550. αβ-*Bisarylmethylenesuccinic Acids. Part II.* The Cyclisation of* αβ-*Bisarylmethylenesuccinic Anhydrides to a Mixture of the Corresponding* 1-*Phenylnaphthalenes.*

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αβ-Bisarylmethylenesuccinic anhydrides substituted dissimilarly in the same position or similarly in different positions are prepared by a two-step Stobbe condensation. They give the corresponding isomeric 1-phenylnaphthalenes on cyclisation. The ratio of the isomers in each of the studied examples depends on the polar nature and position of the substituents in both the α- and β-arylmethylene radicals.

PREVIOUSLY [1] it was shown that the cyclisation of dissimilarly substituted αβ-bisarylmethylenesuccinic anhydrides gives the isomeric 1-phenylnaphthalenes (IV) and (V) in nearly equal proportion. αβ-Disubstituted anhydrides (III) have now been prepared, having either dissimilar substituents in identical positions or similar substituents in different positions of the α- and β-arylidene radicals in order to study the effect of the nature and position of such substituents on the mode of cyclisation and on the ratio of the isomers.

Thus, interaction of an aromatic aldehyde with dimethyl succinate in a boiling solution of potassium t-butoxide in t-butyl alcohol gave the *cis*-β-half esters; [2,3] these or the corresponding acids [4] were methylated to dimethyl *cis*-γ-arylitaconates (I*a*—*c*).[2,3] The *cis*-configuration of esters (I*a* and *b*) was confirmed by their cyclisation to the corresponding naphthalene derivative.[3] Condensation between an aromatic aldehyde and a dimethyl *cis*-γ-arylitaconate (I) at between —15° and 0° in presence of sodium ethoxide gave αβ-bisarylmethylenesuccinic acids (II*a*—*e*). These are relatively unstable and are best handled as dimethyl esters (II; $R = Me$) prepared by use of diazomethane.

The αβ-bisarylmethylenesuccinic acids (II*a*—*e*; $R = H$) were easily converted into their anhydrides (III*a*—*e*) by acetyl chloride, and these on pyrolysis gave mixtures of the isomeric 1-arylnaphthalene-2,3-dicarboxylic anhydrides (IV) and (V) separable by crystallisation.

The dibasic acids (VI*a*—*e*; $R = CO_2H$) derived from these anhydrides (IV*a*—*e*) were decarboxylated with copper-bronze in quinoline to the corresponding 1-arylnaphthalenes (VI*a*—*e*; $R = H$), identical with the products of decarboxylation of 4-aryl-2-naphthoic acids obtained by the isomerisation of the corresponding enol lactones of β-aroyl-α-arylmethylenepropionic acids.[5]

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* Part I, *J. Chem. U.A.R.*, in the press.

[1] Baddar, El-Assal, Doss, and Shehab, *J.*, 1959, 1016.

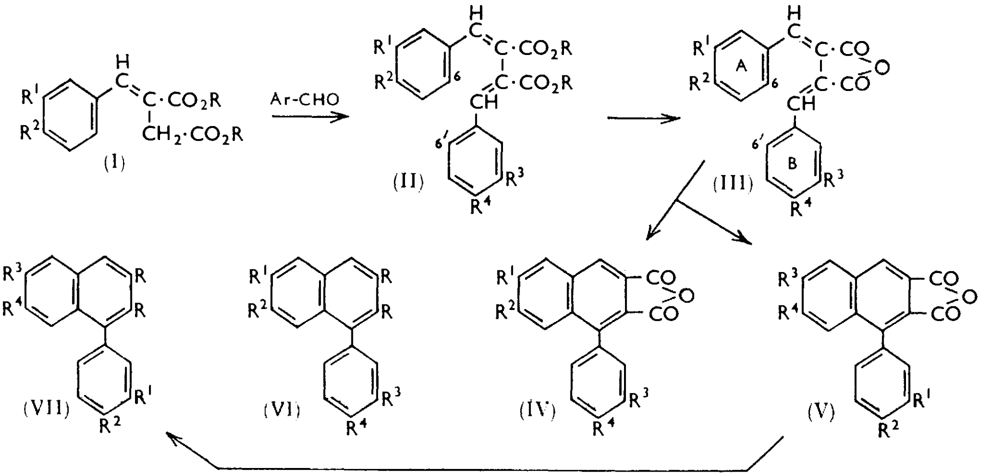
[2] (*a*) El-Assal and El-Abbady, *J.*, 1959, 1024; (*b*) El-Assal and El-Wahhab, *J.*, 1960, 849.

