252. *1-Phenylnaphthalenes. Part I. The Synthesis of 2′ : 5-Dimethoxy-1-phenyl-, 4′ : 7-Dimethoxy-1-phenyl-, and 1-p-Tolyl-7-methyl-naphthalene-2 : 3-dicarboxylic Acids.*

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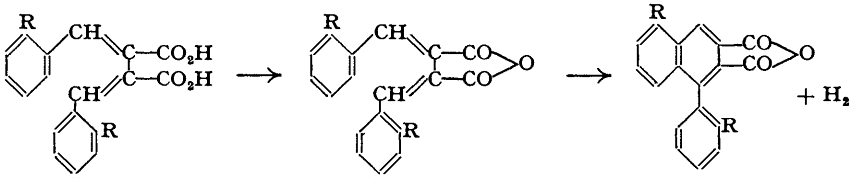
o- and *p*-Methoxybenzaldehyde and *p*-tolualdehyde condense with ethyl succinate to give *di-o-methoxybenzylidene-* (I; R = OMe), *di-p-methoxybenzylidene-*, and *di-p-toluylidene-succinic acid* respectively. The *anhydrides* (II; R = OMe; IV, R = OMe and Me) are converted by the action of heat or light into the corresponding 1-phenylnaphthalene derivatives (III; R = OMe; and V; R = OMe and Me respectively).

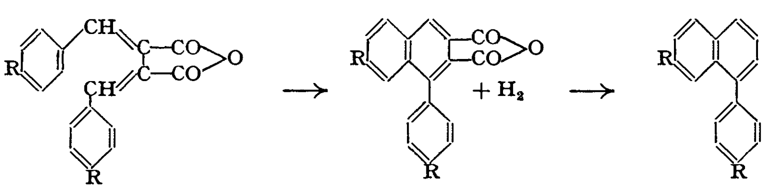
The condensation of benzaldehyde with ethyl succinate in presence of sodium ethoxide was reported by Stobbe and Kloeppel (*Ber.*, 1894, **27**, 2405), Stobbe and Naoúm (*Ber.*, 1904, **37**, 2241), and Stobbe, Ljungren, and Freyberg (*Ber.*, 1926, **59**, 270) to give dibenzylidenesuccinic acid (I; R = H). The anhydride (II; R = H) was converted into 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (III; R = H) on exposure to sunlight (Stobbe, *Ber.*, 1907, **40**, 3372). On distillation with barium hydroxide the dibasic acid (I; R = H) was converted into 1-phenylnaphthalene (Stobbe, *loc. cit.*), owing to cyclisation and decarboxylation.

In the present investigation, the authors repeated the experiments of Stobbe, Ljungren, and Freyberg (*loc. cit.*), but were unable to reproduce their results (35—40% yield). After several trials, using sodium or potassium, or their ethoxides, both in the cold and in the hot, we were able to find the favourable conditions for raising the yield to 15—20% only.

o-Methoxybenzaldehyde was similarly condensed with ethyl succinate to give *di-o-methoxybenzylidenesuccinic acid* (I; R = OMe). The *anhydride* (II; R = OMe) was converted by heat or light into 2′ : 5-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (III; R = OMe), which was identical with the product obtained by heating *o*-methoxyphenylpropiolic acid with acetic anhydride (cf. Baddar, *J.*, 1947, 224).



(I.) (II.) (III.)



