formed needles, m. p. 171—172° (73%) (from benzene) (Found : Br, 45·8. $C_{11}H_{12}O_3Br_2$ requires Br, 45·5%), and the m-iso*propoxy-acid* cubes, m. p. 130—131° (77%) [from toluene–light petroleum (b. p. 50—60°)] (Found : Br, 42·4. $C_{12}H_{14}O_3Br_2$ requires Br, 43·7%).

Methyl αβ-*Dibromo*-m-iso*propoxycinnamate*.—A stirred solution of methyl *m-iso*propoxycinnamate (15·5 g.; 1 mol.) (b. p. 166—168°/10 mm.) in carbon tetrachloride (50 ml.) was brominated in sunlight (4 ml. of bromine). The pale yellow oil left on evaporation of the solvent at room temperature was used for dehydrobromination without purification.

Methyl αβ-*Dibromo*-3 : 4-*diethoxycinnamate*.—An ice-cold, stirred solution of methyl 3 : 4-diethoxycinnamate [prepared from the acid chloride and methyl alcohol (cf. Kindler and Peschke, *Zentr.*, 1934, **105**, *I*, 2582)] in chloroform was brominated as usual. The chloroform was evaporated at room temperature; the residue crystallised from light petroleum (b. p. 100—120°) to give *methyl* αβ-*dibromo*-3 : 4-*diethoxycinnamate*, m. p. 110—111° (Found : Br, 39·5. $C_{14}H_{18}O_4Br_2$ requires Br, 39·0%) (yield, quantitative).

m-*Methoxy-*, m-*Ethoxy-, and* 3 : 4-*Dimethoxy-phenylpropiolic Acid*.—A mixture of the

corresponding dibromocinnamic acid (5 g.) and 25% methyl-alcoholic potash (20 ml.) was evaporated with stirring on a boiling-water bath to dryness. The residue was dissolved in water (charcoal), filtered, cooled, and acidified (cf. Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510). *m*-Methoxyphenylpropiolic acid had m. p. 109—110° (67%) [from chloroform–light petroleum (b. p. 50—60°)] (Jones and James, *loc. cit.*, gave m. p. 109°), and m-*ethoxyphenylpropiolic acid* m. p. 120° (74%) (Found : C, 69·0; H, 5·1. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). 3 : 4-Dimethoxyphenylpropiolic acid (yield, 50% from the ethyl ester) (crystallised from benzene–chloroform, the chloroform being evaporated off on the water-bath) had m. p. 150—151° (decomp.). Perkin and Schiess (*J.*, 1904, **85**, 165) gave m. p. 149°.

m-iso*Propoxy- and* 3 : 4-*Diethoxy-phenylpropiolic Acid.*—The corresponding methyl αβ-dibromocinnamate (0·1 mole) was refluxed with a solution of potassium hydroxide (0·7 mole) in absolute ethyl alcohol (200 ml.) for 7—8 hr. The diluted mixture was cooled in ice and acidified. The precipitate was extracted with ether, then re-extracted by sodium carbonate solution, and the alkaline solution cooled and acidified. The material extracted with chloroform was crystallised from light petroleum (b. p. 80—100°), forming pale cream needles (31%), m. p. 92—93°, of m-iso*propoxyphenylpropiolic acid* (Found : C, 70·3; H, 5·8. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). 3 : 4-*Diethoxyphenylpropiolic acid* (50%) (from benzene) had m. p. 131° (decomp.) (Found : C, 67·0; H, 6·1. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%); this acid was also prepared from the dibromocinnamic ester in 45% yield by the rapid method described above.

m-*Nitrophenylpropiolic Acid.*—αβ-Dibromo-*m*-nitrocinnamic acid (35·5 g.) was left with 10% aqueous sodium hydroxide (80 ml.) at room temperature overnight. The precipitate obtained on acidification was treated with bromine in chloroform (Reich and Koehler, *Ber.*, 1913, **46**, 3727), and the α-bromo-acid (9 g.) was then converted into *m*-nitrophenylpropiolic acid (79%) by 10% aqueous sodium hydroxide (53 ml.) at room temperature overnight (*idem, ibid.*).

