207. *β-Aroyl-α-arylmethylenepropionic Acids. Part I. Conversion of the Lactones of β-Aroyl-α-arylmethylenepropionic Acids into the Corresponding 1-Phenylnaphthalenes.*

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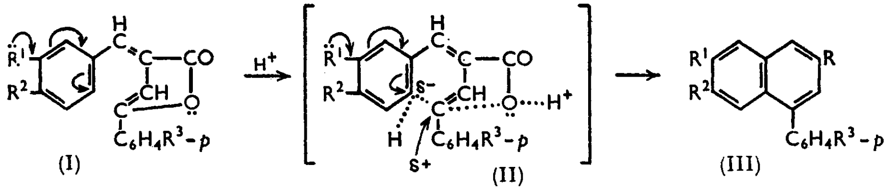
The lactones of β-aroyl-α-arylmethylenepropionic acids are converted into the corresponding 1-phenylnaphthalenes by three methods. However, some lactones fail to isomerise even under drastic conditions.

The conversion of lactones (I) into 1-phenylnaphthalenes (III) was attempted by three methods, two of them described by Howell and Robertson [1] and by Haworth and Sheldrick [2] severally; the third was developed by the authors in this investigation. Those methods are: (i) Passing hydrogen chloride into a suspension of the lactone in boiling methanol for several hours. (ii) Leaving a chloroform solution of the lactone with iodine at room temperature for 5—15 days. (iii) Refluxing the lactone with a mixture of glacial acetic and concentrated hydrochloric acid for a period ranging from 20 minutes to 6 hours. In general, method (iii) proved superior as it gives purer products in shorter times (see Tables). Method (ii) is less often successful than method (i) and gave less pure products.



	R¹	R²	R³
a	–O·CH₂·O–		OMe
b	OMe	OMe	Cl
c	OMe	OMe	H
d	–O·CH₂·O–		Me

	R¹	R²	R³
e	OMe	OMe	OMe
f	OMe	OMe	Me
g	H	OMe	OMe

	R¹	R²	R³
h	H	OMe	H
i	H	H	OMe
j	H	H	H

The structure of methyl 4-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-2-carboxylate (III*a*; R = CO_2Me), obtained by method (i), followed because the derived acid (III*a*; R = CO_2H) was identical with that obtained by the isomerisation with method

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

[2] Haworth and Sheldrick, *J.*, 1935, 636.

(iii), and decarboxylation of this acid gave 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene (III*a*; R = H) identical with the decarboxylation product of 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-2 : 3-dicarboxylic acid which was obtained by the Stobbe condensation.[3]

Methyl 4-*p*-chlorophenyl-6 : 7-dimethoxynaphthalene-2-carboxylate (III*b*; R = CO_2Me) gave on hydrolysis its acid (III*b*; R = CO_2H), identical with the product obtained by method (iii). This acid was decarboxylated to 1-*p*-chlorophenyl-6 : 7-dimethoxynaphthalene (III*b*; R = H). When this compound was dechlorinated by palladised charcoal[4] in tetralin at 205—210°, it gave 6 : 7-dimethoxy-1-phenylnaphthalene[1] (III*c*; R = H).

By method (i) the lactones (I*d, e, f*) gave the esters (III; R = CO_2Me), which were hydrolysed to acids identical with those obtained by method (iii). These acids were decarboxylated to the naphthalenes (III; R = H) whose structures rest on analogy with the above two examples and those in the literature.[1, 2]

Some lactones of type (I) failed to react by any of the three methods. When positions 3 and 4 in the benzylidene radical are occupied by electron-repelling substituents (3 : 4-methylenedioxy, 3 : 4-dimethoxy) the reaction is successful: but it failed with lactones (I*g, h, i, j*) even when attempted by pyrolysis, action of aluminium chloride in nitrobenzene at 20—25° or 100° for several hours or in a sodium chloride melt, or by iodine in chloroform at 20—25° or at the b. p.

The hydrogen chloride reaction appears to be initiated by the attack of a proton on the lactone-oxygen atom. Reaction then proceeds as indicated in formula (II), in a way similar to electrophilic substitution. Since the crude products of isomerisation by method (iii) were pure (m. p. only 1—2° low), the authors believe that the possibility of attachment at the carbon atom 2 is greatly diminished by steric factors.

