206. 1-*Phenylnaphthalenes. Part V.** *The Cyclisation of Diarylidenesuccinic Anhydrides to* 1-*Phenylnaphthalenes.*

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Dissimilarly substituted dibenzylidenesuccinic anhydrides are prepared by a two-step Stobbe condensation. They give, on cyclisation, a mixture of the corresponding two isomeric 1-phenylnaphthalenes in nearly equal proportions.

STOBBE condensation of *p*-chlorobenzaldehyde with diethyl succinate at —15° to —10° in presence of alcohol-free sodium ethoxide[1,2] gave di-*p*-chlorobenzylidenesuccinic acid (II*a*). Its anhydride (III*a*) cyclised in sunlight to 7-chloro-1-*p*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (IV*a*), identical with a specimen prepared by the self-condensation of *p*-chlorophenylpropiolic acid.[3]

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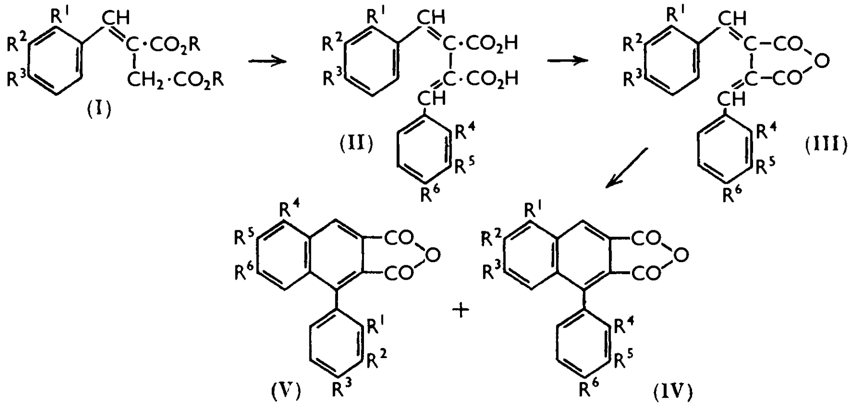
* Part IV, 1958, 986.

[1] Baddar, El-Assal, and Gindy, Part I, *J.*, 1948, 1270.

[2] Baddar, El-Assal, and Doss, *J.*, 1955, 461.

[3] Baddar, El-Assal, and Doss, *J.*, 1959, 1027.

When *o*-methoxybenzaldehyde was condensed with dimethyl succinate in boiling alcoholic sodium ethoxide, it gave *o*-methoxybenzylidenesuccinic acid (I*b*; R = H). Its diethyl ester (I*b*; R = Et) was further condensed with *o*-chlorobenzaldehyde at low temperature in presence of sodium ethoxide[4] to give the diarylidenesuccinic acid (II*b*), whose anhydride (III*b*) cyclised in sunlight or when heated to give a mixture of 1-*o*-chlorophenyl-5-methoxy- (IV*b*) and 5-chloro-1-*o*-methoxyphenyl-naphthalene-2 : 3-dicarboxylic anhydride (V*b*) in nearly equal amounts. The structure of the anhydrides (IV*b* and V*b*) was established by their identity with specimens prepared by the action of *o*-chlorophenylpropioloyl chloride on *o*-methoxyphenylpropiolic acid.[3]



	R¹	R²	R³	R⁴	R⁵	R⁶
a	H	H	Cl	H	H	Cl
b	MeO	H	H	Cl	H	H

	R¹	R²	R³	R⁴	R⁵	R⁶
c	H	H	MeO	H	H	H
d	H	$-O\cdot CH_2\cdot O-$		H	H	OMe

Similarly were prepared the acids (I*c*; R = H) and (II*c*) and the anhydride (III*c*), whose cyclisation afforded the naphthalene-anhydrides (IV*c*) and (V*c*) in nearly equal amount. The structures were proved as in other cases.

Piperonaldehyde gave an acid (I*d*: R = H) which had a much higher m. p. (200—201°) than that reported by Cornforth *et al.*[5] (m. p. 114—115°). The structure of this acid was established by its analysis and that of its dimethyl ester (I*d*; R = Me), and normal condensation of the ester to give the acid (II*d*). In addition, cyclisation of the anhydride (III*d*) in sunlight or by heat gave the anhydrides (IV*d*) and (V*d*) in nearly equal amounts. The dibasic acid derived from the former anhydride gave on decarboxylation 6 : 7-dimethoxy-1-*p*-methoxyphenylnaphthalene, identical with a specimen prepared by the decarboxylation of 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-3-carboxylic acid.[6] The identification of the anhydride (IV*d*) left no doubt concerning the structure of its isomer (V*d*).

