251. *Phenylpropiolic Acids. Part II. The Dimerisation of* p-*Nitro- and* p-*Methoxy-phenylpropiolic Acid.*

By F. G. BADDAR and LANSON SALIB EL-ASSAL.

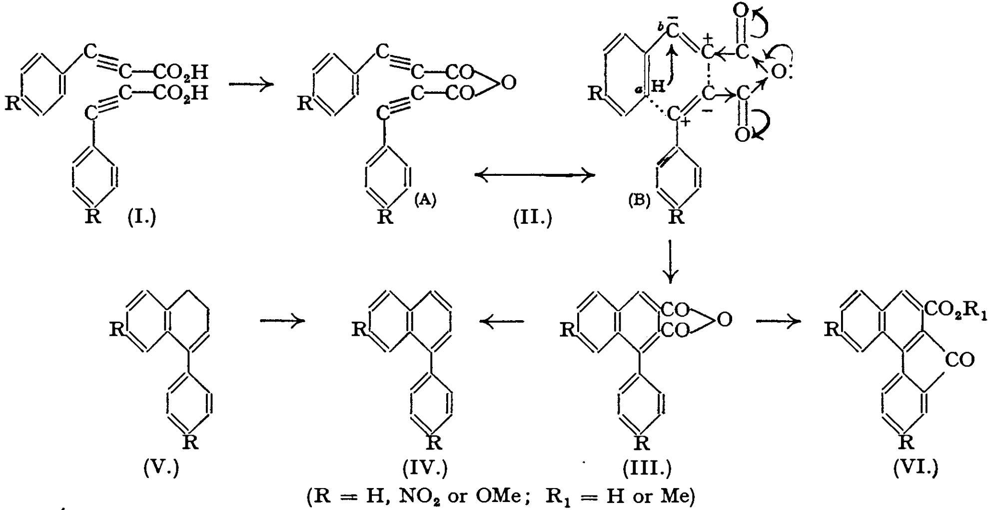
p-Nitrophenylpropiolic acid (I; R = NO_2) is converted by acetic anhydride into 4′ : *7-dinitro-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride* (III; R = NO_2). The dibasic *acid* from this is decarboxylated to 4′ : *7-dinitro-1-phenylnaphthalene* (IV; R = NO_2). This is reduced to 4′ : 7-diamino-1-phenylnaphthalene, which is deaminated to 1-phenylnaphthalene.

p-Methoxyphenylpropiolic acid (I; R = OMe) gives, when similarly treated, the analogous *anhydride* (III; R = OMe), and thence the *acid* and 4′ : *7-dimethoxy-1-phenylnaphthalene* (IV; R = OMe). This is found to be identical with a specimen prepared by dehydrogenation of 4′ : *7-dimethoxy-1-phenyl-3 : 4-dihydronaphthalene* (V; R = OMe). The dimerisation is believed to be preceded by anhydride formation.

IN Part I (Baddar, *J.*, 1947, 224) it was shown that *o*-methoxyphenylpropiolic acid was converted by the action of acetic anhydride or acetyl chloride into 2′ : 5-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride. In the present investigation, the authors have studied the effect of substituents on the mode of dimerisation of phenylpropiolic acids.

p-Nitrophenylpropiolic acid (I; R = NO_2) was converted by boiling acetic anhydride into 4′ : *7-dinitro-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride* (III; R = NO_2). Its structure was determined by decarboxylating its dibasic *acid* to 4′ : *7-dinitro-1-phenylnaphthalene* (IV; R = NO_2), which was reduced to 4′ : *7-diamino-1-phenylnaphthalene*. This gave on deamination 1-phenylnaphthalene, identified as its mononitro-derivative.

p-Methoxyphenylpropiolic acid (I; R = OMe) similarly gave the *anhydride* (III; R = OMe), the dibasic *acid* from which was decarboxylated to 4′ : *7-dimethoxy-1-phenylnaphthalene* (IV; R = OMe), identical with a specimen prepared by dehydrogenation of 4′ : *7-dimethoxy-1-phenyl-3 : 4-dihydronaphthalene* (V; R = OMe), which was prepared from 7-methoxy-α-tetralone and *p*-methoxyphenylmagnesium bromide (cf. Howell and Robertson, *J.*, 1936, 587).