[3] El-Assal and Shehab, unpublished work.

[4] Stobbe, (*a*) *Ber.*, 1894, **27**, 2407; (*b*) *Ber.*, 1908, **41**, 4350.

[5] El-Assal and Shehab, *J.*, 1961, 1658.

As expected, cyclisation of β-(3,4-dimethoxybenzylidene)-α-(3,4-methylenedioxybenzylidene)succinic anhydride (III*e*) gave 1-(3,4-dimethoxyphenyl)-6,7-methylenedioxy-(IV*e*) and 6,7-dimethoxy-1-(3,4-methylenedioxyphenyl)-naphthalene-2,3-dicarboxylic anhydride. Moreover, cyclisation of α-benzylidene-β-*m*-methoxybenzylidenesuccinic anhydride (III*b*) gave the isomer (IV*b*) and unchanged anhydride (III*b*). However, the other anhydrides (III*a*, *c*, and *d*) gave mixtures predominantly of the anhydrides (IV*a*, *c*, and *d*) with very small amounts of the corresponding isomers (V*a*, *c*, and *d*).



I	R^1	R^2
a	H	H
b	OMe	H
c	$-O\cdot CH_2\cdot O-$	

II—VII	R^1	R^2	R^3	R^4
a	H	H	OMe	OMe
b	OMe	H	H	H
c	OMe	H	H	Cl
d	$-O\cdot CH_2\cdot O-$		H	Cl
e	$-O\cdot CH_2\cdot O-$		OMe	OMe

These results are attributed to the electronic nature and position of the substituents in the aromatic nuclei (A) and (B) (see III); an electron-repelling group causes an increase of electron density at positions 2 and 6. The cyclisation by the attachment at position 2 in either nucleus is greatly inhibited by steric factors.[2b,8] Moreover, in the anhydrides (III*c* and *d*), where position 4 of ring (B) is occupied by an electron-attracting group, the electron density at position 6 will be greatly decreased by a $-I$ effect, and hence the attack by the γ position is greatly diminished. The combined effect will lead to the formation predominantly of isomers (IV*a*—*d*).

EXPERIMENTAL

Dimethyl cis-*γ-Phenylitaconate* (I*a*; R = H).—A mixture of *cis*-γ-phenylitaconic acid[4] (20·6 g.), dimethyl sulphate (76 g., 6 mol.), and potassium carbonate (110·5 g., 8 mol.) in acetone (500 ml.) was refluxed for 10 hr. and then worked up as usual.[2] The product distilled at 235—240°/4 mm. to give *dimethyl* cis-*γ-phenylitaconate* as a viscous oil which failed to solidify (Found: C, 66·5; H, 6·1; OMe, 26·1. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6; OMe, 26·5%).

β-*Methyl α-Hydrogen γ-*m*-Methoxyphenylitaconate.*—This was obtained from *m*-methoxybenzaldehyde (13·6 g.,) and methyl succinate (17·5 g., 1·2 mol.) in t-butyl alcohol (25 ml.) and potassium t-butoxide [from metallic potassium (5·8 g.) and the alcohol (75 ml.)] as a dark viscous oil (*ca.* 23 g.).

*cis-γ-*m*-Methoxyphenylitaconic Acid* (I*b*; R = H).—A mixture of β-half ester (5 g.) and 15% (v/v) aqueous alcoholic potassium hydroxide (50 ml.) was refluxed for 2 hr., and then worked up as usual.[2] Acidification of the clear alkaline solution (charcoal) precipitated an acid which was washed with cold water and dried (*ca.* 4·5 g.). Crystallisation from benzene–light petroleum (b. p. 60—70°) gave cis-γ-m-*methoxyphenylitaconic acid*, m. p. 164—165° (Found: C, 61·5; H, 5·3; OMe, 13·1. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1; OMe, 13·1%). The *dimethyl ester* (I*b*; R = Me) was obtained from the acid (6 g.), dimethyl sulphate (13 g.; 4 mol.), and potassium carbonate (35 g.; 6 mol.) in acetone (100 ml.) in the usual manner[2] (12 hours' refluxing) as a viscous oil (Found: C, 63·2; H, 6·0; OMe, 35·6. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1; 3OMe, 35·2%).