EXPERIMENTAL

Di-p-*chlorobenzylidenesuccinic Acid* (II*a*).—A solution of *p*-chlorobenzaldehyde (12·5 g., 2 mol.) and diethyl succinate (8·6 g.; 1 mol.) in dry ether (30 ml.) was added to a suspension of finely powdered, alcohol-free sodium ethoxide (6·8 g., 2 mol.) in dry ether (50 ml.) at −15° to −10°. The temperature was kept thereat for 2 days and at 0° for further 2 days with occasional stirring. After the usual working up,[1, 2] the product was digested with benzene, and the insoluble acid crystallised from acetic acid to give *di*-p-*chlorobenzylidenesuccinic acid* (*ca.* 3 g.), m. p. 225—226° (Found: C, 59·6; H, 3·5; Cl, 19·8. $C_{18}H_{12}O_4Cl_2$ requires C, 59·5; H, 3·3; Cl, 19·7%).

Di-p-*chlorobenzylidenesuccinic Anhydride* (III*a*).—The above acid (1 g.) was refluxed with

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[4] Stobbe, *Annalen*, 1911, **380**, 50.

[5] Cornforth, Gordon, Hughes, and Lions, *J. Proc. Roy. Soc., N.S. Wales*, 1939, **72**, 238.

[6] El-Assal and Shehab, following paper.

acetyl chloride (6 ml.) for 2 hr. and then worked up as usual. The product (*ca.* 0·8 g.) was repeatedly crystallised from benzene–light petroleum (b. p. 40—60°), to give *di-*p*-chlorobenzylidenesuccinic anhydride* in lemon-yellow crystals, m. p. 203—204° (Found: C, 62·8; H, 2·9; Cl, 20·7. $C_{18}H_{10}O_3Cl_2$ requires C, 62·6; H, 2·9; Cl, 20·6%).

*7-Chloro-*1-p*-chlorophenylnaphthalene-*2 : 3*-dicarboxylic Anhydride* (IV*a*).—Di-*p*-chlorobenzylidenesuccinic anhydride (0·5 g.) was cyclised as usual with iodine in sunlight (10 days; October). The product crystallised from benzene, to give *7-chloro-*1-p*-chlorophenylnaphthalene-*2 : 3*-dicarboxylic anhydride* in pale yellow needles, m. p. 266—267° (0·35 g.), undepressed on admixture with an authentic specimen prepared by the self-condensation of *p*-chlorophenylpropiolic acid[3] (Found: C, 62·7; H, 2·3; Cl, 20·5. $C_{18}H_8O_3Cl_2$ requires C, 63·0; H, 2·3; Cl, 20·7%).

Benzylidenesuccinic Acids (I; R = H).—The mixture of the aromatic aldehyde (27 g., 1 mol.), diethyl succinate (32 g., 1·1 mol.) and metallic sodium (5·5 g., 1·2 mol.) in absolute ethanol (150 ml.) was refluxed for 2·5 hr. Alcohol was then removed, 3% sodium hydroxide solution (350 ml.) was added, and the solution was then refluxed for 15 min. On cooling, the insoluble product was removed (either extracted with benzene or filtered off), and the cold alkaline solution (charcoal) was acidified. The precipitated acid was filtered off, washed with water, and dried. The dry acid product was then treated with boiling benzene and the insoluble product was filtered off, dried, and crystallised from a suitable solvent. The *products* are reported in Table 1. Acids (I*b* and *c*) were crystallised from 30% acetic acid, but (I*d*) from glacial acetic acid.

TABLE 1.

Acid	M. p.	Yield (%)	Formula	Found (%) C	H	Required (%) C	H
cis-I*b* †	210—211°	53	$C_{12}H_{12}O_5$	60·9	5·2	61·0	5·2
cis-I*c* †	202—203	57	$C_{12}H_{12}O_5$	61·3	5·35	,,	,,
I*d*[5]	200—201	96	$C_{12}H_{10}O_6$	57·9	3·95	57·6	4·0

† The *cis*-configuration was established by cyclisation to the corresponding 3-hydroxy-2-naphthoic acids (El-Abbady and El-Assal, *J.*, 1959, 1024).

Diethyl o*-Methoxybenzylidenesuccinate* (I*b*; R = Et).—The mixture of the acid (I*b*; R = H) (20 g.), absolute ethanol (70 ml.), benzene (30 ml.), and concentrated sulphuric acid (2 ml.) was refluxed for 15 hr., then worked up as usual. The product was distilled in a vacuum and the lemon-yellow viscous *diethyl* o*-methoxybenzylidenesuccinate* (*ca.* 18 g.), b. p. 280—285°/4 mm., was collected (Found: C, 65·5; H, 7·1. $C_{16}H_{20}O_5$ requires C, 65·75; H, 6·9%).