EXPERIMENTAL

Preparation of the Lactones of β-*Aroyl*-α-*arylmethylenepropionic Acids*.—The mixture of the aromatic aldehyde (1 mol.) and dry sodium β-benzoylpropionate or its derivative (1 mol.) in acetic anhydride was heated on a boiling-water bath for several hours, left overnight, and then worked up as usual.[1, 2] The *lactone* was then crystallised from a suitable solvent. The time of heating and the amount of acetic anhydride had a profound effect on the yield and the purity of the products (see Table 1).

Cyclisation of the Lactones (I).—*Method* (i). Dry hydrogen chloride was passed into a suspension of the lactone (I) in boiling methanol for several hours (complete discharge of the lactone colour). The solution was then concentrated and left to cool. The precipitated colourless ester was filtered off, washed with water, sodium carbonate solution, and water, and dried. Then the ester was crystallised from a suitable solvent. The results are in Table 2.

Method (ii). The solution of the lactone in chloroform was left in diffused light for several days at 20—25°, then washed with sodium thiosulphate solution and sodium carbonate solution. Acidification of the sodium carbonate solution precipitated the acid which was filtered off, washed, dried, and recrystallised. Table 3 gives the results. Lactones (I*a*, *b*, and *d*) gave only traces of acid (III). The crude product needed several crystallisations.

Method (iii). A suspension of lactone (I) in glacial acetic and concentrated hydrochloric acid was heated until the lactone colour disappeared. The precipitated colourless product was filtered off, washed with water, and digested in sodium carbonate solution. The alkaline solution was acidified and the precipitated acid filtered off, washed with water, dried, and recrystallised (Table 4). The products obtained by this method were identical with the hydrolysis products of the corresponding esters obtained by method (i) and with the acids obtained by method (ii).

1-p-*Methoxyphenyl*-6 : 7-*methylenedioxynaphthalene* (III*a*; R = H).—The solution of 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-3-carboxylic acid (III*a*; R = CO_2H) (0·25 g.)

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[3] Baddar, El-Assal, Doss, and Shehab, 1016.

[4] Doss, unpublished work.

TABLE 1.

Lactone	Amounts Salt (g.)	Ac$_2$O (ml.)	Time (hr.)	Solvent *	Colour	M. p.	Yield (%)
I*a*	5 [1, 6]	40	3	C$_6$H$_6$–Pet	Yellow	211—212°	65
I*b*	1·3 [7]	4	1	,,	Orange-yellow	182—183	63
I*c*	6 [8]	80	3	AcOH	Golden-yellow	131—132	81 [1]
I*d*	4·3 [9]	40	3	CHCl$_3$	Orange	214—215	98
I*e*	2·3 [1, 6]	20	6	AcOH	Orange-yellow	174—175	91
I*f*	2·15 [9]	30	3	,,	Orange	144—145	90
I*g*	2·3 [1, 6]	5	6	,,	Greenish-yellow	177—178	83
I*h*	2 [8]	5	3	C$_6$H$_6$	Orange-yellow	168—169	71 [5]
I*i*	2·3 [1, 6]	15	3	,,	Greenish-yellow	176—177	90 [1]
I*j*	6 [8]	15	6	AcOH	Orange-yellow	150—151	53 [5]

Lactone	Formula	Found (%) C	H	OMe	Cl	Required (%) C	H	OMe	Cl
I*a*	$C_{19}H_{14}O_5$	71·2	4·5	9·1	—	70·8	4·35	9·6	—
I*b*	$C_{19}H_{15}O_4Cl$	66·8	4·6	17·6	9·7	66·6	4·4	18·1	10·4
I*c*	$C_{19}H_{16}O_4$	—	—	—	—	—	—	—	—
I*d*	$C_{19}H_{14}O_4$	74·7	4·7	—	—	74·5	4·6	—	—
I*e*	$C_{20}H_{18}O_5$	71·3	5·5	27·0	—	71·0	5·3	27·5	—
I*f*	$C_{20}H_{18}O_4$	74·2	5·65	19·65	—	74·5	5·6	19·25	—
I*g*	$C_{19}H_{16}O_4$	74·3	5·3	19·6	—	74·0	5·2	20·1	—

* Pet = Light petroleum (b. p. 60—80°).

TABLE 2. *Method* (i), *giving esters* (III; R = CO$_2$Me).