αβ-*Bisarylmethylenesuccinic Acids* (II; R = H).—A solution of dimethyl *cis*-γ-arylitaconate (I; R = Me) (16—18 g.) and a suitable aromatic aldehyde (10—12 g.; 1 mol.) in ether (50 ml.) was added to a suspension (at −18°) of sodium ethoxide (5—6 g.; 1 mol.) in ether (100 ml.). The reactants were then kept at between −15° and −10° for 3 days, and for a further 2 days at just below 0°, and finally at room temperature (20—25°) for several hours and then worked up as previously described.[1,6] The aqueous alkaline layer was boiled for 15 min., cooled, and filtered. Acidification precipitated an acid.

These acids (Table 1) clearly tended to decompose to the anhydrides (Table 2) when heated or treated with solvents that cause dehydration. They were therefore characterised as *dimethyl esters* (III; R = Me). Dimethyl sulphate did not give suitable products and diazomethane was therefore used according to the following procedure:

The αβ-bisarylmethylenesuccinic acid (II; R = H) (*ca.* 3 g.) in ether (20 ml.) was added portionwise to a cooled solution of diazomethane [from methylnitrosourea sulphate (10 g.) in ether (30 ml.)], kept in an ice-box overnight, and then worked up in the usual manner. The results are summarised in Table 1.

TABLE 1.

αβ-Bisarylmethylenesuccinic acids (II; R = H) and their corresponding dimethyl esters (II; R = Me).

Acid	M. p.	Yield (%)	Ester	Solv.	M. p.	Yield (%)
a	179—181°	60	*a*	MeOH	83—84°	70
b	212—215	70	*b*	MeOH	85—86	86
c	112—115	75	*c*	MeOH	82—83	70
d	190—195	90	*d*	MeOH	150—151	90
e	170—173	95	*e*	C_6H_6–Pet	174—175	75

	Found (%)					Required (%)			
Ester	C	H	OMe	Cl	Formula	C	H	OMe	Cl
a	69·2	5·6	32·2	—	$C_{22}H_{22}O_6$	69·4	5·75	32·5	—
b	71·3	5·9	28·2	—	$C_{21}H_{20}O_5$	71·6	5·65	26·4	—
c	64·75	5·1	24·0	9·0	$C_{21}H_{19}O_5Cl$	65·2	4·9	24·0	9·2
d	62·45	4·6	15·8	8·6	$C_{21}H_{18}O_6Cl$	62·8	4·5	15·4	8·8
e	64·5	5·3	40·0	—	$C_{23}H_{22}O_8$	64·8	5·2	39·1	—

Pet = light petroleum (b. p. 40—60°).

αβ-*Bisarylmethylenesuccinic Anhydride* (III).—The dry crude acid (*ca.* 4 g.) and acetyl chloride (10 ml.) were refluxed for 4—5 hr. and then left overnight at 20—25°. The product was washed with light petroleum (b. p. <40°) and crystallised from benzene or light petroleum to give the αβ-*bisarylmethylenesuccinic anhydrides* (III) described in Table 2.

TABLE 2.

αβ-Bisarylmethylenesuccinic anhydrides (III).

			Found (%)					Required (%)			
(III)	M. p.	Yield (%)	C	H	OMe	Cl	Formula	C	H	OMe	Cl
a	137—138°	92	71·0	4·8	18·05	—	$C_{20}H_{16}O_6$	71·1	4·75	18·45	—
b	139—140	90	74·9	4·6	10·4	—	$C_{19}H_{14}O_4$	74·5	4·6	10·1	—
c	111—112	95	66·6	3·8	9·0	10·2	$C_{19}H_{13}O_4Cl$	66·9	3·8	9·1	10·4
d	145—146	80	64·0	3·3	—	9·9	$C_{19}H_{11}O_5Cl$	64·3	3·1	—	10·0
e	191—192	90	66·3	4·2	16·1	—	$C_{21}H_{16}O_7$	66·3	4·2	16·3	—

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

Cyclisation of αβ-*Bisarylmethylenesuccinic Anhydrides* (III) *to the Corresponding* 1-*Arylnaphthalene*-2,3-*dicarboxylic Anhydrides* (IV) *and* (V).—The anhydride (III) (*ca.* 3 g.) was heated at 265—270° for 3·5—4 hr. When cold, the glassy product was extracted with boiling benzene. This either dissolved both products, which were then separated by crystallisation, the anhydride (IV) being the less soluble, or the anhydride (IV) dissolved and the isomer (V) was left as residue.