(IV.) (V.) (VI.)

p-Methoxybenzaldehyde and *p*-tolualdehyde condensed also with ethyl succinate to give *di-p-methoxybenzylidene-* and *di-p-toluylidene-succinic acid* respectively. Their *anhydrides* (IV; R = OMe and Me) were converted by heat or light into 4′ : 7-dimethoxy-1-phenyl- (V; R = OMe) and 1-p-*tolyl-7-methyl-naphthalene-2 : 3-dicarboxylic anhydride* (V; R = Me) respectively. The anhydride (V; R = OMe) was found to be identical with the product obtained by refluxing *p*-methoxyphenylpropiolic acid with acetic anhydride (cf. Baddar and El-Assal, preceding paper). The dibasic *acid* from (V; R = Me), however, was decarboxylated to 1-*p*-tolyl-7-methylnaphthalene (VI; R = Me), which was found to be identical with a specimen prepared by the dehydrogenation of 1-*p*-tolyl-7-methyl-3 : 4-dihydronaphthalene, obtained by the action of 7-methyl-α-tetralone on *p*-tolylmagnesium iodide (cf. Baddar and El-Assal, *loc. cit.*).

The conversion of the dibenzylidene derivatives (II; R = H and OMe; and IV; R = OMe and Me) into the corresponding 1-phenylnaphthalenes (III; R = H and OMe; and V; R = OMe and Me respectively) appears to proceed by the elimination of hydrogen, followed by the activation of the molecule and cyclisation, as stated by Baddar and El-Assal (*loc. cit.*).

EXPERIMENTAL.

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

*Di-*o*-methoxybenzylidenesuccinic Acid* (I; R = OMe).—A suspension of freshly prepared, powdered, alcohol-free sodium ethoxide (6·4 g.; 2 mols.) in dry ether (70 c.c.) was cooled to − 18°, while thoroughly stirred. A solution of ethyl succinate (8·3 g.; 1 mol.) and *o*-methoxybenzaldehyde (13·0 g.; 2 mols.) in dry ether (30 c.c.) was quickly added, and the mixture stirred for 12 hours, the temperature being kept between − 14° and − 10°. The temperature was then raised to 0°, and the mixture kept for 3 days, with occasional stirring. The product was then decomposed with water, the ether distilled off, and the aqueous alkaline layer refluxed for 1 hour, to hydrolyse any ester present. The solution was extracted with ether to remove neutral substances, and the precipitated acids were taken up in ether, and re-extracted from the ethereal solution with dilute potassium hydroxide solution (charcoal). The product, precipitated on acidification, was purified by extracting it with boiling water two or three times. The insoluble portion was repeatedly crystallised from glacial acetic acid, from which *di-*o*-methoxybenzylidenesuccinic acid* was obtained in colourless monoclinic crystals, m. p. 259—260° (decomp.). On slow heating, it began to melt at 200°, probably owing to anhydride formation [Found: C, 67·9; H, 5·2; *M* (Rast), 358. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%; *M*, 354]; yield, 3·6 g. (*ca.* 20%). It gave with concentrated sulphuric acid a yellow solution with a faint green fluorescence.

Dibenzylidenesuccinic Acid (I; R = H).—This was similarly prepared as mentioned above in a 15—20% yield. The acid was purified, however, by precipitating it as its barium salt (cf. Stobbe and Naoúm, *loc. cit.*).

*Di-*o*-methoxybenzylidenesuccinic Anhydride* (II; R = OMe).—The acid (I; R = OMe) (4·5 g.) was refluxed with acetyl chloride (30 c.c.) for 1—2 hours. The solution was concentrated to about one-third of its original volume, then ether was added, and the mixture left overnight. The orange-yellow crystalline precipitate was collected and crystallised from benzene, from which *di-*o*-methoxybenzylidenesuccinic anhydride* separated in orange-yellow crystals, m. p. 195·5—196·5° (efferv.) (Found: C, 71·2; H, 4·9. $C_{20}H_{16}O_5$ requires C, 71·4; H, 4·8%); yield, 4·1 g. (98%). It dissolved in concentrated sulphuric acid to a yellow solution.

