323. *β-Aroyl-α-arylmethylenepropionic Acids. Part II.* The Synthesis and the Mechanism of Isomerisation of their Enol Lactones.*

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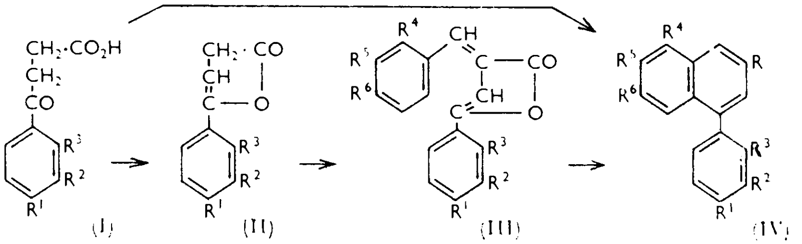
β-Aroylpropionic acids or their sodium salts are converted by warm acetic anhydride into the corresponding lactones (II) which condense with aromatic aldehydes to give the corresponding α-arylmethylene-lactones (III) (Perkin's conditions). Isomerisation of those of the latter lactones that have a *m*-alkoxyaryl group on the α-methylene-radical, to give the corresponding phenylnaphthalenes, supports the mechanism suggested previously.

Borsche[1] suggested that condensation of aromatic aldehydes with β-aroylpropionic acids (I) or their sodium salts at the α-position, to give β-aroyl-α-arylmethylenepropionic acid lactones (III), occurred by intermediate formation of the γ-aryl-crotonolactones (II) derived from enol forms, and Hag *et al.*[2] isolated one such lactone (IId). The aims of the present work were to isolate several such lactones, convert them under the conditions of the original condensation into lactones (III), and, thereby, to study the effect of substituents on the mode of their isomerisation to 4-phenyl-2-naphthoic acids (IV).



I, II)

	R^1	R^2	R^3
a	H	H	H
b	OMe	H	H
c	Me	H	H
d	OMe	OMe	H
e	Cl	H	H
f	H	H	OMe

(III, IV)

	R_1	R_2	R_3	R_4	R_5	R_6
a	OMe	H	H	H	H	H
b	OMe	H	H	OMe	H	H
c	OMe	H	H	H	OMe	H
d	OMe	H	H	H	H	OMe
e	OMe	H	H	H	OMe	OMe
f	OMe	H	H	H	$-O{\cdot}CH_2{\cdot}O-$	
g	Me	H	H	H	OMe	OMe
h	Me	H	H	H	$-O{\cdot}CH_2{\cdot}O-$	
i	Me	H	H	H	H	H
j	OMe	OMe	H	H	OMe	OMe
k	OMe	OMe	H	H	$-O{\cdot}CH_2{\cdot}O-$	
l	OMe	OMe	H	H	OMe	H
m	H	H	H	H	OMe	H
n	Cl	H	H	H	OMe	H
o	Me	H	H	H	OMe	H
p	H	H	OMe	H	OMe	H
q	Cl	H	H	H	$-O{\cdot}CH_2{\cdot}O-$	
r	H	H	H	H	$-O{\cdot}CH_2{\cdot}O-$	
s	H	H	H	H	NO_2	H

When the aroylpropionic acids (Ib, c, and d) or their sodium salts were gradually heated to 70—80° in acetic anhydride, the corresponding lactones (IIb, c, and d) were obtained in 90—95% yield[3,4] (see Table 1). Heating at 100° alone gave oils and resins at the expense of the yield and purity of the lactones, perhaps owing to preferential interaction of the produced enol-form of the acids and the acetic anhydride at high temperatures. Heating the acids (Ib, c, and d) at about 20° above their melting points also

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* Part I, *J.*, 1959, 1020.

[1] Borsche, *Ber.*, 1914, **47**, 1108.

[2] Hag, Kapur, and Ray, *J.*, 1933, 1087.

[3] Fittig and Ginsberg, *Annalen*, 1898, **299**, 11, 18.

