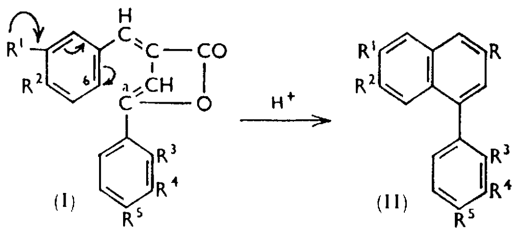
551. *β-Aroyl-α-arylmethylenepropionic Acids. Part III.*[1] *The Isomerisation of the Enol Lactones of β-Aroyl-α-*m*-methylbenzylidenepropionic Acids to the Corresponding 4-Aryl-2-naphthoic Acids, and the Ultraviolet Absorption Spectra of their Methyl Esters.*

By LANSON S. EL-ASSAL and (MRS.) AWATEF H. SHEHAB.

PREVIOUSLY,[1] we concluded that the only factor governing the successful isomerisation of the enol lactones (I) of β-aroyl-α-arylmethylenepropionic acids to the corresponding 4-aryl-2-naphthoic acids (II; R = CO_2H) was the presence of an electron-repelling group in the *m*-position of the α-arylmethylene radical. We have therefore studied the effect



(I) (II)

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*
R^1	Me	Me	Me	Me	Me	Me	OMe	OMe	OMe	OMe	OMe	OMe	–O·CH$_2$·O–	–O·CH$_2$·O–
R^2	H	H	H	H	H	H	H	H	H	OMe	OMe	OMe		
R^3	H	H	H	H	H	OMe	H	OMe	H	H	H	H	H	H
R^4	H	H	H	H	OMe	H	H	H	H	H	H	H	H	OMe
R^5	H	OMe	Me	Cl	OMe	H	H	H	OMe	H	OMe	Cl	OMe	OMe

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[1] Part II, El-Assal and Shehab, *J.*, 1961, 1658.

of a weaker electron-repelling group (*e.g.*, *m*-methyl) on the isomerisation, and confirmed the structure of the products, especially those which have been deduced by analogy.[1,2,3,4a] The enol lactones (I*b*—*e*) [1] were isomerised to 4-aryl-2-naphthoic acids (II*b*—*e*; R = CO_2H) by boiling glacial acetic and concentrated hydrochloric acid [1,2] but in poor yields (Table 2). Since the products appeared to be substantially pure, and as the yields were not improved by variations in experimental conditions we believe that the activity at position 2 is greatly diminished by steric factors.

4-Aryl-2-naphthoic acids (II*b*—*e*; R = CO_2H) on decarboxylation with copper-bronze in quinoline gave the corresponding 1-arylnaphthalenes (II*b*—*d*; R = H) (see Table 4).

The structure of the methyl esters (II; R = CO_2Me), previously deduced by analogy,[1,2] are supported by the similarity of their ultraviolet absorption spectra with those of the synthetic [3,4] esters (III*j*—*l*; R = CO_2Me).

EXPERIMENTAL

4-Aryl-4-hydroxy-2-benzylidenebut-3-enoic acid lactones (I). The β-aroylpropionic acid or its sodium salt (ca. 1—1·5%), *m*-tolualdehyde (1·2 mol.), and sodium acetate (1 mol.) in acetic anhydride (4—5 ml.) were heated to 60—80° during 2 hr., kept thereat for 5 hr., left overnight at 25—30°, and then worked up.[1,2] Crystallisation from glacial acetic acid gave the lactones (I) described in Table 1.

TABLE 1.

4-Aryl-4-hydroxy-2-benzylidenebut-3-enoic acid lactones (I*a*—*f*).

			Found (%)					Required (%)			
(I)	M. p.	Yield (%)	C	H	OMe	Cl	Formula	C	H	OMe	Cl
a	116—117°	60	81·7	5·2	—	—	$C_{18}H_{14}O_2$	82·4	5·3	—	—
b	125—126	98	78·4	5·5	10·4	—	$C_{19}H_{16}O_3$	78·1	5·5	10·6	—
c	147—148	95	82·5	5·7	—	—	$C_{19}H_{16}O_2$	82·6	5·8	—	—
d	202—204	60	72·7	4·4	—	12·8	$C_{18}H_{13}O_2Cl$	72·85	4·4	—	12
e	134—135	70	74·2	5·6	19·1	—	$C_{20}H_{18}O_4$	74·5	5·6	19·25	—
f	112—113	70	77·6	5·3	10·4	—	$C_{19}H_{16}O_3$	78·1	5·5	10·6	—

Isomerisation of lactones (I) *to 4-aryl-2-naphthoic acids* (III; R = CO_2H). The lactone (*ca.* 2 g.) was refluxed in glacial acetic acid and concentrated hydrochloric acid (1 : 1v/v) (30 ml.) for 2 hr., followed by the addition of 4 ml. of the acid mixture every 4 hr. during 30—32 hr., and then left to cool. The precipitate was washed with water and digested with sodium carbonate solution. The insoluble material (original lactone) was recovered and identified (m. p. and mixed m. p.). Acidification of the alkaline solution (charcoal) precipitated material which on crystallisation from glacial acetic acid gave the *4-aryl-7-methyl-2-naphthoic acids* (III; R = CO_2H) (Table 2).

