The Stobbe Condensation with Dimethyl Homophthalate. II.

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The condensation of some heterocyclic aldehydes with dimethyl homophthalate in the presence of either sodium hydride or potassium t-butoxide as condensing agents gave either the (E)- or the (Z)-half-ester (1b) as the predominant product. The structure and configuration of the products has been established by both chemical and spectroscopic tools.

In a previous investigation (1a), the Stobbe condensation of dimethyl homophthalate with heterocyclic ketones has been reported. This work deals with the exploitation of the above condensation using heterocyclic aldehydes and aiming for the synthesis of new heterocyclic systems. The study was also intended to explore the factors influencing the formation of the stereoisomeric half-esters produced. Thus, thiophene-, 5-methylthiophene-, and furan-2-carboxaldehydes were condensed with dimethyl homophthalate in the presence of either sodium hydride (2) or potassium t-butoxide (3) as condensing agents. In every case one solid crystalline (E)-half-ester Ia-c was isolated in excellent yield (ca. 90%). However, 1-methylpyrrole-2-carboxaldehyde was similarly condensed to give the (Z)-half-ester Id in 90% yield. On the other hand, indole-3-carboxaldehyde failed to undergo this condensation using the sodium hydride method, whereas with potassium t-butoxide as condensing agent, the (Z)-half-ester Ie was obtained in about 90% yield.
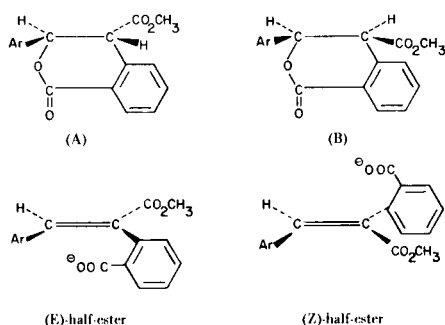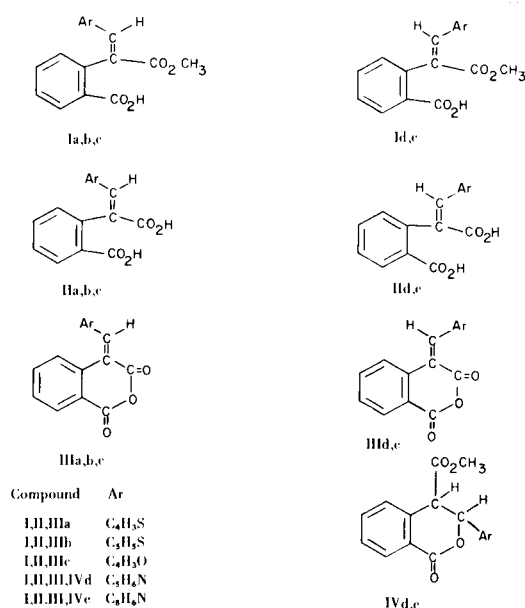

It is noteworthy to mention that the formation of one stereoisomer or the other is affected by the non-bonded interactions (which are both steric and/or polar in origin) involved in the formation of the diastereomeric condensate anions, which lead to the formation of the corresponding diastereomeric δ-lactones A and B (4,5). Repulsive forces between the π-sextet of the heterocyclic ring and the nega-

tive field of the carbonyl oxygen in the ester group favour the formation of the intermediate lactone A. This is also favoured by steric effect, where the bulky heterocyclic ring tends to be cis to the small hydrogen atom. The above view was corroborated by the observation that the (E)-half-esters Ia-c are the preponderant products in the condensation of thiophene-, 5-methylthiophene-, and furan-2-carboxaldehydes. In the condensation of 1-methylpyrrole-2-, and indole-3-carboxaldehydes, the formation of the intermediate lactone A should be also favoured. However, the preferential formation of the (Z)-half-esters Id,e may be interpreted by considering the stability of the final products. By constructing space-filling models for these half-esters, it was found that their (E)-configuration is highly strained. This is due to the steric interference between the ortho-carboxyphenyl and the bulky substituted heterocyclic groups. Accordingly, it seems that during the alkaline cleavage of the intermediate lactone A, isomerisation takes place leading to the most stable configuration, viz, the (Z)-configuration.

Chemical and spectroscopic evidence can be cited as strong support for the structure and configuration of the above half-esters. Thus the products Ia-e were saponified to the corresponding dibasic acids IIa-e. The infrared spectra of these acids (Table I) show one absorption band, which can be assigned both to α,β-unsaturated and aromatic acids (6a). The electronic spectra (Table I) of these acids resemble those of the corresponding half-esters. They show, however, a slight hypsochromic shift, as well as a hypochromic effect. The nmr spectrum of IIa indicates the presence of the olefinic and aromatic protons (cf. the Experimental). Chemical evidence for the structure of the above acids was obtained from their conversion to the corresponding esters or anhydrides. Thus methylation of the diacids IIa,c gave the corresponding diesters, which exhibit carbonyl stretching bands characteristic of α,β-unsaturated and aromatic esters (6a). Compelling evidence

for the structure of the ester derived from IIa was obtained from its nmr spectrum, which shows chemical shifts characteristic of carbmethoxy and aromatic protons. The above acids were easily converted to the corresponding anhydrides IIIa-c, by the action of acetyl chloride or acetic anhydride. Supporting evidence for their structure is forthcoming from the infrared spectra (Table I), which show two absorption bands characteristic of six-membered ring anhydrides condensed to aromatic systems (7). The electronic spectra of the anhydrides are in favour of their highly conjugated structure (Table I).