[4] Kugel, *Annalen*, 1898, **299**, 54.

produced the lactones, but less well. The structure of these lactones was confirmed by their infrared stretching frequencies 1800 ± 2 cm.$^{-1}$ characteristic of βγ-unsaturated lactones[5] (see Table 1).

The lactones (IIb, c, and d) condensed readily when heated with aromatic aldehydes (Perkin's conditions), to give the corresponding lactones (III) in satisfactory yields (see Table 2). Heating above 100°[1,2] gave inferior purity and yield.

These results place beyond doubt the mechanism suggested by Borsche.[1] The reactivity of the α-methylene group under the effect of the neighbouring polarised carbonyl group has now been assessed by such condensations.

The lactones (IIIb, c, and k—s) were prepared by the present method in satisfactory yields, and isomerised to pure 4-phenyl-2-naphthoic acids (IV; R = CO_2H) in boiling glacial acetic and concentrated hydrochloric acid[6] (see Table 4), the results being better than those of others.[6] Since the crude acids were pure (m. p. only 1—2° low), we believe the possibility of attachment at $C_{(2)}$ to be greatly diminished by steric factors.

Decarboxylation of the naphthoic acids (IVb, c, and k—s; R = CO_2H) with copper-bronze in quinoline gave the corresponding 1-phenylnaphthalenes (IV; R = H) (see Table 6). 6-Methoxy-1-phenyl- (IVm; R = H) and -1-*p*-tolyl-naphthalene (IVc; R = H) gave oils that were identified as the crystalline nitro-derivatives. Dechlorination[6] of 1-*p*-chlorophenyl-6-methoxy- (IVn; R = H), and -6,7-methylenedioxy-naphthalene (IVq; R = H) by palladised charcoal in tetralin at 205—210° yielded 6-methoxy- and 6,7-methylenedioxy-1-phenylnaphthalene, whose nitro-derivatives were identical with those obtained from the decarboxylation products of acids (IVm and r; R = CO_2H). This showed that isomerisation of the lactones (IIIm, n, q, and r) occurred by attachment at the same position 6 of their α-arylmethylene radical, independently on the nature of the *para*-substituent in the β-aroyl radical. The structures of five of the 1-phenylnaphthalenes were established by identity with authentic specimens.[7]

The successful isomerisation of lactones (IIIk, q, and r) in which the 3,4-positions are occupied by electron-repelling groups supports our previous observation.[6] However, the reaction of lactones (IIIc, k, l, m, n, and o), which have only *one* electron-repelling group in the *meta*-position of their α-arylmethylene radical, proves that the only effective factor is this electron-repelling group independently of the nature and position of the substituents in the β-aroyl-radical (see Table 4). This was supported by the failure of the lactones (IIIb and s) to isomerise (see Part I[6] for further examples).

We believe that isomerisation of the lactones of type (III) by hydrogen chloride in glacial acetic acid is initiated by attack of the proton on the lactone-oxygen atom, the C–O bond gradually weakening until heterolysis sets in. As a result, the partial positive charge developed at the γ-carbon atom attacks the centre which is made electronegative by the electron-repelling substituent R^5 (as in electrophilic substitution) and so leads to formation of 4-phenyl-2-naphthoic acids (IV; R = CO_2H).

EXPERIMENTAL

Microanalyses were by Dr. A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mulheim (Ruhr), Germany.

Preparation of 4-*Aryl*-4-*hydroxybut*-3-*enoic Acid Lactones* (II).—*Method* (i). The β-aroylpropionic acid (I) (*ca.* 2 g.) was heated in acetic anhydride (4—5 ml.) to 70—80° during 2 hr., kept thereat for a further 3 hr., then left overnight at 20—25°. The precipitate was filtered off, washed with dry light petroleum (b. p. <40°), and crystallised from light petroleum (b. p. 60—70°), to give the *lactones* (II) in light or reddish-brown flakes which depress the m. p. of their parent acids.

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[5] Cf. Bellamy, " The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1956, p. 153.

