Phenylpropiolic Acids. Part IV. The Self-condensation of* o- *and* p-*Tolyl- and* o-*Chlorophenyl-propiolic Acids.*

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o- and *p*-Tolylpropiolic acids are converted by acetic anhydride into 7-methyl-1-*p*-tolyl- and 5-methyl-1-*o*-tolyl-naphthalene-2 : 3-dicarboxylic anhydride, identical with the cyclisation products from di-*p*-methyl- and di-*o*-methyl-benzylidenesuccinic anhydride, respectively. The first two anhydrides are converted by aluminium chloride into 3′ : 7- and 1′ : 5-dimethyl-3 : 4-benzofluorenone-1-carboxylic acid, respectively, and the former acid is decarboxylated to 3′ : 7-dimethyl-3 : 4-benzofluorenone. Fusion of the 3′ : 7-dimethyl-acid with potassium hydroxide gives 7-methyl-1-(2-carboxy-*p*-tolyl)naphthalene-3-carboxylic acid and a trace of the 2 : 3-dicarboxylic acid. Concentrated sulphuric acid converts the former into 6 : 9-dimethyl*meso*benzanthrone-2-carboxylic acid which is decarboxylated to 6 : 9-dimethyl*meso*benzanthrone.

o-Chlorophenylpropiolic acid, when similarly treated, gives 5-chloro-1-*o*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride. However, di-*o*-chlorobenzylidenesuccinic anhydride fails to cyclise to the corresponding anhydride.

In Parts I, II, and III (*J.*, 1947, 224; 1948, 1267; 1951, 1844) it was shown that phenylpropiolic acids were converted by acetic anhydride into the corresponding 1-phenylnaphthalene derivatives. The present investigation deals with other *o*- and *p*-substituted phenylpropiolic acids where the substituent is an electron-repelling or -attracting group.

When *p*- and *o*-tolylpropiolic acids were refluxed with acetic anhydride, they gave 7-methyl-1-*p*-tolyl- (II; R = H, R′ = Me) and 5-methyl-1-*o*-tolylnaphthalene-2 : 3-dicarboxylic anhydride (II; R = Me, R′ = H), identical with the products obtained by the action of sunlight on di-4-methyl- (III; R = H, R′ = Me) and di-2-methyl-benzylidenesuccinic anhydride (III; R = Me, R′ = H), respectively. Both anhydrides were converted by aluminium chloride in nitrobenzene into 3′ : 7- (IV; R = H, R′ = Me) and 1′ : 5-dimethyl-3 : 4-benzofluorenone-1-carboxylic acid (IV; R = Me, R′ = H), respectively. The former acid was decarboxylated with copper-bronze in quinoline to 3′ : 7-dimethyl-3 : 4-benzofluorenone, and when fused with potassium hydroxide gave 7-methyl-1-(2-carboxy-*p*-tolyl)naphthalene-3-carboxylic acid (V; R = H, R′ = Me) together with a trace of the isomeric acid (VI; R = H, R′ = Me). This result agrees with Baddar and Gindy's view (*J.*, 1944, 450; 1948, 1231) that the factors determining the point of cleavage of 3 : 4-benzofluorenones are of polar origin, depending on the electron density at carbon atoms (*a*) and (*b*). The acid (V; R = H, R′ = Me) was cyclised by 90% sulphuric acid (cf. Baddar, *J.*, 1941, 310) to 6 : 9-dimethyl*meso*benzanthrone-2-carboxylic acid (VII; R = H, R′ = Me); the formation of a trace of 3′ : 7-dimethyl-3 : 4-benzofluorenone-1-carboxylic acid (IV; R = H, R′ = Me) could not be completely excluded (cf. Baddar, *loc. cit.*).

Fusion of either 7-methyl-1-*p*-tolylnaphthalene-2 : 3-dicarboxylic anhydride (II; R = H, R′ = Me) or 3′ : 7-dimethyl-3 : 4-benzofluorenone-1-carboxylic acid (IV; R = H, R′ = Me) with aluminium chloride–sodium chloride (cf. Baddar, *loc. cit.*) gave a mixture of isomeric *meso*benzanthronecarboxylic acids from which no pure product could be isolated—it is possible that the methyl group migrates under the influence of aluminium chloride.