The above anhydrides had been also formed upon lactonisation of the (E)-half-esters Ia-c with sodium acetate, acetic acid, acetic anhydride mixture. Conversely however, the (Z)-half-esters Id,e gave upon such treatment the ex-
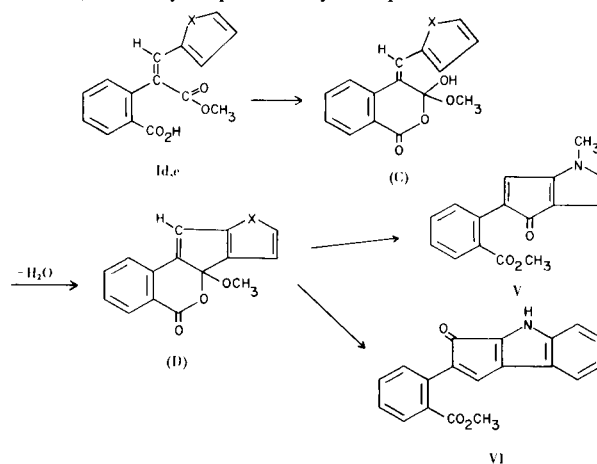
ical amount of fused zinc chloride (10), led to the formation of the cyclic ketonic esters V and VI. The structure of these esters was substantiated by their spectral data. The infrared spectra (Table I) show two absorption bands, which can be ascribed to α,β-unsaturated five-membered ring ketones (6d) and aryl esters (6c). The electronic spectra of these esters (Table I) support their structural analogy (8). The bathochromic shift as well as the hyperchromic effect (compared to similar carbocyclic ketonic esters) is attributed to the enhanced conjugation affected by the unshared electron pairs on the heteroatoms. The nmr spectra (cf. Experimental) show chemical shifts, which can be attributable to the carbmethoxy, olefinic and aromatic protons; each absorption area is proportional to the number of protons it represents.

The above cyclisation reaction can be protrayed by assuming that an intramolecular ester exchange took place, which has been enhanced by the suitably situated carboxyl and carbmethoxyl groups for ring formation (11). This can be succinctly explained by the possible formation of

Compound	Ar
I,II,IIIa	C_4H_3S
I,II,IIIb	C_5H_4S
I,II,IIIc	C_4H_3O
I,II,III,IVd	C_5H_6N
I,II,III,IVe	C_8H_6N

pected lactonic esters IVd,e. These show absorption bands in the infrared region (Table I), ascribed to α,β-unsaturated δ-lactones and saturated esters (6b,c). The electronic spectra of these lactones (Table I) are also in favour of the suggested structure (8). Adequate evidence for the structure of the lactonic ester IVd is obtained from its nmr spectrum, which shows two 3Hs characteristic of the carbmethoxy and N-methyl groups. Furthermore, each of the two aliphatic protons of the lactonic ring is indicated by a 1 Hd.

The formation of the above lactones can be attributable to the formation of a carbonium ion that results from the addition of a proton to the double bond of the half-ester. The so-formed carbonium ion has a built-in nucleophile (the carboxyl group), which attacks the positive centre to form the δ-lactone IV (9).

The cyclisation of the (Z)-half-esters Id,e using acetic acid, acetic anhydride mixture in the presence of a catalyt-
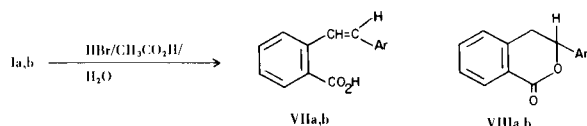
the hypothetical pseudo-ester C as an intermediate, which undergoes a cyclodehydration to the lactone D, which in turn rearranges to give V or VI (12,13).

A different behaviour has been observed with the (E)-half-esters Ia-c, which gave upon such treatment the corresponding anhydrides IIIa-c. Although no definite evidence has been obtained for the mechanism of this reaction, there is a possibility for intramolecular nucleophilic participation by the carboxylic group in the displacement reaction at the carbonyl carbon of the ester group (14).

The proclivity of the half-esters Ia-e for undergoing lactonisation under strong acidic conditions has been tested, by refluxing them with hydrobromic acid, acetic acid, water mixture. The half-esters Ic-e failed to give any definite product. Somewhat different behaviour has been observed with Ia,b, which gave the unsaturated acids VIIa,b, together with the neutral lactones VIIIa,b.