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

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

Hag *et al.*[2] obtained the lactone (IId) in yellow silky needles (from hot water), m. p. 114—115° (contrast Table 1; colourless with faint blue tint), and we believe that their compound is a dilactone or an anhydride.[3,4]

Infrared measurements were carried in Nujol mull for the lactones (IIb and c) and in chloroform for the lactone (IId) by the use of Infracord model 137 (Perkin-Elmer).

Method (ii). β-Aroylpropionic acids (I) were heated about 20° above their m. p. (oil-bath) for 3—4 hr., cooled, and extracted with dry light petroleum (b. p. 60—80°). On concentration and repeated crystallisation from the same solvent, the products gave the lactones (II) but in much lower yield than for method (i).

TABLE 1. *Lactones* (II).

	M. p.	Yield (%)	$\nu_{max.}$ (cm.$^{-1}$)	Found (%) C	H	OMe	Formula	Required (%) C	H	OMe
IIb	103—104°	93	1798	69·7	5·25	16·6	$C_{11}H_{10}O_3$	69·5	5·3	16·3
IIc	92—93	95	1800	75·5	5·8	—	$C_{11}H_{10}O_2$	75·9	5·75	—
IId	94—95	92	1802	65·7	5·7	28·9	$C_{12}H_{12}O_4$	65·45	5·45	28·2

TABLE 2. *Lactones* (III).

Lactone (III)	From lactone (II)	Solvent *	Colour	M. p.	Yield (%)	Ref.
a	IIb	C_6H_6	Greenish-yellow	176—177°	90	*a*
b	IIb	AcOH	Reddish-brown	164—165	60	†
c	IIb	AcOH	Yellowish-green	157—158	75	†
d	IIb	AcOH	Greenish-yellow	177—178	85	6
e	IIb	AcOH	Orange-yellow	174—175	92	6
f	IIb	C_6H_6–Pet	Yellow	211—212	85	6
g	IIc	AcOH	Orange	144—145	90	6
h	IIc	$CHCl_3$	Orange	214—215	98	6
i	IIc	C_6H_6–Pet	Yellow	133—134	65	1
j	IId	Aq.AcOH	Green	148—150	92	*b*
k	IId	Ac_2O	Golden-yellow	228—229	93	†
	IId	AcOH	Greenish-brown	143—144	89	†

Lactone (III)	Found (%) C	H	OMe	Formula	Calcd. (%) C	H	OMe
a	77·6	5·1	11·6	$C_{18}H_{14}O_3$	77·7	5·0	11·15
b	74·3	5·3	19·7	$C_{19}H_{16}O_4$	74·0	5·2	20·1
c	73·6	5·0	19·9	$C_{19}H_{16}O_4$	74·0	5·2	20·1
d	74·3	5·25	19·6	$C_{19}H_{16}O_4$	74·0	5·2	20·1
e	71·3	5·5	27·0	$C_{20}H_{18}O_5$	71·0	5·3	27·5
f	71·2	4·5	9·1	$C_{19}H_{14}O_5$	70·8	4·35	9·6
g	74·2	5·65	19·65	$C_{20}H_{18}O_4$	74·5	5·6	19·25
h	74·7	4·7	—	$C_{19}H_{14}O_4$	74·5	4·6	—
i	82·6	5·2	—	$C_{18}H_{14}O_2$	82·4	5·3	—
j	68·8	5·5	33·1	$C_{21}H_{20}O_6$	68·5	5·4	33·7
k	68·4	4·6	17·2	$C_{20}H_{16}O_6$	68·2	4·55	17·6
l	71·4	5·15	28·0	$C_{20}H_{18}O_5$	71·0	5·3	27·5

* Pet. = Light petroleum (b. p. 60—70°). † These lactones were identical with those prepared by the modified direct method (ii) in this investigation (see Table 3).

a, Howell and Robertson, *J.*, 1936, 587. *b*, Haworth and Sheldrick, *J.*, 1935, 636.