5-Chloro-1-*o*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (II; R = Cl, R′ = H) was obtained either (*a*) by heating *o*-chlorophenylpropiolic acid with acetic anhydride, or (*b*) by refluxing *o*-chlorophenylpropioloyl chloride with *o*-chlorophenylpropiolic acid in benzene (cf. Baddar and El-Assal, Part III). However, the structure of the anhydride

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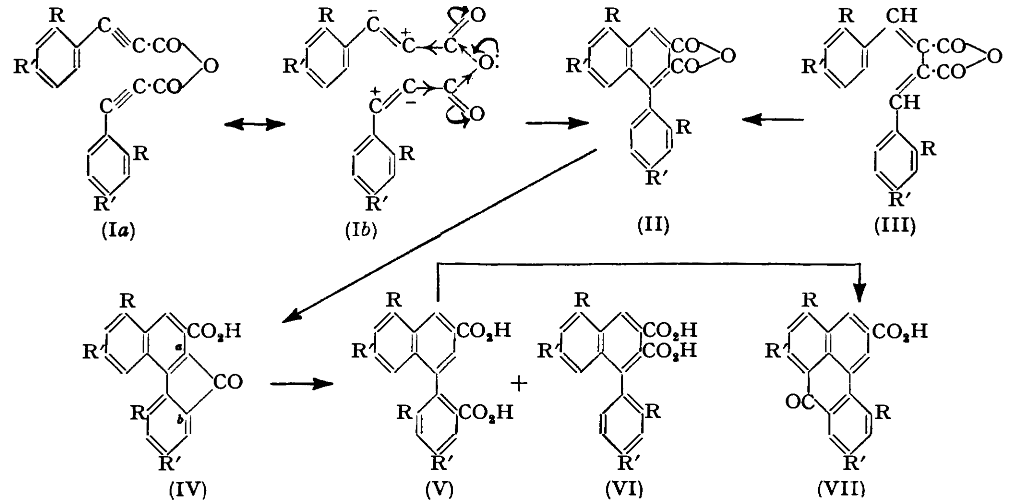
* Part III, *J.*, 1951, 1844.

was established by the following facts : (i) It was insoluble in sodium carbonate solution but readily dissolved in boiling sodium hydroxide solution; the precipitated dibasic acid was converted back into the original anhydride when boiled with acetic anhydride, which indicated that it is an *o*-dibasic acid. (ii) Its solution in sodium hydrogen carbonate failed to discharge the colour of potassium permanganate solution, excluding the *cyclo*butadiene structure (cf. Baddar and El-Assal, Parts I—III). Attempted conversion of the anhydride (II; R = Cl, R′ = H) into the corresponding 3 : 4-benzofluorenone derivative (IV; R = Cl, R′ = H) by means of aluminium chloride in nitrobenzene either cold or at 150° was unsuccessful, probably owing to deactivation of the 6′-position of the phenyl group by the (—*I*) effect of the chlorine atom in the 2′-position.



o-Chlorobenzaldehyde was condensed with diethyl succinate to give di-2-chlorobenzylidenesuccinic acid. Its anhydride (III; R = Cl, R′ = H) gave, at 300° or on exposure of its benzene solution to sunlight, a mixture of products from which no pure 5-chloro-1-*o*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (II; R = Cl, R′ = H) could be isolated.

Attempted reaction of *o*-nitrophenylpropiolic acid under similar conditions gave an uncrystallisable material (see following paper).

EXPERIMENTAL

p- *and* o-*Methylcinnamic Acids*.—These were prepared from the corresponding tolualdehydes and malonic acid (Walling and Wolfstirn, *J. Amer. Chem. Soc.*, 1947, **69**, 852) in 60—70% yield. From ethanol or benzene, both acids crystallised in shining crystals, with respective m. p.s 199—200° (Stoermer, Grium, and Leage, *Ber.*, 1917, **50**, 979, gave m. p. 198—199°) and 175—176° (Auwers, *Annalen*, 1917, **413**, 265, gave 174—175°).