Self-condensation of m-*Methoxyphenylpropiolic Acid.*—The acid (5 g.) was refluxed with acetic anhydride (10 ml.) for 3 hr., and the cold solution then diluted with ether and left overnight. The yellow precipitate (3·5 g.; 74%) was washed with ether and the solution in glacial acetic acid (25 ml.) left overnight. The precipitate was repeatedly crystallised from glacial acetic acid, giving yellow 8-*methoxy*-1-m-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (*ca.* 1 g.), m. p. 230—230·5° (Found : C, 70·9; H, 4·0. $C_{20}H_{14}O_5$ requires C, 71·9; H, 4·2%). It was soluble in benzene and in boiling 20% sodium hydroxide solution but practically insoluble in ether. Its alkaline solution did not discharge the colour of potassium permanganate. The *dimethyl* ester had m. p. 123—125° [from light petroleum (b. p. 80—100°)] (Found : C, 69·2; H, 5·1. $C_{22}H_{20}O_6$ requires C, 69·5; H, 5·25%). Its *imide*, prepared by heating the anhydride (0·5 g.) with ammonium carbonate (10 g.) at 240—250° (cf. Baddar, *loc. cit.*), had m. p. 208·5—210° (Found : N, 4·55. $C_{20}H_{15}O_4N$ requires N, 4·2%).

A second crop, m. p. 165—185°, obtained from the acetic acid solution, crystallised from the same solvent to give colourless 6-*methoxy*-1-m-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (*ca.* 1 g.), m. p. 179—179·5° (Found : C, 71·7; H, 4·1%), moderately soluble in acetic acid, soluble in benzene, and insoluble in ether; it dissolved easily in cold 20% sodium hydroxide solution.

The mixed m. p. of the two isomers was 160—200° which was that of the original crude condensation product.

5-*Acetamido*-2-*naphthol.*—A mixture of 6-hydroxy-1-naphthylamine hydrochloride (19·5 g.) (from the base, prepared according to Brown *et al.*, *J. Amer. Chem. Soc.*, 1929, **51**, 1766), fused sodium acetate (10 g.), glacial acetic acid (20 ml.), and acetic anhydride (10 ml.) was warmed gently with stirring on the water-bath for 1 min. The acetyl derivative was precipitated with water and crystallised from alcohol, forming needles, m. p. 215—216° (cf. Sachs, *Ber.*, 1906, **39**, 3025).

1-*Acetamido*-6-*methoxynaphthalene.*—Methyl sulphate (50 g.) was slowly added to a stirred solution of 5-acetamido-2-naphthol (40 g.) in methyl alcohol (100 ml.), the solution being kept alkaline by dropwise addition of 9% sodium hydroxide solution. The stirred mixture was kept for a further hr., and diluted with water; the precipitated ether crystallised from alcohol (yield, 70%) and had m. p. 140° (cf. Sachs, *loc. cit.*).

6-*Methoxy*-1-*naphthylamine Hydrochloride.*—The above acetyl derivative (43 g.) was refluxed for 1 hr. with 25% methyl-alcoholic sodium hydroxide (100 ml.); the mixture was diluted with water, and the base hydrochloride precipitated from the dried ether extract with dry hydrogen chloride. The free base crystallised from light petroleum (cf. Cohen, Cook, Hewett, and Girard, *J.*, 1934, 653).

5-*Bromo*-3-*nitrobenzoic Acid.*—A mixture of *m*-nitrobenzoic acid (42 g.), concentrated

sulphuric acid (500 ml.), silver sulphate (39·2 g.), and bromine (15·5 ml.) was stirred at 100° for 7—8 hr. (cf. Derbyshire and Waters, *J.*, 1950, 573). The mixture was poured on ice, and the solid filtered off and extracted with sodium carbonate solution. 5-Bromo-3-nitrobenzoic acid was precipitated on acidification and formed needles (yield, 80%), m. p. 162°, from dilute alcohol. Hübner (*Annalen*, 1884, **222**, 166) and Blanksma (*Chem. Weekblad*, 1912, **9**, 862) gave m. p.s 161° and 162°, respectively.

3-*Amino*-5-*bromobenzoic Acid*.—Concentrated hydrochloric acid (65 ml.) was gradually added to 5-bromo-3-nitrobenzoic acid (37 g.) and tin (35·5 g.), and the mixture heated on a boiling-water bath for 2—3 hr. The product was made slightly alkaline with ammonia solution and filtered, and the filtrate treated with acetic acid till just acid. The precipitate gave colourless 3-amino-5-bromobenzoic acid, m. p. 220—222°, on crystallisation from alcohol. Hübner (*loc. cit.*), and McAlister and Kenner (*J.*, 1928, 1913), gave m. p.s 215° and 220—222°, respectively.