The lactones (IIb, c, and d) are insoluble in cold sodium hydrogen carbonate and 5% sodium carbonate solution but dissolve in hot or boiling alkali solution to give the parent acids (identical m. p. and mixed m. p.s); the lactone ring breaks on storage with exposure to moisture or in boiling with water (several minutes) (contrast Hag *et al.*[2]).

Preparation of 4-*Aryl*-2-*arylmethylene*-4-*hydroxybut*-3-*enoic Acid Lactones* (III).—*Two-step method* (i). A mixture of the aromatic aldehyde (1·2 mol.), 4-aryl-4-hydroxybut-3-enoic acid lactone (1 mol.), and sodium acetate (1 mol.) in acetic anhydride (2 mol.) was heated to 70—80° during 2 hr., kept thereat for a further 5 hr., and left overnight at 20—25°. The precipitate was filtered off, washed with water, dried, and recrystallised. The products, lactones (III), were identical with those described in the literature and those prepared by the modified method of this investigation (identical m. p. and mixed m. p.) (see Table 2).

Isomerisation of the lactone (IIIj) by our method gave 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-naphthoic acid (IVj; R = CO_2H), which on decarboxylation with copper-bronze in quinoline gave 1-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene[8] (IVj; R = H).

Modified direct method (ii). A mixture of β-aroylpropionic acid (I) or its sodium salt (1 mol.), aromatic aldehyde (1·2 mol.), and sodium acetate (1 mol.) in acetic anhydride (6 mol.) was heated to 60—80° during 2 hr., kept thereat for a further 4 hr., left overnight at 25—30°, and worked up in the usual manner.[6] The product, on crystallisation from acetic acid, gave the β-aroyl-α-arylmethylenepropionic acid lactones (III) described in Table 3.

Isomerisation of Lactones (III) *to* 4-*Phenyl*-2-*naphthoic Acids* (IV; R = CO_2H).—The lactone (III) (1 g.) was refluxed in glacial acetic and concentrated hydrochloric acid (1 : 1 v/v) (50 ml.) for 2—6 hr. (see Table 4) (to disappearance of the lactone colour) and then left to cool. The precipitate was filtered off, washed with water, and digested in sodium carbonate solution, and the insoluble product (traces) was removed. Acidification of the clear alkaline filtrates (charcoal) precipitated acids which on crystallisation from acetic acid gave nearly colourless crystals of the 4-phenyl-2-naphthoic acids (IV; R = CO_2H), described in Table 4. The acids were best analysed after esterification and recovery by hydrolysis.

TABLE 3. *Lactones* (III) *prepared by method* (ii).

Lactone (III)	From acid (I)	and benzaldehyde	Colour	M. p.	Yield (%)
b	b	*o*-Methoxy-	Yellowish-brown	159—160°	50
c	b	*m*-Methoxy	Yellowish-green	159—160	75
k	a	3,4-Methylenedioxy-	Yellow	175—176	50
l	d	*m*-Methoxy-	Green	144—145	86
m	a	*m*-Methoxy-	Orange-yellow	117—118	76
n	e	*m*-Methoxy-	Yellow	171—172	60
o	c	*m*-Methoxy-	Bright-red	152—153	60
p	f	*m*-Methoxy-	Yellow	143—144	50
q	e	3,4-Methylenedioxy-	Yellow	255—256	65
r	d	3,4-Methylenedioxy-	Golden-yellow	228—229	95
s	a	*m*-Nitro-	Yellowish-brown	204—205	50