Lactone No.	(g.)	Time (hr.)	MeOH (ml.)	M. p.[a]	Yield (%)	Formula	Found (%) C	H	OMe	Required (%) C	H	OMe
I*a*	1	2	15	154—155°	76	$C_{20}H_{16}O_5$	71·2	5·0	18·0	71·4	4·8	18·45
I*b*	0·5	6	30	165—166 [b]	80	$C_{20}H_{17}O_4Cl$ *	67·4	4·8	25·0	67·3	4·8	26·0
I*c*	—	4	—	124 [1]	—	—	—	—	—	—	—	—
I*d*	1	30	30	151—152 [c]	80	$C_{20}H_{16}O_4$	75·3	5·1	—	75·0	5·0	—
I*e*	0·5	8	30	139—140	96	$C_{21}H_{20}O_5$	71·65	5·75	35·1	71·5	5·7	35·2
I*f*	0·5	6	30	146—147	96	$C_{21}H_{20}O_4$	75·5	6·2	26·8	75·0	5·95	27·3

* Cl: Found, 10·2. Reqd., 9·7%. [a] Cryst. from MeOH, except as stated. [b] From C$_6$H$_6$. [c] From light petroleum (b. p. 60—70°).

TABLE 3. *Cyclisation by method* (ii).

Lactone No.	g.	I	CHCl$_3$ (ml.)	Time (days)	Solvent	M. p.	Yield (%)
I*c*	1·7	1·7	20	5	MeOH	265°	41·2 [1]
I*e*	0·5	0·2	10	5	AcOH	231—232	90
I*f*	1	0·4	20	15	,,	244—245	90

in quinoline (4 ml.) containing copper-bronze (0·1 g.) was refluxed for 30 min. More copper-bronze (0·1 g.) was added and heating continued for a further hour. Working up as usual and repeated crystallisation from light petroleum (b. p. 40—60°) gave 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene (0·18 g.) in pale brown rosettes, m. p. 108—109°, undepressed on admixture with a specimen prepared by the decarboxylation of 1-*p*-methoxyphenyl-6 : 7-methylenedioxynaphthalene-2 : 3-dicarboxylic acid prepared by a two-step Stobbe condensation [3] (Found: C, 78·0; H, 5·2, OMe, 12·0. Calc. for $C_{18}H_{14}O_3$: C, 77·7; H, 5·0; OMe, 11·15%).

1-p-*Chlorophenyl*-6 : 7-*dimethoxynaphthalene* (III*b*; R = H).—The carboxylic acid (III*b*; R = CO$_2$H) (1 g.) and copper-bronze (2 × 0·4 g.) in quinoline (10 ml.) gave, after distillation, a fraction of b. p. 216—220°/4 mm. Crystallisation from light petroleum (b. p. $<$40°) gave 1-p-*chlorophenyl*-6 : 7-*dimethoxynaphthalene* (0·6 g.), m. p. 98—99° (Found: C, 72·3; H, 5·3; OMe, 20·1; Cl, 11·2. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·4; OMe, 20·8; Cl, 11·9%).

[5] Borsche, *Ber.*, 1914, **47**, 1108.
[6] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1936, **58**, 2314.
[7] Skraup and Schwamberger, *Annalen*, 1928, **462**, 148.
[8] *Org. Synth.*, 1933, **13**, 12.
[9] Barnett and Sanders, *J.*, 1933, 434.

TABLE 4. *Cyclisation of lactones* (I) *to acids* (III) *by method* (iii).

Lactone		Acids				
No.	g.	AcOH (ml.)	HCl (ml.)	Time (hr.)	M. p.[a]	Yield (%)
I*a*	0·2	5	5	2	255—256°	98
I*b*	0·2	5	5	0·3	255—256	95
I*c*	0·5	10	10	3	267—268[b]	80
I*d*	1	15	30	5	271—272	90
I*e*	0·5	10	10	2	231—232	100
I*f*	0·2	5	5	2	244—245	100

		Found (%)				Required (%)			
No.	Formula	C	H	OMe	Cl	C	H	OMe	Cl
I*a*	$C_{19}H_{14}O_5$	71·3	4·5	9·0	—	70·8	4·3	9·6	—
I*b*	$C_{19}H_{15}O_4Cl$	66·3	4·35	16·3	10·0	66·55	4·4	18·1	10·3
I*d*	$C_{19}H_{14}O_4$	74·1	4·6	—	—	74·5	4·6	—	—
I*e*	$C_{20}H_{18}O_5$	70·85	5·45	26·2	—	71·0	5·3	27·5	—
I*f*	$C_{20}H_{18}O_4$	74·6	5·95	19·4	—	74·5	5·6	19·25	—

[a] Cryst. from AcOH unless otherwise stated. [b] From aq. AcOH; Howell and Robertson [1] gave m. p. 265° (see Table 3).