αβ-*Dibromo*-β-p-*tolylpropionic Acid*.—This was prepared as described by Gattermann (*Annalen*, 1906, **347**, 358), but with use of chloroform instead of carbon disulphide, in 70% yield; m. p. 193—194° (Gattermann gave m. p. 192°).

αβ-*Dibromo*-β-o-*tolylpropionic Acid*.—Similarly prepared from *o*-methylcinnamic acid (12 g.) and bromine (4 ml.) in carbon tetrachloride (100 ml.), and crystallised from benzene–light petroleum (b. p. 40—60°), this *acid* (70%) had m. p. 162—163° (Found : C, 37·7; H, 2·9; Br, 51·5. $C_{10}H_{10}O_2Br_2$ requires C, 37·3; H, 3·1; Br, 49·7%).

αβ-*Dibromo*-β-o-*chlorophenylpropionic Acid*.—This was prepared from *o*-chlorocinnamic acid (Stoermer, *Ber.*, 1911, **44**, 659) (5 g.) and bromine (1·5 ml.) in hot glacial acetic acid (50 ml.), and crystallised from benzene–light petroleum (b. p. 40—60°); it had m. p. 184—185° (*ca.* 8·5 g.) (Stoermer gave m. p. 184°) (Found : C, 31·8; H, 2·1; Hal., 57·0. Calc. for $C_9H_7O_2ClBr_2$: C, 31·5; H = 2·1; Hal., 57·0%).

Arylpropiolic Acids.—The following acids were prepared from the corresponding αβ-dibromophenylpropionic acids exactly as described by Reimer (*J. Amer. Chem. Soc.*, 1942, **64**, 2510) for phenylpropiolic acid: *p*-Tolylpropiolic acid, needles (from benzene), m. p. 149—150°; Gattermann (*loc. cit.*) gave m. p. 148—149° (95%). o-*Tolylpropiolic acid,* light-brown aggregates, m. p. 94—95° (95%) [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 74·7; H, 5·1. $C_{10}H_8O_2$ requires C, 75·0; H, 5·0%). Attempted preparation of this acid by the method of *Org. Synth.*, 1932, **12**, 60, gave a poor yield of an impure product which was difficult to purify. *o*-Chlorophenylpropiolic acid (93%) crystallised from benzene in aggregates, m. p. 132—133° (decomp.) (Found: C, 59·6; H, 2·6; Cl, 19·4. Calc. for $C_9H_5O_2Cl$: C, 59·8; H, 2·9; Cl, 19·4%); Otto (*J. Amer. Chem. Soc.*, 1934, **56**, 1393) gave m. p. 131—132°. The acid *chloride,* b. p. 120—125°/1 mm., was a pale yellow liquid which solidified on cooling at 0° (Found: Cl, 37·0. $C_9H_4OCl_2$ requires Cl, 35·0%).

7-*Methyl*-1-p-*tolylnaphthalene*-2 : 3-*dicarboxylic Anhydride* (II; R = H, R′ = Me).—*p*-Tolylpropiolic acid (5 g.) was refluxed with acetic anhydride (12 ml.) for 4—5 hr., cooled, and diluted with ether; the precipitated anhydride was filtered off, m. p. 268—269° (*ca.* 4 g.), and crystallised from benzene–light petroleum (b. p. 40—60°) in pale yellow, shining crystals, m. p. and mixed m. p. 268—269°; Baddar, El-Assal, and Gindy (*J.*, 1948, 1272) gave m. p. 266—267°. The *dimethyl ester,* prepared by diazomethane and crystallised from methyl alcohol, had m. p. 140—141° (Found: C, 75·6; H, 5·6. $C_{22}H_{20}O_4$ requires C, 75·8; H, 5·7%).

3′ : 7-*Dimethyl*-3 : 4-*benzofluorenone*-1-*carboxylic Acid* (IV; R = H, R′ = Me).—A powdered mixture of the above anhydride (II; R = H, R′ = Me) (3 g.) and aluminium chloride (15 g.) was gradually added (30 min.) to stirred nitrobenzene (35 ml.), the temperature being kept below 50°. The mixture was then heated on a boiling-water bath for a further 6 hr. The product was hydrolysed as usual, nitrobenzene was removed with steam, the precipitated dark-brown product was filtered off and treated with ammonia, and the insoluble orange ammonium salt was filtered off and acidified. The liberated deep red acid was crystallised from xylene or benzene, giving 3′ : 7-*dimethyl*-3 : 4-*benzofluorenone*-1-*carboxylic acid* in red needles, m. p. 292—293° (*ca.* 2·9 g.) (Found: C, 79·2; H, 4·9. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·7%). Its *methyl ester,* prepared with diazomethane in ether–dioxan, crystallised from benzene–light petroleum (b. p. 40—60°) in fine orange needles (84% yield), m. p. 224—225° (Found: C, 80·3; H, 5·1. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%).