Lactone	Found (%)					Required (%)			
(III)	C	H	OMe	Cl or N	Formula	C	H	OMe	Cl or N
b	74·3	5·15	19·8	—	$C_{19}H_{16}O_4$	74·0	5·2	20·1	—
c	73·6	5·1	19·9	—	$C_{19}H_{16}O_4$	74·0	5·2	20·1	—
k	73·6	4·2	—	—	$C_{18}H_{12}O_4$	74	4·1	—	—
l	70·5	5·2	26·9	—	$C_{20}H_{18}O_5$	71·0	5·3	27·5	—
m	77·6	5·1	11·2	—	$C_{18}H_{14}O_3$	77·7	5·0	11·15	—
n	69·1	4·4	9·7	11·0	$C_{18}H_{13}ClO_3$	69·1	4·2	9·9	11·4
o	77·6	5·5	9·3	—	$C_{19}H_{16}O_3$	78·1	5·5	10·6	—
p	73·5	5·3	19·8	—	$C_{19}H_{16}O_4$	74·0	5·2	20·1	—
q	65·9	3·5	—	9·8	$C_{18}H_{11}ClO_4$	66·15	3·4	—	10·9
r	68·2	4·6	17·4	—	$C_{20}H_{16}O_6$	68·2	4·55	17·6	—
s	69·2	3·95	—	5·0	$C_{17}H_{11}NO_4$	69·6	3·75	—	4·8

TABLE 4. *Production of* 4-*phenyl*-2-*naphthoic acids* (IV) *from the lactones* (III)

Reaction (hr.)	Acid (IV; R = CO_2H)	M. p.	Yield (%)	Found (%) C	H	OMe	Formula	Required (%) C	H	OMe
3	c	224—225°	100	74·0	5·1	19·9	$C_{19}H_{16}O_4$	74·0	5·2	20·1
5	k	277—278	95	73·3	4·4	—	$C_{18}H_{12}O_4$	74	4·2	—
6	l	192—193	100	70·65	5·1	27·4	$C_{20}H_{18}O_3$	71·0	5·3	27·5
3·5	m	199—200	89	77·1	4·8	11·1	$C_{18}H_{14}O_3$	77·7	5·0	11·15
3	n	215—216	100	69·3	4·3	10·1	$C_{18}H_{13}ClO_3$ *	69·1	4·1	9·9
1·5	o	221—222	96	77·8	5·6	11·1	$C_{19}H_{16}O_3$	78·1	5·5	10·8
6	p	254—255	90	73·5	5·2	21·3	$C_{19}H_{16}O_4$	74·0	5·2	20·2
3	q	265—266	100	66·2	3·6	10·4	$C_{18}H_{11}ClO_4$ †	66·15	3·4	10·9
1·5	r	266—267	89	67·8	4·6	16·7	$C_{20}H_{16}O_6$	68·2	4·55	17·6

* Found: Cl, 10·4. Reqd.: Cl, 11·0%. † Found: Cl, 10·4. Reqd.: Cl, 10·9%.

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

Some of the sodium salts of these acids were insoluble in cold water; these were filtered off and reconverted into the acids which were dried in a vacuum at 90—100° before analysis.

The methyl esters (Table 5) were prepared by means of methanol–sulphuric acid, diazomethane, or methyl sulphate–potassium carbonate in acetone, and recrystallised from methanol or benzene–light petroleum (b. p. 60—70°).

1-*Phenylnaphthalenes* (IV; R = H).—A stirred mixture of an acid (IV; R = CO_2H) (*ca.* 0·5 g.) and copper-bronze (0·25 g.) in quinoline (10 ml.) was heated to the b. p. during 30 min. More copper-bronze (0·25 g.) was added in portions during 90 min. with continued stirring and heating. The mixture was cooled, poured into dilute hydrochloric acid, and repeatedly extracted with ether. Working up the extract in the usual way gave a residue which solidified on trituration with warm light petroleum (b. p. <40°) and crystallised to give the 1-phenylnaphthalene (IV; R = H) in light-brown crystals (see Table 6) which did not depress the m. p. of the authentic specimen.[7] Yields were 70—80%.