(R = H, NO_2 or OMe; R_1 = H or Me)

4′ : 7-Dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride was converted, under the influence of aluminium chloride in nitrobenzene, into 3′ : 7-*dimethoxy*-3 : 4-*benzfluorenone*-1-*carboxylic acid* (VI; R = OMe; R_1 = H) (cf. Part I, *loc. cit.*). Under similar conditions, the nitro-derivative (III; R = NO_2) was recovered unchanged, and resinified on heating.

The fact that unsubstituted and substituted phenylpropiolic acids (see Part I, *loc. cit.*, for references) gave only 1-phenylnaphthalene derivatives, independently of the nature of the substituent, may be explained by assuming that dimerisation is preceded by anhydride formation [II(A); R = H, OMe, or NO_2]. The hydrogen attached to carbon atom (*a*) migrates as a proton to carbon atom (*b*), then the excited structure II(B) cyclises as indicated by the dotted lines.

This is supported by the following facts: (1) All the reagents used for converting phenylpropiolic acids into 1-phenylnaphthalene-2 : 3-dicarboxylic anhydrides, such as acetic anhydride, acetyl chloride, or phosphorus oxychloride, are anhydride-forming reagents. (2) Phenylpropiolic anhydride, prepared by treating an ethereal solution of propiolyl chloride with silver propiolate, dimerised readily when heated on the water-bath, exposed to sun-light, or even kept at room temperature, forming 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride. Contrary to Bucher (*J. Amer. Chem. Soc.*, 1908, **30**, 1264; footnote), phenylpropiolic acids were recovered unchanged under these conditions.

EXPERIMENTAL.

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

p-*Nitrophenylpropiolic Acid* (I; R = NO_2).—The finely powdered phenylpropiolic acid (10 g.) was added portionwise to fuming nitric acid (100 c.c.; *d* 1·52), which had been cooled to − 18°, and the mixture stirred for one hour (cf. Reich, *Compt. rend.*, 1916, **162**, 129). The product was crystallised from 60% ethyl alcohol, from which *p*-nitrophenylpropiolic acid was obtained in prismatic needles, m. p. 201—202°; yield, 7 g. (54%). Müller (*Annalen*, 1882, **212**, 139) and Drewsen (*ibid.*, p. 154) give m. p.s 181° and 198°, respectively. It gave on oxidation with alkaline potassium permanganate *p*-nitrobenzoic acid.

4′ : 7-*Dinitro*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic Anhydride* (III; R = NO_2).—*p*-Nitrophenylpropiolic acid (4 g.) was refluxed with acetic anhydride (18 c.c.) for 2 hours, cooled, and the crystalline precipitate filtered off. On crystallisation from glacial acetic acid, 4′ : 7-*dinitro*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic anhydride* was obtained in reddish-brown crystals, m. p. 325—326° (Found: C, 59·2; H, 2·1; N, 8·2. $C_{18}H_8O_7N_2$ requires C, 59·3; H, 2·2; N, 7·7%); yield, 65%. The *acid*, prepared by refluxing the anhydride with dilute sodium hydroxide solution, crystallised from glacial acetic acid in pale yellowish-brown crystals, m. p. above 320° (Found: C, 56·6; H, 2·7; N, 6·9; equiv., 192·7. $C_{18}H_{10}O_8N_2$ requires C, 56·5; H, 2·6; N, 7·3%; equiv., 191).

The *diethyl* ester, prepared by refluxing the acid (2 g.) with absolute ethyl alcohol (20 c.c.), and concentrated sulphuric acid (5 c.c.) for 3 hours, crystallised from ethyl alcohol in light yellowish-brown flakes, m. p. 177—178° [Found: C, 60·1; H, 4·1; N, 6·3; *M* (Rast), 430. $C_{22}H_{18}O_8N_2$ requires C, 60·3; H, 4·1; N, 6·4%; *M*, 438]; yield, 70%.