TABLE 2.

Production of 4-aryl-7-methyl-2-naphthoic acids (III; R = CO_2H) from lactones (I).

			Found (%)					Required (%)			
(III; R = CO_2H)	M. p.	Yield (%)	C	H	OMe	Cl	Formula	C	H	OMe	Cl
b	221—222°	50	77·7	5·3	10·1	—	$C_{19}H_{16}O_3$	78·1	5·5	10·6	—
c	185—186	60	82·5	6·7	—	—	$C_{19}H_{16}O_2$	82·6	5·8	—	—
d	228—229	30	72·3	4·5	—	11·6	$C_{18}H_{13}O_2Cl$	72·85	4·4	—	12
e	190—192	50	74·3	5·8	19·1	—	$C_{20}H_{18}O_4$	74·5	5·6	19·3	—

These acids were dried in a vacuum at 60—80°/4 mm. before analysis. Details of the *methyl esters*, prepared by use of dimethyl sulphate and potassium carbonate in acetone in nearly quantitative yield, are given in Table 3.

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

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

[4] (*a*) Baddar, El-Assal, Doss, and Shehab, *J.*, 1959, 1016; (*b*) Baddar, El-Assal, and Doss, *J.*, 1955, 461; (*c*) Baddar, El-Assal, and Gindy, *J.*, 1948, 1270.

TABLE 3.

Methyl esters (III; R = CO_2Me).

(III; R = CO_2Me)	M. p.	Found (%) C	H	OMe	Cl	Formula	Required (%) C	H	OMe	Cl
b	97—98°	78·5	5·6	20·05	—	$C_{20}H_{18}O_3$	78·4	5·8	20·3	—
c	110—111	82·2	6·0	—	—	$C_{20}H_{18}O_2$	82·7	6·2	—	—
d	130—131	73·3	5·0	9·5	10·6	$C_{19}H_{15}O_2Cl$	73·9	4·9	10·0	11·5
e	79—80	74·7	6·0	26·2	—	$C_{21}H_{20}O_4$	75	5·95	27·7	—

1-*Phenylnaphthalenes* (III; R = H). Decarboxylation with copper–bronze in boiling quinoline, as described in Part III, and crystallisation from light petroleum or methanol, gave 1-*phenylnaphthalenes* (III; R = H) (see Table 4).

TABLE 4.

1-Phenylnaphthalenes (III; R = H).

(III; R = H)	M. p.	Yield (%)	Found (%) C	H	OMe	Cl	Formula	Required (%) C	H	OMe	Cl
b	72—73°	75	86·4	6·4	11·8	—	$C_{18}H_{16}O$	87·1	6·45	12·5	—
c	78—79	73	93·0	6·8	—	—	$C_{18}H_{16}$	93·1	6·9	—	—
d	75—76	76	81·2	5·2	—	13·65	$C_{17}H_{13}Cl$	80·8	5·1	—	14·1

TABLE 5.

Spectrographic data of methyl 4-aryl-2-naphthoates (III; R = CO_2Me).

(III; R = CO_2Me)	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$	Ref.
b	237	47,614	272	5983	
	~295	7536	323	2284	
c	243	53,475	266	3799	
	~290	7762	320	1725	
g	242	57,631	273	730	1
	~284	1077	314	692	
h	241	59,143	275	10,679	1
	~280	11,089	315	821	
i	241	45,500	278	7000	1
	~287	7000	320	1400	
j	257·5	50,123	278	6355	1
k	257·5	54,810	282	8374	1, 2, 3
l	257·5	61,709	280	6066	1
m	258·5	39,961	288	8155	1, 2
n	256·5	47,903	282	12,917	1, 2

Spectrographic data. Absorption spectra were measured in methanol by the use of a Perkin-Elmer model 4000 spectrophotometer. The results are summarised in Table 5.

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UNIVERSITY COLLEGE FOR GIRLS AT HELIOPOLIS,
A'IN-SHAMS UNIVERSITY, CAIRO, EGYPT, U.A.R.

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