In this way there were obtained: from α-benzylidene-β-(3,4-dimethoxybenzylidene)succinic anhydride (III*a*) 6,7-*dimethoxy*-1-*phenylnaphthalene*-2,3-*dicarboxylic anhydride* (IV*a*), m. p. 222—223° (85%) (from glacial acetic acid) (Found: C, 71·8; H, 4·3; OMe, 17·9. $C_{20}H_{14}O_5$ requires C, 72·3; H, 4·2; 2OMe, 18·5%), and 1-(3,4-*dimethoxyphenyl*)*naphthalene*-2,3-*dicarboxylic anhydride* (V*a*), m. p. 247—248° (Found: C, 72·5; H, 4·1; OMe, 18·8%); from α-benzylidene-β-*m*-methoxybenzylidenesuccinic anhydride (III*b*) 6-*methoxy*-1-*phenylnaphthalene*-2,3-*dicarboxylic anhydride* (IV*b*) (main product), m. p. 223—224° (Found: C, 76·5; H, 4·05; OMe, 9·8. $C_{19}H_{12}O_4$ requires C, 75·0; H, 3·9; OMe, 10·2%), (80%); from α-*p*-chlorobenzylidene-β-*m*-methoxybenzylidenesuccinic anhydride (III*c*) 1-p-*chlorophenyl*-6-*methoxynaphthalene*-2,3-*dicarboxylic anhydride* (IV*c*), m. p. 226—227° (68%) (Found: C, 67·3; H, 3·5; Cl, 10·5; OMe, 8·9. $C_{19}H_{11}O_4Cl$ requires C, 67·4; H, 3·3; Cl, 10·5; OMe, 9·15%), and 7-*chloro*-1-m-*methoxyphenylnaphthalene*-2,3-*dicarboxylic anhydride* (V*c*), m. p. 252—253° (Found: C, 67·5; H, 3·4; Cl, 10·7; OMe, 9·5%); from α-*p*-chlorobenzylidene-β-(3,4-methylenedioxybenzylidene)-succinic anhydride (III*d*) 1-p-*chlorophenyl*-6,7-*methylenedioxynaphthalene*-2,3-*dicarboxylic anhydride* (IV*d*), m. p. 292—293° (from glacial acetic acid) (85%) (Found: C, 64·6; H, 2·65; Cl, 9·2. $C_{19}H_9O_5Cl$ requires C, 64·7; H, 2·8; Cl, 10·1%), and 7-*chloro*-1-(3,4-*methylenedioxyphenyl*)*naphthalene*-2,3-*dicarboxylic anhydride* (V*d*), m. p. 272—273° (Found: C, 64·5; H, 2·7; Cl, 10·2%); and from α-(3,4-dimethoxybenzylidene)-β-(3,4-methylenedioxybenzylidene)-succinic anhydride (III*e*) 1-(3,4-*dimethoxyphenyl*)-6,7-*methylenedioxynaphthalene*-2,3-*dicarboxylic anhydride* (IV*e*), m. p. 267—268° (50%) (Found: C, 66·2; H, 3·8; OMe, 15·45. $C_{21}H_{14}O_7$ requires C, 66·6; H, 3·7; OMe, 16·4%), and 6,7-*dimethoxy*-1-(3,4-*methylenedioxyphenyl*)*naphthalene*-2,3-*dicarboxylic anhydride* (V*e*) (50%), m. p. 287—288° (Found: C, 66·35; H, 3·7; OMe, 16·1%).

1-*Arylnaphthalene*-2,3-*dicarboxylic Acids* (VI*a*—*e or* VII*e*; R = CO_2H) *and their Dimethyl Esters*.—A suspension of an anhydride (VI*a*—*e* or VII*e*) (*ca.* 2 g.) in 20% sodium hydroxide solution (20 ml.) was heated for 10—20 min. The clear alkaline solution (charcoal) was cooled (ice-bath) and carefully acidified with ice-cold concentrated hydrochloric acid. The precipitate was washed with cold water and dried (*ca.* 1·9 g.) (see Table 3).