5-*Bromo*-3-*hydroxybenzoic Acid*.—The amino-acid (21·6 g.), in 10% (v/v) sulphuric acid (200 ml.), was diazotised with sodium nitrite (7 g.), and the solution boiled with dilute sulphuric acid (1 : 1, v/v) (120 ml.) for 15 min. The precipitated acid was crystallised from water, 5-*bromo*-3-*hydroxybenzoic acid* being obtained in needles, m. p. 238—239° (yield nearly quantitative) (Found : C, 38·8; H, 2·55; Br, 36·8. $C_7H_5O_3Br$ requires C, 38·7; H, 2·3; Br, 36·9%).

5-*Bromo*-3-*methoxybenzoic Acid*.—This acid was prepared with methyl sulphate and after crystallisation from alcohol had m. p. 190—191° (73%) (Found : Br, 34·6. $C_8H_7O_3Br$ requires Br, 34·6%). Its methyl ester (from the acid chloride and methyl alcohol) had b. p. 156—157°/4 mm.

5-*Methoxy*-3-(6-*methoxy*-1-*naphthyl*)*benzoic Acid*.—1-Iodo-6-methoxynaphthalene (5·7 g.; 1 mol.) (cf. Cohen, Cook, Hewett, and Girard, *loc. cit.*) was heated with methyl 5-bromo-3-methoxybenzoate (4·9 g.; 1 mol.) and copper-bronze (7·5 g.) at 230—240° for 4 hr., and the product worked up as reported by Baddar and Gindy (*J.*, 1948, 1231). The benzene solution, after being freed from the diphenic acid, was evaporated, and the residue was esterified (diazomethane) and distilled. The fraction, b. p. 260—270°/4 mm. (0·62 g.), was hydrolysed with alcoholic potassium hydroxide, the solution acidified, and the precipitate dried in a vacuum at 100° for about 2 hr. On repeated crystallisation from methyl alcohol, the *benzoic acid* formed cubes (10%), m. p. 166—167° (shrinking at 162°) (Found : C, 73·5; H, 5·2%; *M*, 278. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%; *M*, 308). Inferior results were obtained if condensation was effected at 260—270°.

6-*Methoxy*-1-m-*methoxyphenylnaphthalene*.—(i) The benzoic acid (0·5 g.), quinoline (5 ml.), and copper-bronze (0·1 g.) were stirred and gradually heated to 200—210°. Copper-bronze (0·3 g.) was added portionwise during 1 hr. and the mixture heated for a further hr. The brownish-yellow 6-methoxy-1-*m*-methoxyphenylnaphthalene (0·24 g.) had b. p. 220—230°/4 mm. It was identified as the x-*mononitro*-derivative (cf. Baddar and El-Assal, *J.*, 1948, 1267), which crystallised from methyl alcohol in yellow crystals, m. p. 170—172° (Found : N, 4·9. $C_{18}H_{15}O_4N$ requires N, 4·53%).

(ii) 6-Methoxy-1-*m*-methoxyphenylnaphthalene-2 : 3-dicarboxylic acid (1·0 g.) was decarboxylated as in (i), to give 6-methoxy-1-*m*-methoxyphenylnaphthalene, b. p. 230—240°/4 mm. (0·23 g.). This gave a mononitro-derivative, m. p. and mixed m. p. with the above specimen, 170—172° (Found : N, 4·8%).

Condensation of m-*Ethoxyphenylpropiolic Acid*.—This acid (5 g.) was refluxed with acetic anhydride (12·5 ml.) for 3 hr., and treated as before. The precipitate was filtered off, and washed with ether (yield, *ca.* 4·0 g.; 83%); it had m. p. 135—160°. A hot benzene solution (*ca.* 25 ml.) slowly (45 min.) deposited colourless material which was separated by decantation; the m. p., 156—166°, was raised to 172—173° (*ca.* 1·3 g.) on repeated crystallisation from benzene. 6-*Ethoxy*-1-m-*ethoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (Found : C, 73·4; H, 4·6. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%) was soluble in hot acetic acid and in hot sodium hydroxide solution but practically insoluble in ether, and insoluble in sodium carbonate.