2′ : 5-Dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic Anhydride (III; R = OMe).—This was prepared from the anhydride (II; R = OMe) in a nearly quantitative yield, by either heating it at 280—285° for 2 hours, or exposing its benzene or chloroform solution, containing a trace of iodine, to sunlight for two days (March). The product was crystallised from glacial acetic acid, from which 2′ : 5-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride separated in straw-yellow, tabular, prismatic crystals, m. p. 245—246° (Found: C, 71·8; H, 4·3; OMe, 18·2. Calc. for $C_{20}H_{14}O_5$: C, 71·8; H, 4·2; OMe, 18·6%). The m. p. was not depressed on admixture with the product obtained by heating *o*-methoxyphenylpropiolic acid with acetic anhydride (cf. Baddar, *loc. cit.*).

*Di-*p*-methoxybenzylidenesuccinic Acid.*—A suspension of powdered, freshly prepared, alcohol-free sodium ethoxide (6·8 g.; 2 mols.) in dry ether (70 c.c.) was mechanically stirred, while cooled in a freezing mixture to between − 18° and − 15°. A solution of *p*-methoxybenzaldehyde (13·6 g.; 2 mols.) and ethyl succinate (8·8 g.; 1 mol.) in dry ether (30 c.c.) was quickly added, and the mixture kept at this temperature for 6 hours. The temperature was then raised to 0°, kept thereat for 2 days, and then finally at room temperature (30—35°) for another day, with occasional stirring. The product was worked up as for the *o*-methoxy-derivative, and then extracted with hot benzene to remove the soluble resinous acids. The insoluble product was crystallised from glacial acetic acid, from which *di-*p*-methoxybenzylidenesuccinic acid* separated in colourless crystals, m. p. 260—261° (quick heating) (Found: C, 67·7; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%).

*Di-*p*-methoxybenzylidenesuccinic Anhydride* (IV; R = OMe).—The powdered acid (0·2 g.) was refluxed with acetyl chloride (4 c.c.) for 4 hours, then the acetyl chloride was removed, and ether added. The ethereal solution was left overnight, and the crystalline precipitate was collected, and crystallised from benzene–light petroleum (b. p. 55—65°), from which *di-*p*-methoxybenzylidenesuccinic anhydride* separated in orange-yellow flakes, m. p. 179—180° [Found: C, 71·6; H, 4·7; *M* (Rast), 319. $C_{20}H_{16}O_5$ requires C, 71·4; H, 4·8%; *M*, 336]; yield, 90%.

4′ : 7-Dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic Anhydride (V; R = OMe).—This was obtained from the anhydride (IV; R = OMe) by either heating it at 205—210° for 2 hours, or exposing its benzene or chloroform solution, containing traces of iodine, to sun-light for 4 days (July). In both cases, the product was crystallised from glacial acetic acid or benzene–light petroleum (b. p. 60—70°) to give 4′ : 7-dimethoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydride in straw-yellow, tabular, prismatic crystals, m. p. 216—217°, undepressed when mixed with a specimen obtained by refluxing *p*-methoxyphenylpropiolic acid with acetic anhydride (cf. Baddar and El-Assal, *loc. cit.*) (Found: C, 71·6; H, 4·4; OMe, 17·5. Calc. for $C_{20}H_{14}O_5$: C, 71·8; H, 4·2; OMe, 18·6%).

*Di-*p*-toluylidenesuccinic Acid.*—A suspension of powdered, alcohol-free sodium ethoxide (6·8 g.; 2 mols.) in dry ether (80 c.c.) was cooled to between − 18° and − 15°, while thoroughly stirred. A solution of *p*-tolualdehyde (12·0 g.; 2 mols.) and ethyl succinate (8·8 g.; 1 mol.) in dry ether (30 c.c.) was quickly added, and the reaction carried out as in the case of di-*p*-methoxybenzylidenesuccinic acid. The dry acid was extracted with a little hot benzene, and the insoluble product was crystallised from 70% acetic acid, from which *di-*p*-toluylidenesuccinic acid* separated in light yellowish-brown crystals, m. p.

219—220° (quick heating), and 217—218° (slow heating), probably owing to anhydride formation (Found : C, 73·9; H, 5·8. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%); yield, 1·8 g. (20%).