The *dimethyl esters* (Table 3) were prepared by use of diazomethane, use of dimethyl sulphate not always giving a clean product.

TABLE 3.

1-Arylnaphthalene-2,3-dicarboxylic acids (VI*a*—*e* and VII*e*; R = CO_2H) and their dimethyl esters.

Acid (R = CO_2H)	M. p.*	Yield (%)	Ester (R = CO_2Me)	Solvent	M. p.
VI*a*	210—212°	78	VI*a*	MeOH	129—130°
VI*b*	215—217	98	VI*b*	MeOH	122—123
VI*c*	125—130	97	VI*c*	MeOH	87—88
VI*d*	198—205	70	VI*d*	C_6H_6–Pet	166—167
VI*e*	155—160	76	VI*e*	MeOH	139—140
VII*e*	165—170	75	VII*e*	C_6H_6–Pet	164—165

	Found (%)					Required (%)			
Ester	C	H	Cl	OMe	Formula	C	H	Cl	OMe
VI*a*	69·4	5·3	—	33·05	$C_{22}H_{20}O_6$	69·5	5·3	—	32·6
VI*b*	71·7	5·2	—	25·8	$C_{21}H_{18}O_5$	72·0	5·1	—	26·6
VI*c*	65·3	4·5	8·9	24·3	$C_{21}H_{17}O_5Cl$	65·6	4·4	9·2	24·2
VI*d*	63·2	3·9	9·0	15·0	$C_{21}H_{15}O_6Cl$	63·5	3·8	8·9	15·8
VI*e*	65·5	4·8	—	30·2	$C_{23}H_{20}O_8$	65·1	4·7	—	29·2
VII*e*	65·5	4·65	—	30·5	$C_{23}H_{20}O_8$	65·1	4·7	—	29·2

Pet = light petroleum (b. p. 50—70°).

* Of crude material.

Preparation of 1-*Arylnaphthalenes* (VI*a*—*e* and VII*e*; R = H).—The crude dry acid (VI*a*—*e* and VII*e*; R = CO_2H) (*ca.* 0·3 g.) in quinoline (5 ml.) was stirred with copper–bronze (0·15 g.) and heated to 205—210° during 45 min. The temperature was kept thereat for a further 45 min., and more copper–bronze (0·15 g.) added portionwise. The heating and stirring were continued for a further hour. Working up in the usual manner gave the 1-*arylnaphthalenes* (Table 4), identical with those prepared by the decarboxylation of 4-aryl-2-naphthoic acids obtained by isomerisation of the enol lactones of β-aroyl-α-arylmethylenepropionic acids.

TABLE 4.

1-Arylnaphthalenes (VI*a*—*e* and VII*e*; R = H).

Compound (R = H)	M. p.	Yield (%)	Ref.	Found (%)				Formula	Calcd. (%)			
				C	H	Cl	OMe		C	H	Cl	OMe
VI*a*	110—111°	75	5, 7, 8	81·5	6·2	—	24·2	$C_{18}H_{16}O_2$	81·8	6·1	—	23·5
VI*c*	72—73	55	5	76·1	5·1	12·8	10·8	$C_{17}H_{13}OCl$	76·0	4·85	13·2	11·5
VI*d*	113—114	90	5	71·8	4·15	12·5	—	$C_{17}H_{11}O_2Cl$	72·2	3·95	12·6	—
VI*e*	134—135	66	5	73·85	5·3	—	19·9	$C_{19}H_{16}O_4$	74·0	5·2	—	20·1
VII*e*	169—170			73·75	5·3	—	20·4	$C_{19}H_{16}O_4$	74·0	5·2	—	20·1

6-*Methoxy*-1-*phenylnaphthalene* (VI*b*).—This was obtained by a similar decarboxylation of 6-methoxy-1-phenylnaphthalene-2,3-dicarboxylic acid (VI*b*; R = CO_2H) as an oil which failed to crystallise even after distillation at 245—250°/5 mm. Therefore, it was nitrated[5] to give a mononitro-derivative, m. p. and mixed m. p 147—148°.

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[7] Howell and Robertson, *J.*, 1936, 587.

[8] El-Assal and Shehab, *J.*, 1959, 1020.