The original benzene mother-liquor was evaporated to dryness, and the residue was repeatedly crystallised from the minimum of acetic acid, giving 8-*ethoxy*-1-m-*ethoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (*ca.* 1·3 g.) in yellow crystals, m. p. 164—165°, depressed to 135—160° on admixture with the first isomer (Found : C, 72·5; H, 4·9%). It was insoluble in sodium carbonate, but soluble in boiling 20% sodium hydroxide solution to give a colourless disodium salt. The alkaline solution did not discharge the colour of potassium permanganate. Its *imide*, prepared as usual (at 210—220°) and crystallised from glacial acetic acid, was obtained in pale yellow crystals, m. p. 238·5—239·5° (Found : N, 4·5. $C_{22}H_{19}O_4N$ requires N, 3·9%).

1-*Acetamido*-6-*ethoxynaphthalene*.—5-Acetamido-2-naphthol (40 g.) was ethylated in 76%

yield with ethyl sulphate (61·6 g.) in a similar manner to that adopted for its methylation. On crystallisation from dilute alcohol, 1-*acetamido*-6-*ethoxynaphthalene* was obtained in needles, m. p. 155—156° (Found : C, 73·0; H, 6·4. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·55%).

6-*Ethoxy*-1-*naphthylamine*.—An alcoholic solution (230 ml.) of the acetyl derivative (23·0 g.) was refluxed with concentrated sulphuric acid (46 ml.) for 1·5 hr., the mixture diluted with water, and the base liberated by sodium hydroxide. 6-*Ethoxy*-1-*naphthylamine* formed needles (53%) (from light petroleum), m. p. 104—105° (Found : N, 7·8. $C_{12}H_{13}ON$ requires N, 7·5%).

6-*Ethoxy*-1-*iodonaphthalene*.—This *compound*, prepared as usual (cf. Cohen, Cook, Hewett, and Girard, *loc. cit.*), formed a pale yellow oil, b. p. 182—184°/4 mm., 200—202°/10 mm. (30%), which solidified on cooling. It crystallised from light petroleum (b. p. 60—80°) in aggregates, m. p. 74—75° (Found : I, 41·8. $C_{12}H_{11}OI$ requires I, 42·6%).

3-*Bromo*-5-*ethoxybenzoic Acid*.—3-Bromo-5-hydroxybenzoic acid (21·7 g.) was ethylated in 70% yield with ethyl sulphate (31·0 g.) as usual; 3-*bromo*-5-*ethoxybenzoic acid* had m. p. 152° (from alcohol) (Found : Br, 33·0. $C_9H_9O_3Br$ requires Br, 32·7%). The *methyl ester* (from the acid chloride and methyl alcohol) formed needles (96%), m. p. 59—60° (from methyl alcohol) (Found : C, 46·8; H, 4·6. $C_{10}H_{11}O_3Br$ requires C, 46·3; H, 4·3%).

5-*Ethoxy*-3-(6-*ethoxy*-1-*naphthyl*)*benzoic Acid*.—This was prepared like the dimethoxy-compound (cf. Baddar and Gindy, *loc. cit.*). The intermediate ester was distilled and the fraction, b. p. 230—240°/4 mm. (0·55 g.), was hydrolysed with alcoholic potassium hydroxide. The acid precipitated on acidification was dried at 100° in a vacuum for 1 hr. and then crystallised from methyl alcohol to give the *ethoxybenzoic acid* (8%), m. p. 180—181° (Found : C, 74·9; H, 6·2. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). The material insoluble in benzene was purified by repeated crystallisation from glacial acetic acid to give 3 : 3′-*diethoxydiphenyl*-5 : 5′-*dicarboxylic acid*, m. p. 293—294° (Found : C, 64·7; H, 5·4. $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·45%).

Decarboxylation of 6-*Ethoxy*-1-m-*ethoxyphenylnaphthalene*-2 : 3-*dicarboxylic Acid*.—The acid was decarboxylated as described for the dimethoxy-dicarboxylic acid, and the product distilled, giving the pale yellow 6-ethoxy-1-*m*-ethoxyphenylnaphthalene, b. p. 210—220°/4 mm. This failed to solidify, and on nitration gave a mixture. Its structure was elucidated by heating it (0·25 g.) with magnesium iodide (from 0·2 g. of magnesium powder) at 210—220° for 2 hr. The dihydroxy-compound was then methylated with diazomethane, and the product was nitrated with nitric acid (*d* 1·42) in glacial acetic acid. The nitro-derivative was identical (m. p. and mixed m. p.) with the mononitro-derivative of 6-methoxy-1-*m*-methoxyphenylnaphthalene.