4′ : 7-*Dinitro*-1-*phenylnaphthalene* (IV; R = NO_2).—4′ : 7-Dinitro-1-phenylnaphthalene-2 : 3-dicarboxylic acid (2·0 g.) was dissolved in hot quinoline (15 c.c.), and heated to 210—220°. Copper-bronze (0·5 g.) was then added, and the mixture stirred for 45 minutes. The reaction mixture was poured into cold dilute hydrochloric acid, and the precipitated product filtered off, and repeatedly extracted with boiling benzene. The benzene extract was washed with sodium hydroxide solution, and the product crystallised from glacial acetic acid or benzene–light petroleum (b. p. 60—70°), from which 4′ : 7-*dinitro*-1-*phenylnaphthalene* was obtained in orange-red crystals, m. p. 201—202° (Found: C, 65·3; H, 3·4; N, 9·6. $C_{16}H_{10}O_4N_2$ requires C, 65·3; H, 3·4; N, 9·5%); yield, 1·2 g. (78%).

The acid, precipitated on the acidification of the alkaline extract, crystallised from 80% acetic acid to give rod-shaped crystals, m. p. 260—261°. This was most probably 4′ : 7-*dinitro*-1-*phenylnaphthalene*-2- or -3-*carboxylic acid* (Found: C, 60·2; H, 3·3; N, 7·9. $C_{17}H_{10}O_6N_2$ requires C, 60·3; H, 3·0; N, 8·3%).

4′ : 7-*Diamino*-1-*phenylnaphthalene*.—Zinc dust (20 g.) was added portionwise during 30 minutes to a boiling mixture of 4′ : 7-dinitro-1-phenylnaphthalene (1·0 g.), ethyl alcohol (120 c.c.), and concentrated hydrochloric acid (80 c.c.). The mixture was refluxed for a further hour, with occasional shaking, and poured into ice-cold 30% sodium hydroxide solution (400 c.c.). The liberated base was extracted with ether, dried, and the base precipitated as its hydrochloride by passing a dry current of hydrogen chloride through the dry ethereal solution. The base (0·6 g.) was liberated with sodium hydroxide, but changed to a dark-brown, sticky solid on standing, so was converted (Schotten–Baumann method) into its *dibenzoyl* derivative, which crystallised from benzene in fine pale pink crystals, m. p. 249—250° (Found: C, 80·7; H, 5·1; N, 6·7. $C_{30}H_{22}O_2N_2$ requires C, 81·4; H, 5·0; N, 6·3%).

1-*Phenylnaphthalene*.—1-Phenylnaphthalene-2′-carboxylic acid (0·4 g.) was decarboxylated by refluxing it with quinoline (4 c.c.), and copper-bronze (0·14 g.) for 1·5 hours. The product was worked up as usual, and purified by distillation in a vacuum, b. p. 180—200°/10 mm.; yield, 90%.

1-Phenylnaphthalene-2 : 3- and -2′ : 3-dicarboxylic acid were similarly decarboxylated, but in poorer yield, owing to incomplete decarboxylation.

4-Nitro-1-phenylnaphthalene, prepared according to Weiss and Woidich (*Monatsh.*, 1925, **46**, 453), crystallised from benzene–light petroleum (b. p. 60—70°) in brownish-yellow crystals, m. p. 131—132° (Found: N, 5·6. Calc. for $C_{16}H_{11}O_2N$: N, 5·6%).