3′ : 7-*Dimethyl*-3 : 4-*benzofluorenone.*—The acid (IV; R = H, R′ = Me) (0·5 g.) was decarboxylated by heating the stirred mixture with copper-bronze (0·06 g.) in quinoline (15 ml.) for 2 hr. at 205—210°. The 3′ : 7-*dimethyl*-3 : 4-*benzofluorenone* crystallised from methyl alcohol in orange prismatic crystals, m. p. 145—146° (Found: C, 87·7; H, 5·4. $C_{19}H_{14}O$ requires C, 88·3; H, 5·4%); yield *ca.* 0·3 g.

7-*Methyl*-1-(2-*carboxy*-p-*tolyl*)*naphthalene*-3-*carboxylic Acid* (V; R = H, R′ = Me).—The acid (IV; R = H, R′ = Me) (1 g.) was heated with molten potassium hydroxide (7 g.) for 30 min. at 230—240° and worked up as usual (cf. Baddar and Gindy, *J.*, 1948, 1231). The product, m. p. 312—313° (1 g.), was refluxed with acetyl chloride for 30 min., acetyl chloride removed, ether added, and the insoluble 7-methyl-1-*p*-tolylnaphthalene-2 : 3-dicarboxylic anhydride (II; R = H, R′ = Me) filtered off (trace; identified by m. p. and mixed m. p.). The residue left on distillation of ether crystallised from acetic acid, giving 7-*methyl*-1-(2-*carboxy*-p-*tolyl*)*naphthalene*-3-*carboxylic acid* (V; R = H, R′ = Me), m. p. 325—326° (Found: C, 75·1; H, 4·9. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

6 : 9-*Dimethyl*meso*benzanthrone*-2-*carboxylic acid* (VII; R = H, R′ = Me).—A mixture of the acid (V; R = H, R′ = Me) (1 g.) and cold concentrated sulphuric acid (5 ml.) was kept at 20—25° for 3 days. The solution was added to crushed ice, and the precipitated yellow product (*ca.* 0·95 g.) was crystallised from nitrobenzene, giving 6 : 9-*dimethyl*meso*benzanthrone*-2-*carboxylic acid* in yellow crystals, m. p. >350° (Found: C, 79·4; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·7%). Its *methyl ester,* prepared from diazomethane in ether–dioxan, crystallised from methyl alcohol in pale yellow prismatic needles, m. p. 218—219° (Found: C, 79·7; H, 4·8. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·0%).

6 : 9-*Dimethyl*meso*benzanthrone.*—The acid (VII; R = H, R′ = Me) (1 g.) was decarboxylated with copper-bronze (0·08 g.) and quinoline (5 ml.); 6 : 9-*dimethyl*meso*benzanthrone* was obtained in orange needles (*ca.* 0·3 g.), m. p. 114—115° (from methanol) (Found: C, 87·8; H, 5·4. $C_{19}H_{14}O$ requires C, 88·3; H, 5·4%).

Fusion of 3′ : 7-*Dimethyl*-3 : 4-*benzofluorenone*-1-*carboxylic Acid* (IV; R = H, R′ = Me) *with Aluminium Chloride–Sodium Chloride.*—The acid (0·5 g.) was added to a stirred molten mixture of aluminium chloride (5 g.) and sodium chloride (1 g.) at 140—150° (oil-bath) and kept thereat for 2·5 hr. The product was decomposed with dilute hydrochloric acid, filtered off, and extracted with ammonia, and the extract (charcoal) acidified. The precipitated *meso*-benzanthronecarboxylic acid mixture, crystallised from nitrobenzene, had m. p. >350°; esterification gave two fractions, m. p.s 195—205° and 205—212°. Fractional crystallisation failed to resolve the mixture.