6-Methoxy-1-phenyl- (IVm; R = H), and -1-*p*-tolyl-naphthalene (IVo; R = H) were oils and were identified as their nitro-derivatives, which were prepared by means of nitric acid (*d* 1·42) in acetic acid at 25—30° (3·5 hr.). They had, respectively, m. p. 147—148° (from acetic acid) (Found: C, 73·2; H, 4·6; OMe, 10·8; N, 5·15. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·65; OMe, 11·1; N, 5·0%), and m. p. 143—145° [from light petroleum (b. p. 60—70°)] (Found: C, 73·5; H, 5·2; OMe, 10·65; N, 5·0. $C_{18}H_{15}O_3N$ requires C, 73·0; H, 5·1; OMe, 10·6; N, 4·75%).

TABLE 5. *Methyl 4-phenyl-2-naphthoates* (IV; R = CO_2Me).

		Found (%)					Required (%)			
Ester	M. p.	C	H	OMe	Cl	Formula	C	H	OMe	Cl
c	103—104°	74·5	5·55	28·3	—	$C_{20}H_{18}O_4$	74·5	5·6	28·9	—
k	170—171	74·3	4·6	10·5	—	$C_{19}H_{14}O_4$	74·5	4·6	10·1	—
l	138—139	71·4	5·75	34·8	—	$C_{21}H_{20}O_5$	71·3	5·7	35·2	—
m	77—78	78·2	5·6	21·05	—	$C_{19}H_{16}O_3$	78·1	5·5	21·2	—
n	130—131	69·7	4·8	18·4	10·5	$C_{19}H_{15}ClO_3$	69·8	4·6	18·7	10·9
o	93—94	78·1	5·8	19·8	—	$C_{20}H_{18}O_3$	78·4	5·9	20·3	—
p	155—156	74·1	5·4	29·3	—	$C_{20}H_{18}O_4$	74·5	5·6	28·9	—
q	166—167	66·55	3·9	9·7	9·15	$C_{19}H_{13}ClO_4$	66·95	3·8	9·1	10·4
r	175—176	68·6	5·0	25·1	—	$C_{21}H_{18}O_6$	68·85	4·9	25·3	—

TABLE 6. 1-*Phenylnaphthalenes* (IV; R = H).

			Found (%)					Required (%)			
Compound	Solvent	M. p.	C	H	OMe	Cl	Formula	C	H	OMe	Cl
c	Pet.[a]	85—86°	81·5	6·1	22·15	—	$C_{18}H_{16}O_2$	81·8	6·0	23·5	—
k	MeOH	134—135	73·85	5·3	19·9	—	$C_{19}H_{16}O_4$	74·0	5·2	20·1	—
n	Pet[b]	72—74	75·8	4·8	11·4	13·6	$C_{17}H_{13}ClO$	76	4·8	11·5	13·2
q	MeOH	113—114	71·8	4·15	—	12·5	$C_{17}H_{11}ClO_2$	72·2	3·9	—	12·6
r	MeOH	87—88	82·4	5·0	—	—	$C_{17}H_{12}O_2$	82·25	4·8	—	—

[a, b] Light petroleum of b. p. (*a*) 60—70°, (*b*) 50—60°.

Dechlorination of 1-p-*Chlorophenyl*-6-*methoxynaphthalene* (IVn; R = H).—1-*p*-Chlorophenyl-6-methoxynaphthalene (0·15 g.), dry tetralin (0·5 ml.), and 10% palladised charcoal (0·6 g.) were heated at 205—210° until the evolution of hydrogen chloride stopped (*ca.* 4 hr.). The cooled product was extracted with boiling benzene. Removal of the solvent in a vacuum left 6-methoxy-1-phenylnaphthalene (*ca.* 0·1 g.) that was identified as its nitro-derivative, m. p. and mixed m. p. 147—148° (Found: C, 73·4; H, 4·5; OMe, 11·0; N, 4·9%).

1-*p*-Chlorophenyl-6,7-methylenedioxynaphthalene (IVq; R = H) (0·07 g.), tetralin (0·3 ml.), and 10% palladised charcoal (0·03 g.) similarly gave 6,7-methylenedioxy-1-phenylnaphthalene (IVr; R = H), m. p. and mixed m. p. 87—88° (from methanol) (Found: C, 82·3; H, 4·9%).

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