Deamination of 4′ : 7-*Diamino*-1-*phenylnaphthalene*.—The mixture of the finely powdered

4′ : 7-diamino-1-phenylnaphthalene (0·5 g.) and concentrated sulphuric acid (3 c.c.) was cooled in a freezing mixture, with stirring. A solution of sodium nitrite (0·5 g.) in glacial acetic acid (2 c.c.) was slowly added during 15 mins., followed by glacial acetic acid (2 c.c.) added dropwise during 15 mins. The stirring was continued for a further 30 mins., and then the diazonium solution was slowly added to a vigorously stirred suspension of finely powdered, freshly prepared cuprous oxide (0·65 g.) in alcohol (10 c.c.). The reaction was accompanied by evolution of heat, but the temperature was not allowed to exceed 70°. The stirring was continued for an hour, then the reaction mixture was poured into water (100 c.c.), and the precipitated product filtered off. Both the precipitate and the filtrate were extracted with benzene, and the product distilled in a vacuum to give a yellowish-brown viscous oil (0·2 g.), b. p. 180—200°/10 mm. This was identified as 1-phenylnaphthalene by converting it into its 4-nitro-derivative, m. p. 131—132°, undepressed on admixture with an authentic specimen (Found : N, 5·9. Calc. for $C_{16}H_{11}O_2N$: N, 5·6%).

Methyl p-*Methoxycinnamate*.—This was obtained in 95% yield from the acid chloride and methyl alcohol; m. p. 94—95°. Perkin (*J.*, 1881, **39**, 439) gives m. p. 89°.

p-*Methoxyphenylpropiolic Acid* (I; R = OMe).—Powdered pure methyl αβ-dibromo-β-(*p*-methoxyphenyl)propionate (40 g.), m. p. 150—151°, was slowly added to cold 20% alcoholic potassium hydroxide (150 c.c.), the mixture heated under reflux for 10 hours, and worked up as usual (cf. Part I, *loc. cit.*). The product was contaminated with an acid containing bromine, and was therefore purified by repeated fractional crystallisation from benzene, from which *p*-methoxyphenylpropiolic acid was obtained in colourless prismatic needles, m. p. 142—143° (Found : C, 68·1; H, 4·7; OMe, 15·2. Calc. for $C_{10}H_8O_3$: C, 68·2; H, 4·6; OMe, 17·6%); yield, 9 g. (45%). Reychler (*Bull. Soc. chim.*, 1897, **17**, 512) gives m. p. 132—139°.

4′ : 7-*Dimethoxy*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic Anhydride* (III; R = OMe).—*p*-Methoxyphenylpropiolic acid (8·5 g.) was refluxed with acetic anhydride (25 c.c.) for 4 hours, cooled, and the precipitated anhydride filtered off (cf. Part I, *loc. cit.*). On crystallisation from glacial acetic acid the *anhydride* was obtained in straw-yellow, tabular, prismatic crystals, m. p. 216—217° [Found : C, 71·9; H, 4·45; OMe, 17·3; *M* (Rast), 345. $C_{20}H_{14}O_5$ requires C, 71·8; H, 4·2; OMe, 18·6%; *M*, 334]; yield, 6·6 g. (82%). This anhydride (0·5 g.) was refluxed with 20% sodium hydroxide solution (15 c.c.), filtered, cooled in ice, and acidified. The precipitated 4′ : 7-*dimethoxy*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic acid* crystallised from glacial acetic acid in colourless crystals, m. p. 239—240° (Found : C, 67·6; H, 4·8. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). Its *dimethyl* ester, prepared in dioxan solution by means of diazomethane in ether, crystallised from benzene–light petroleum (b. p. 60—70°) in colourless crystals, m. p. 126—127° (Found : C, 69·6; H, 5·2. $C_{22}H_{20}O_6$ requires C, 69·5; H, 5·3%).

Methyl 3′ : 7-*Dimethoxy*-3 : 4-*benzfluorenone*-1-*carboxylate* (VI; R = OMe; R_1 = Me).—The powdered mixture of the anhydride (III; R = OMe) (3 g.) and aluminium chloride (15 g.) was slowly added to ice-cold nitrobenzene (36 c.c.), and the reaction was carried out as described in Part I (*loc. cit.*). The dry crude acid (2·9 g.), being difficultly soluble in most organic solvents, was directly esterified by allowing its suspension in dioxan (25 c.c.) to stand at room temperature (20—30°) for 3 days with ethereal diazomethane. The precipitated dark-brown product was filtered off, and washed with hot ammonium hydroxide. On crystallisation from dioxan–ethyl alcohol, *methyl* 3′ : 7-*dimethoxy*-3 : 4-*benzfluorenone*-1-*carboxylate* separated in red prismatic needles, m. p. 191—192° (Found : C, 72·1; H, 4·5. $C_{21}H_{16}O_5$ requires C, 72·4; H, 4·6%). Hydrolysis of this ester with alcoholic potassium hydroxide afforded the pure acid.