6 : 7-*Dimethoxy*-1-*phenylnaphthalene* (III*c*; R = H).—1-*p*-Chlorophenyl-6 : 7-dimethoxynaphthalene (0·15 g.), tetralin (0·5 ml.), and 40% palladised charcoal (0·3 g.) were heated at 205—210° (nitrobenzene bath) for 3·5 hr.[4] The product was extracted with benzene and filtered from the catalyst. Recovery of the product and crystallisation from light petroleum (b. p. 40—60°) gave 6 : 7-dimethoxy-1-phenylnaphthalene in rosettes, m. p. 107—109°, undepressed on admixture with a specimen prepared by the decarboxylation of 6 : 7-dimethoxy-4-phenylnaphthalene-2-carboxylic acid [1] (III*c*; R = CO_2H) (Found: C, 81·3; H, 6·1; OMe, 23·7. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1; OMe, 23·5%).

6 : 7-*Methylenedioxy*-1-p-*tolylnaphthalene* (III*d*; R = H).—The acid (III*d*; R = CO_2H) (0·5) (Table 4) was similarly decarboxylated with copper-bronze (2 × 0·2 g.) in quinoline (4 ml.). The product (*ca.* 0·4 g.), on repeated crystallisation from light petroleum (b. p. 60—80°), gave 6 : 7-*methylenedioxy*-1-p-*tolylnaphthalene*, m. p. 121—122° (Found: C, 82·3; H, 5·4. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%).

Methyl 6 : 7-*Dimethoxy*-4-p-*methoxyphenylnaphthalene*-2-*carboxylate* (III*e*; R = CO_2Me).—*Method* (A). The acid (III*e*: R = CO_2H) (0·7 g.) was esterified by concentrated sulphuric acid (4 ml.) in boiling methanol (10 ml.) (4 hr.). The methyl ester (III*e*; R = CO_2Me) was obtained in colourless crystals (from methanol), m. p. and mixed m. p. with the product from method (i), 139—140°. *Method* (B). The acid (0·5 g.), dimethyl sulphate (0·75 g.), and potassium carbonate (2 g.) in acetone (20 ml.) were refluxed for 12 hr., then worked up as usual. The ester had m. p. and mixed m. p. 139—140°.

6 : 7-*Dimethoxy*-1-p-*methoxyphenylnaphthalene* (III*e*; R = H).—A stirred mixture of the acid (III*e*; R = CO_2H) (0·5 g.) and copper-bronze (0·4 g.) in quinoline (4 ml.) was heated on a sand-bath for 1 hr. and then worked up as usual. The brown semisolid product distilled at 170—175°/2 mm. (*ca.* 0·3 g.) and the solidified distillate crystallised from methanol, to give 6 : 7-*dimethoxy*-1-p-*methoxyphenylnaphthalene*, plates, m. p. 96—97° (Found: C, 77·3; H, 6·1; OMe, 31·4. $C_{19}H_{18}O_3$ requires C, 77·55; H, 6·1; OMe, 31·6%).

Methyl 6 : 7-*Dimethoxy*-4-p-*tolylnaphthalene*-2-*carboxylate* (III*f*; R = CO_2Me).—Prepared by either method, as above, from the acid, this ester had m. p. and mixed m. p. 146—147°.

6 : 7-*Dimethoxy*-1-p-*tolylnaphthalene* (III*f*; R = H).—Copper-bronze (0·2 g.) was added to a stirred solution of 6 : 7-dimethoxy-4-*p*-tolylnaphthalene-2-carboxylic acid (0·5 g.) in quinoline (4 ml.) and the whole was heated in an ethyl cinnamate bath (265—275°). A further amount of copper-bronze (0·2 g.) was then added, and heating and stirring were continued for further 2 hr. The product (0·2 g.) recrystallised from methanol, to give pale brown 6 : 7-*dimethoxy*-1-p-*tolylnaphthalene*, m. p. 98—99° (Found: C, 81·8; H, 6·5; OMe, 22·1. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5; OMe, 22·3%).

The authors thank Professor F. G. Baddar for facilities and for his interest.

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