Diethyl p*-methoxybenzylidenesuccinate* (I*c*; R = Et), prepared as was its *o*-methoxy-isomer, had b. p. 285—290°/4 mm. (11 g.) (Found: C, 65·8; H, 7·0%).

Dimethyl Piperonylidenesuccinate (I*d*; R = Me).—A mixture of the acid (I*d*; R = H) (25 g.), dimethyl sulphate (50·5 g.), and potassium carbonate (100 g.) in acetone (150 ml.) was heated for 12 hr., then worked up as usual. The fraction of the product boiling at 224—228°/6 mm. was triturated with ether, giving a colourless solid. On crystallisation from benzene–light petroleum (b. p. 40—60°) it gave *dimethyl piperonylidenesuccinate* in rosettes (17 g.), m. p. 77—78° (Found: C, 60·25; H, 5·1. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·0%).

Dissimilarly Substituted Dibenzylidenesuccinic Acids (II).—A solution of the aromatic aldehyde (~ 7 g., 1 mol.) and the ester (I; R = Et) (1 mol.) in ether (*ca.* 25 ml.) was added to a suspension of sodium ethoxide (3·5 g., 1·1 mol.) in ether (*ca.* 130 ml.) at −18°, kept between −15° and −10° for 3 days, then finally at room-temperature (20—25°) for several hours with occasional stirring. The product was worked up as usual.[2] The product insoluble in benzene was crystallised from a suitable solvent and the results are summarised in Table 2.

TABLE 2.

Acid	Solvent	M. p.	Yield (%)	Found (%) C	H	Cl	Required (%) C	H	Cl
II*b*	Aq. AcOH	232—233°	52	63·15	4·1	9·8	63·6	4·2	9·9
II*c*	,,	231—232	87	69·8	5·0	—	70·4	4·9	—
II*d* *	AcOH	224—227	70	—	—	—	—	—	—

* The cooling in this case was at −18° to −15° for 24 hr. and then at 0° for a further 3 days. The acid was gradually transformed into its anhydride on repeated crystallisation from glacial acetic acid as indicated by the lowering of its m. p. and by a change of colour; it was best analysed as its anhydride.

α-o-*Chlorobenzylidene*-β-o-*methoxybenzylidenesuccinic Anhydride* (III*b*), prepared in the usual manner, had m. p. 98—100° [lemon-yellow crystals from benzene–light petroleum (b. p. below 40°)] (Found: C, 66·6; H, 3·85; Cl, 10·0. $C_{19}H_{13}O_4Cl$ requires C, 66·95; H, 3·8; Cl, 10·4%).

Cyclisation of α-o-*Chlorobenzylidene*-β-o-*methoxybenzylidenesuccinic Anhydride.*—(i) The anhydride (2 g.) was cyclised by iodine in sunlight in the usual manner (14 days, Ohio, U.S.A.). The product (*ca.* 1·5 g.) was fractionally crystallised, to give 1-o-*chlorophenyl*-5-*methoxynaphthalene*-2 : 3-*dicarboxylic anhydride* (IV*b*) in lemon-yellow crystals, m. p. 251—252°, undepressed on admixture with a specimen prepared by the action of *o*-chlorophenylpropioloyl chloride on *o*-methoxyphenylpropiolic acid [3] (Found: C, 67·3; H, 3·1; Cl, 10·7. $C_{19}H_{11}O_4Cl$ requires C, 67·35; H, 3·25; Cl, 10·5%). The benzene mother-liquor was concentrated and the precipitated product (*ca.* 0·55 g.) repeatedly crystallised from the same solvent, to give 5-*chloro*-1-o-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (V*b*), m. p. 199—200°, undepressed on admixture with a specimen prepared by the action of *o*-chlorophenylpropioloyl chloride on *o*-methoxyphenylpropiolic acid [3] (Found: C, 66·9; H, 3·25; Cl, 10·6%). (ii) The anhydride (III*b*) (2 g.) was heated at 280—290° for 2 hr., then worked up as in (i). The product (*ca.* 1·4 g.; m. p. 175—215°) precipitated from ether was fractionally crystallised from benzene to give 1-*o*-chlorophenyl-5-methoxy- (IV*b*) and 5-chloro-1-*o*-methoxy-phenylnaphthalene-2 : 3-carboxylic anhydride (V*b*), identified by m. p. and mixed m. p.