Di-2-methylbenzylidenesuccinic Acid.—A mixture of diethyl succinate (8·7 g.; 1 mol.) and *o*-tolualdehyde (12 g.; 2 mol.) in dry ether (30 ml.) was quickly added to a stirred suspension of powdered, freshly prepared, alcohol-free sodium ethoxide (6·8 g.; 2 mol.) in dry ether (50 ml.) cooled at −15° to −18°. The mixture was kept below 0° for 4 days and then at 20—25° for several hours with occasional stirring, then worked up as usual (cf. Baddar, El-Assal, and Gindy, *J.*, 1948, 1270). The product crystallised from glacial acetic acid to give *di-2-methylbenzylidenesuccinic acid*, m. p. 223—224° (Found: C, 74·1; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%); yield *ca.* 4 g. The *dimethyl ester* (diazomethane in ether–dioxan) formed needles, m. p. 105—107° (from methyl alcohol) (Found: C, 75·2; H, 6·0. $C_{22}H_{22}O_4$ requires C, 75·75; H, 6·4%).

Di-2-methylbenzylidenesuccinic Anhydride (III; R = Me, R′ = H).—A suspension of the above acid (0·5 g.) in acetyl chloride (3 ml.) was refluxed till it dissolved, then acetyl chloride was distilled off and the residue triturated with ether, filtered off, and dried (*ca.* 0·4 g.). The *anhydride* was obtained in monoclinic, lemon-yellow crystals, m. p. 154—155° [from benzene–light petroleum (b. p. 50—60°)] (Found: C, 79·3; H, 5·1. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%).

5-Methyl-1-o-tolylnaphthalene-2 : 3-dicarboxylic Anhydride (II; R = Me, R′ = H).—(*a*) A solution of the anhydride (III; R = Me, R′ = H) (0·5 g.) in benzene (5 ml.) and a tiny crystal of iodine were left in sunlight for 12 days (November) in a Pyrex tube. Distillation of the benzene left a residue which was heated in a vacuum at 100° for 2 hr. Repeated crystallisation from benzene–light petroleum (b. p. 50—60°) gave *5-methyl-1-o-tolylnaphthalene-2 : 3-dicarboxylic anhydride* in pale yellow needles, m. p. 162—163°, depressed to 110—120° on admixture with the original anhydride (II; R = Me, R′ = H) (Found: C, 79·6; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·7%). (*b*) *o*-Tolylpropiolic acid (5 g.) was refluxed with acetic anhydride (10 ml.) for 4—5 hr., acetic anhydride was then evaporated off (reduced pressure), and the residue treated with ether, filtered off, washed, and dried; it had m. p. 160—161° (*ca.* 2·5 g.). 5-Methyl-1-*o*-tolylnaphthalene-2 : 3-dicarboxylic anhydride formed pale yellow needles, m. p. and mixed m. p. 162—163° [from benzene–light petroleum (b. p. 50—60°)] (Found: C, 78·9; H, 4·8%).

1′ : 5-Dimethyl-3 : 4-benzofluorenone-1-carboxylic Acid (IV; R = Me, R′ = H).—Powdered anhydride (II; R = Me, R′ = H) (0·5 g.) and aluminium chloride (2·5 g.) were added portion-wise to stirred nitrobenzene (6 ml.), and the temperature was allowed to rise to 50—60° and kept thereat for a further 10 hr., and the product worked up as usual. It was digested with ammonia solution, and the extract filtered and acidified. The precipitate (0·45 g.) gave *1′ : 5-dimethyl-3 : 4-benzofluorenone-1-carboxylic acid* in deep red needles, m. p. 236—237° (from benzene) (Found: C, 78·9; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·7; H, 4·7%).