Condensation of m-iso*Propoxyphenylpropiolic Acid*.—The propiolic acid (2·7 g.) was refluxed with acetic anhydride (7 ml.) for 3 hr. The solution was concentrated under reduced pressure, and diluted with ether. The pale yellow precipitate was washed with ether and dried; it had m. p. 135—142° (1·7 g.; 63%). The mixture was dissolved in acetic acid (*ca.* 10 ml.) and left overnight. The precipitate consisted of two types of crystals which were mechanically separated : (*a*) fine yellow needles, m. p. 167—168°, and (*b*) slightly coloured aggregates, m. p. 156—158°. The mother-liquor was evaporated, and the residue crystallised from the minimum of acetic acid. One isomer (0·52 g.) was recrystallised from glacial acetic acid, giving 8-iso*propoxy*-1-m-iso*propoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* in fine yellow crystals, m. p. 172—173° (Found : C, 72·9; H, 5·6. $C_{24}H_{22}O_5$ requires C, 73·8; H, 5·6%). The 3′ : 6-*di*iso*propoxy*-isomer (0·52 g.) crystallised from glacial acetic acid in nearly colourless crystals, m. p. 163—164°, depressed to 135—142° on admixture with the first isomer (Found : C, 74·0; H, 5·5%). Neither isomer in alkaline solution discharged the colour of potassium permanganate. The constitution of the two isomers rested entirely on analogy.

Condensation of 3 : 4-*Diethoxyphenylpropiolic Acid*.—The propiolic acid (5 g.) was heated with acetic anhydride (12·5 ml.) on a boiling-water bath for 4 hr. and worked up as usual. The 6 : 7-*diethoxy*-1-(3′ : 4′-*diethoxyphenyl*)*naphthalene*-2 : 3-*dicarboxylic anhydride* (3·5 g.) crystallised from acetic acid in greenish-yellow crystals, m. p. 216—217° (Found : C, 69·0; H, 5·9. $C_{26}H_{26}O_7$ requires C, 69·3; H, 5·8%). The acetic anhydride–ether mother-liquor was concentrated, then decomposed with water. The precipitate was filtered off and extracted with dilute cold sodium carbonate solution. The residue, m. p. 154—184° (0·55 g.), was crystallised from acetic acid, and the product (0·4 g.), m. p. 200—214°, was repeatedly crystallised from acetic acid to give the 3′ : 4′ : 7 : 8-*tetraethoxy-anhydride* in colourless crystals, m. p. 220·5—222·5°, depressed to 194—195° on admixture with the first isomer (Found : C, 68·3; H, 5·9%). It was soluble in boiling 20% sodium hydroxide solution, and its alkaline solution did not discharge the colour of potassium permanganate.

Dimethyl 6 : 7-*Diethoxy*-1-(3′ : 4′-*diethoxyphenyl*)*naphthalene*-2 : 3-*dicarboxylate*, prepared by

use of diazomethane, crystallised from light petroleum (b. p. 80—100°) in colourless crystals, m. p. 130—131° (Found : C, 67·4; H, 6·12. $C_{28}H_{32}O_8$ requires C, 67·7; H, 6·45%).

Condensation of 3 : 4-*Dimethoxyphenylpropiolic Acid.*—The propiolic acid was heated with acetic anhydride as mentioned by Haworth and Sheldrick (*loc. cit.*). The precipitate (3·5 g.; from 5 g.), m. p. 305—309° (shrinking at 302°), was repeatedly crystallised from nitrobenzene or *o*-dichlorobenzene, giving 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride in greenish-yellow crystals, m. p. 316—317° (shrinking at 314°) (Found : 66·8; H, 4·6. Calc. for $C_{22}H_{18}O_7$: C, 67·0; H; 4·6%). Haworth and Sheldrick (*loc. cit.*) gave m. p. 305—306°. The crystals showed extinction and pleochroism, probably belonging to the orthorhombic system.

The acetic anhydride–ether mother-liquor contained only unchanged 3 : 4-dimethoxyphenylpropiolic acid.

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