α-*Benzylidene*-β-p-*methoxybenzylidenesuccinic Anhydride* (III*c*).—This *compound* was obtained from the acid (5 g.) and acetyl chloride (15 ml.) in the usual manner as lemon-yellow crystals [from benzene–light petroleum (b. p. below 40°)], m. p. 153—154° (*ca.* 4·5 g.) (Found: C, 74·2; H, 4·8. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

Cyclisation of α-*Benzylidene*-β-p-*methoxybenzylidenesuccinic Anhydride.*—The above anhydride (III*c*) (2 g.) was cyclised with iodine in the usual manner (14 days; Ohio, U.S.A.). The product (*ca.* 1·8 g.), m. p. 210—220°, on fractional crystallisation from benzene, gave 1-p-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (V*c*) (*ca.* 0·5 g.) in lemon-yellow crystals, m. p. 259—260°, undepressed on admixture with a specimen prepared by the action of *p*-methoxyphenylpropioloyl chloride on phenylpropiolic acid [3] (Found: C, 74·8; H, 4·2. $C_{19}H_{12}O_4$ requires C, 75·0; H, 3·95%). Concentration of the original benzene mother-liquor precipitated a product (0·48 g.) which on repeated crystallisation from the same solvent gave 7-*methoxy*-1-*phenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (IV*c*) in pale yellow crystals, m. p. 267—268°, undepressed on admixture with an authentic specimen [3] (Found: C, 74·85; H, 4·0%).

α-p-*Methoxybenzylidene*-β-*piperonylidenesuccinic Anhydride* (III*d*).—The *anhydride* (*ca.* 3·5 g.), prepared from its acid (II*d*) (4·5 g.) in the usual manner, was repeatedly crystallised from benzene in orange rosettes, m. p. 182—183° (Found: C, 68·6; H, 4·15; OMe, 8·4. $C_{20}H_{14}O_6$ requires C, 68·6; H, 4·0; OMe, 8·85%).

Cyclisation of α-p-*Methoxybenzylidene*-β-*piperonylidenesuccinic Anhydride.*—(i) The solution of the anhydride (III*d*) (1 g.) in benzene (10 ml.) was treated with iodine in the usual manner (14 days; Cairo). The precipitated product (*ca.* 0·2 g.), m. p. 272—274°, was boiled with 10% sodium hydroxide solution (5 ml.) to remove traces of the second isomer, and the insoluble product was filtered off, washed, and dried. On crystallisation from acetic acid, 7-*methoxy*-1-(3 : 4-*methylenedioxyphenyl*)*naphthalene*-2 : 3-*dicarboxylic anhydride* (V*d*) was obtained in light brown crystals, m. p. 277—278° (Found: C, 68·85; H, 3·75; OMe, 8·4. $C_{20}H_{12}O_6$ requires C, 68·9; H, 3·5; OMe, 8·9%). Distillation of the original benzene mother-liquor left a brown semi-solid, which on trituration with ether was transformed into crystals (*ca.* 0·3 g.), m. p. 272—274°. On repeated crystallisation from benzene it gave lemon-yellow 1-p-*methoxyphenyl*-6 : 7-*methylenedioxynaphthalene*-2 : 3-*dicarboxylic anhydride* (IV*d*) (0·25 g.), m. p. 275—276°, depressed on admixture with a specimen of its isomer (V*d*) (Found: C, 69·0; H, 3·6; OMe, 8·4%). (ii) The anhydride (III*d*) (1·5 g.) was heated at 205—210° (nitrobenzene-bath) for 3 hr. The glassy mass was triturated with ether, and the insoluble solid was filtered off (*ca.* 1·1 g.), then treated with boiling benzene. The insoluble product (*ca.* 0·5 g.) was treated as described in (i) and crystallised from acetic acid, to give 7-methoxy-1-(3 : 4-methylenedioxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride identified by m. p. and mixed m. p. Concentration of the benzene solution precipitated a solid which after repeated crystallisation from the same solvent gave 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-2 : 3-dicarboxylic anhydride (0·52 g.), identified by m. p. and mixed m. p.

1-p-*Methoxyphenyl*-6 : 7-*methylenedioxynaphthalene.*—A solution of the above acid (0·2 g.) (prepared from its anhydride) in quinoline (5 ml.) was stirred with copper-bronze (0·1 g.) while gradually heated to 205—210° (nitrobenzene-bath) during 30 min. The temperature was kept thereat for 30 min. during which a further amount of copper-bronze (0·1 g.) was added portionwise. The heating and stirring were continued for a further hour, then the whole was worked up as usual. The brown viscous oily product was transformed on trituration with light petroleum (b. p. 40—60°) into a solid, m. p. 103—104° (*ca.* 0·1 g.). On repeated crystallisation from the same solvent it gave 1-p-*methoxyphenyl*-6 : 7-*methylenedioxynaphthalene* in pale brown crystals, m. p. 108—109°, undepressed on admixture with a specimen prepared by the decarboxylation of 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-3-carboxylic acid [6] (Found: C, 77·8; H, 5·2; OMe, 13·6. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0; OMe, 12·15%).

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