Di-p-*toluylidenesuccinic Anhydride* (IV; R = Me).—This was similarly prepared by refluxing the acid (0·5 g.) with acetyl chloride (2 c.c.) for 1 hour. On crystallisation from benzene–light petroleum (b. p. 55—65°) *di*-p-*toluylidenesuccinic anhydride* was obtained in yellow prismatic crystals, m. p. 177—178° (Found : C, 78·9; H, 5·1. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%); yield, 95%.

1-p-*Tolyl*-7-*methylnaphthalene*-2 : 3-*dicarboxylic Anhydride* (V; R = Me).—This was similarly prepared by either heating di-*p*-toluylidenesuccinic anhydride at 205—210° for one hour, or exposing its benzene solution to sunlight for 8 days (March). On crystallisation from benzene–light petroleum (b. p. 55—65°) 1-p-*tolyl*-7-*methylnaphthalene*-2 : 3-*dicarboxylic anhydride* was obtained in colourless crystals, m. p. 266—267° [Found : C, 79·0; H, 4·6; *M* (Rast), 297. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·7%; *M*, 302].

1-p-*Tolyl*-7-*methylnaphthalene*-2 : 3-*dicarboxylic Acid*.—The anhydride (V; R = Me) was boiled with dilute sodium hydroxide solution for 10 minutes. The acid precipitated on acidification was crystallised from benzene, from which 1-p-*tolyl*-7-*methylnaphthalene*-2 : 3-*dicarboxylic acid* separated in colourless fine needles, m. p. 270—271° (Found : C, 74·5; H, 5·3. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

1-p-*Tolyl*-7-*methylnaphthalene* (VI; R = Me).—1-*p*-Tolyl-7-methyl-3 : 4-dihydronaphthalene was prepared from 7-methyl-α-tetralone (3·6 g.) and *p*-tolylmagnesium iodide (from 5·4 g. of *p*-iodotoluene) in ether (50 c.c.). The reaction was carried out as in the case of the 4′ : 7-dimethoxy-derivative (cf. Baddar and El-Assal, *loc. cit.*), and the product was obtained as a pale-yellow viscous oil, b. p. 175—180°/4 mm., which failed to crystallise.

Dehydrogenation of this compound (0·7 g.) with powdered selenium (0·6 g.) at 280—285° for 15 hours gave an ether-soluble product, from which 1-*p*-tolyl-7-methylnaphthalene was obtained as a pale-yellow fluorescent viscous oil, b. p. 170—180°/2 mm. (0·2 g.), which failed to solidify. Nitration of this substance (0·36 g.) in acetic acid (6 c.c.) with nitric acid (1·5 c.c.; *d* 1·42) (cf. Howell and Robertson, *J.*, 1936, 587) at room temperature, in the course of 4 hours, gave a *mononitro*-derivative, which separated from light petroleum (b. p. 55—65°) in yellowish-brown crystals, m. p. 94—95° (Found : C, 77·5; H, 5·7; N, 5·0. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·5; N, 5·1%).

Decarboxylation of 1-p-*Tolyl*-7-*methylnaphthalene*-2 : 3-*dicarboxylic Acid*.—The acid was decarboxylated in a similar manner to that adopted for the 4′ : 7-dimethoxy-derivative (cf. preceding paper). The product was purified by distillation in a vacuum to give 1-*p*-tolyl-7-methylnaphthalene as a yellowish-brown fluorescent oil, b. p. 170—180°/2 mm. (yield, 60%). The product was nitrated, in an exactly similar manner to that mentioned above, to give a mononitro-derivative, m. p. 94—95°, undepressed when mixed with an authentic specimen (Found : C, 77·5; H, 5·5; N, 4·9. Calc. for $C_{18}H_{15}O_2N$: C, 78·0; H, 5·5; N, 5·1%).

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