4′ : 7-*Dimethoxy*-1-*phenyl*-3 : 4-*dihydronaphthalene* (V; R = OMe).—Ice-cold *p*-methoxyphenylmagnesium bromide, prepared from *p*-bromoanisole (3·3 g.; 1·2 mols.) and magnesium metal (0·45 g.; 1·3 atoms) in dry ether (25 c.c.), was treated dropwise with a solution of 7-methoxy-α-tetralone (2·5 g., 1 mol.) in 25 c.c. of ether during ½ hour. The reaction mixture was left over-night at room temperature, and then refluxed for 2 hours. The product was hydrolysed with ice-cold ammonium chloride solution, subjected to steam distillation to remove unchanged materials, and finally purified by vacuum distillation. The fraction of b. p. 195—205°/4 mm. was crystallised from methyl alcohol, from which 4′ : 7-*dimethoxy*-1-*phenyl*-3 : 4-*dihydronaphthalene* separated in colourless tabular prismatic crystals, m. p. 77—78° (Found : C, 80·9; H, 6·8; OMe, 20·8. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8; OMe, 23·3%); yield, 1·4 g. (37%).

4′ : 7-*Dimethoxy*-1-*phenylnaphthalene* (IV; R = OMe).—A mixture of 4′ : 7-dimethoxy-1-phenyl-3 : 4-dihydronaphthalene (0·2 g.) and powdered selenium (0·2 g.) was heated at 280—285° for 15 hours (cf. Howell and Robertson, *loc. cit.*). The product was extracted with ether, and then purified by crystallisation from methyl alcohol, from which 4′ : 7-*dimethoxy*-1-*phenylnaphthalene* was obtained in colourless monoclinic crystals, m. p. 87—88° (Found : C, 81·8; H, 6·2. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Decarboxylation of 4′ : 7-*Dimethoxy*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic Acid*.—This was carried out in an exactly similar manner to that described for 2′ : 5-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic acid (Part I, *loc. cit.*). The product was distilled in a vacuum, b. p. 200—210°/5 mm., then crystallised from methyl alcohol, from which 4′ : 7-dimethoxy-1-phenylnaphthalene was obtained in colourless crystals, m. p. 87—88°, undepressed on admixture with an authentic specimen (Found : C, 81·2; H, 6·2. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%); yield, 44%.

Phenylpropiolic Anhydride (II; R = H).—An ethereal solution of phenylpropiolyl chloride (Ruhemann and Merriman, *J.*, 1905, **87**, 139) was mixed with powdered silver phenylpropiolate (Glaser, *Annalen*, 1870, **154**, 148) and kept over-night at 15—20° with occasional shaking. The ethereal solution was filtered, and the ether removed at room temperature, under reduced pressure, to give phenylpropiolic anhydride as a light-brown viscous oil. It could not be purified by distillation, as it was converted on heating into 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride. The precipitated silver chloride was found to be contaminated with the anhydride (III; R = H).

Conversion of Phenylpropiolic Anhydride into 1-*Phenylnaphthalene*-2 : 3-*dicarboxylic Anhydride*.—This conversion was effected by either (*a*) heating phenylpropiolic anhydride on the water-bath for

15—20 mins., or (*b*) exposing its benzene solution (trace of iodine) to sun-light for several days. In both cases 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride was obtained as a crystalline product, m. p. 255—256°. Partial conversion was also effected at room temperature. Under similar conditions, phenylpropiolyl chloride was recovered unchanged.

FOUAD I UNIVERSITY, CAIRO, EGYPT.

[*Received, September* 13*th*, 1947.]