5-Chloro-1-o-chlorophenylnaphthalene-2 : 3-dicarboxylic Anhydride (II; R = Cl, R′ = H).—(*a*) *o*-Chlorophenylpropiolic acid (5 g.) was refluxed with acetic anhydride (20 ml.) for 6 hr., and then worked up as usual. The resulting *anhydride* (*ca.* 3 g.) crystallised from benzene–light petroleum (b. p. 40—60°) in needles, m. p. 193—194° (Found: C, 62·8; H, 2·3; Cl, 18·3. $C_{18}H_8O_3Cl_2$ requires C, 62·9; H, 2·3; Cl, 17·7%). (*b*) A mixture of *o*-chlorophenylpropiolic acid (1·0 g.) and its acid chloride (0·9 g.) in benzene (20 ml.) was refluxed for 30 hr. The benzene was distilled off, the residue treated with ether, and the insoluble product filtered off and dried, m. p. 186—188° (*ca.* 0·8 g.). On crystallisation as before, the anhydride formed needles, m. p. and mixed m. p. 193—194°. Its dibasic acid (0·5 g.) was esterified with diazomethane in ether; the *dimethyl ester* had m. p. 153—154° (from methyl alcohol) (Found: C, 62·1; H, 3·6; Cl, 17·6. $C_{20}H_{14}O_4Cl_2$ requires C, 61·6; H, 3·6; Cl, 18·2%).

When a finely powdered mixture of the anhydride (II; R = Cl, R′ = H) (2 g.) and ammonium carbonate (12·0 g.) was heated for an hour at 200—210°, the product was extracted with warm sodium hydroxide solution, the alkaline extract (charcoal) acidified, and the precipitate crystallised from glacial acetic acid, the *imide* was obtained in yellow needles, m. p. 218—219° depressed to 165—170° on admixture with the original anhydride (Found: C, 63·0; H, 2·3; Cl, 20·8; N, 4·0. $C_{18}H_9O_2NCl_2$ requires C, 63·1; H, 2·6; Cl, 20·8; N, 4·1%).

Di-2-chlorobenzylidenesuccinic Acid.—A solution of diethyl succinate (8 g.) and *o*-chlorobenzaldehyde (12·5 g.) in dry ether (30 ml.) was quickly added to a stirred suspension of dry, alcohol-free sodium ethoxide (3·5 g.) in dry ether (50 ml.) cooled at −15° to −18°, and the reaction completed as before. The mixture was shaken with cold water, and the ether layer separated from the aqueous alkaline layer (*A*). Distillation of the ether left a residue which was hydrolysed with 20% sodium hydroxide solution. The insoluble neutral product in the alkaline solution (*B*) was re-extracted with ether, and the ethereal solution washed and dried (Na_2SO_4). Distillation of ether left a pale yellow oil which slowly solidified and crystallised from ethyl alcohol to give *o*-chlorobenzyl alcohol, needles, m. p. and mixed m. p. 71—72° (cf. Carothers and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1681).

Acidification of the aqueous alkaline solution (*B*) (charcoal) precipitated an acid which was filtered off, washed, and dried, m. p. 125—126° (*ca.* 1 g.). This on two crystallisations from benzene gave needles, m. p. 130—131° depressed to 112—117° on admixture with *o*-chlorobenzoic acid. The structure of this acid is under investigation.

The alkaline solution (*A*) (charcoal) was refluxed for an hour till hydrolysis was complete and then worked up as usual (cf. Baddar and El-Assal, *loc. cit.*). The acid product was treated several times with hot benzene, and the insoluble product filtered off and crystallised from glacial acetic acid to give *di-2-chlorobenzylidenesuccinic acid*, m. p. 233—234° (Found : C, 59·1; H, 3·2; Cl, 19·4. $C_{18}H_{12}O_4Cl_2$ requires C, 59·5; H, 3·3; Cl, 19·5%); yield *ca.* 3 g. When the benzene mother-liquor evaporated slowly, it gave a few crystals embedded in a viscous oil. Those were mechanically separated and crystallised from the same solvent, forming needles, m. p. 130—131°, identical with the above unidentified product.

Di-2-chlorobenzylidenesuccinic Anhydride (III; R = Cl, R′ = H).—Prepared as usual and repeatedly crystallised from benzene–light petroleum (b. p. 40—60°), this *anhydride* formed lemon-yellow crystals, m. p. 184—185° (80%), (Found: C, 62·5; H, 2·9; Cl, 20·2. $C_{18}H_{10}O_3Cl_2$ requires C, 62·6; H, 2·9; Cl, 20·5%).

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