Table I

Compd.	ν C=O (cm⁻¹) (Potassium bromide)	λ max (Ethanol)	log E	Compd.	ν C=O (cm⁻¹) (Potassium bromide)	λ max (Ethanol)	log E
Ia	1707,1685	313	4.20	IVd	1720,1700	222	4.12
Ib	1720,1681	320	4.29			338	4.25
Ic	1720,1685	310	4.28	IVe	1735	250	4.21
Id	1720,1690	335	4.35			295	3.86
Ie	1700,1680	335	4.23	V	1724	265	4.29
	3300 (ν NH)					348	4.16
IIa	1698	300	4.14	VI	1720	282	4.17
IIb	1695	307	4.15			325	3.93
IIc	1685	300	4.25	VIIa	1690	230	4.18
IId	1685	330	4.21		1600 (C=C)		
IIe	1682	280	3.97	VIIb	1693	230	4.13
	(3380 ν NH)	327	4.09		1605 (C=C)		
IIIa	1745,1704	220	4.26	VIIIa	1760	230	4.29
		385	4.22			275	3.32
IIIb	1742,1708	220	4.14	VIIIb	1768	282	3.31
		400	4.12			---	---
IIIc	1760,1720	220	4.32		(chloroform)		
		380	4.22				
IIId	1760,1720	225	3.99				
		430	4.11				
IIIe	1743,1700	220	4.54				
		275	4.18				
		430	4.49				

Spectroscopic evidence has been adduced in favour of the structure of the above products. The acids VIIa,b show two absorption bands in their infrared spectra (Table I), which can be correlated to α,β-unsaturated acids (6a) and olefinic double bonds (6f). On the other hand, the lactones VIIIa,b showed only one band (Table I) which can be ascribed to α,β-unsaturated δ-lactones (6b). The electronic spectra of the above compounds (Table I) lend a further support for their structures. An ample evidence for the structure of the acid VIIb and the saturated lactone VIIIa is derivable from their nmr spectra. The acid VIIb shows chemical shifts characteristic of the aromatic methyl group and the olefinic protons. The spectrum of the lactone VIIIa shows a 2Hd and a 1Ht, which can be attributed to the methylene and methine protons respectively.

EXPERIMENTAL

Microanalyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, B. R. D. The nmr spectra have been run on a T-60A spectrometer in deuteriochloroform, with TMS as internal standard. The infrared (potassium bromide or chloroform) and the electronic spectra (ethanol) were measured on a Unicam SP-1000 and a Unicam SP-8000 spectrophotometers, respectively.

The Stobbe Condensation.

a) Sodium hydride method.

A mixture of the heterocyclic aldehyde (0.1 mole), dimethyl homophthalate (0.15 mole) and sodium hydride (0.15 mole of 50% dispersion in oil), in dry benzene (200 ml.) was stirred at room temperature till the reaction was ended, and then worked up (2).

b) Potassium t-Butoxide Method.

The heterocyclic aldehyde (0.1 mole) and the dimethyl homophthalate (0.12 mole) in t-butyl alcohol (15 ml.) were mixed and then gradually added during 15 minutes to a heated solution of potassium t-butoxide [from metallic potassium (5.8 g.) and t-butyl alcohol (85 ml.)]; and the mixture was refluxed for further 30 minutes, then worked up (3).

(E)-Methyl o-Carboxyphenyl-3-(2'-thienyl)prop-2-enoate (Ia).

The condensation with thiophene-2-carboxaldehyde gave Ia, crystallised from benzene in pale yellow crystals, (yield, 95%); nmr: δ 3.72 (s, 3, CO₂CH₃), 7.95 (s, 1, olefinic).

(E)-Methyl o-Carboxyphenyl-3-(5'-methyl-2'-thienyl)prop-2-enoate (Ib).

The condensation of 5-methylthiophene-2-carboxaldehyde produced Ib, crystallised from benzene in pale yellow crystals, (yield, 96%); nmr: δ 2.34 (s, 3, Ar-CH₃), 3.76 (s, 3, CO₂CH₃) and 7.95 (s, 1, olefinic).

(E)-Methyl o-Carboxyphenyl-3-(2'-furyl)prop-2-enoate (Ic).

The condensation of furan-2-carboxaldehyde gave Ic, crystallised from benzene in pale yellow crystals, (yield, 82%); nmr: δ 3.73 (s, 3, CO₂CH₃) and 8.72 (s, 1, olefinic).

Table II

Compd.	M.p. °C	Formula	Anal.	C, %	H, %	S, %	OCH₃ %
Ia	173-174	$C_{15}H_{12}O_4S$	Calcd.	62.49	4.20	11.12	10.77
			Found	62.63	4.30	10.97	10.47
Ib	191-192	$C_{16}H_{14}O_4S$	Calcd.	63.57	4.67	10.61	10.27
			Found	63.44	4.55	10.87	10.54
Ic	130°	$C_{15}H_{12}O_5$	Calcd.	66.18	4.45	----	11.40
			Found	66.17	4.23	----	11.02
IIa	215	$C_{14}H_{10}O_4S$	Calcd.	61.30	3.65	11.69	----
			Found	60.88	3.77	11.31	----
IIb	219 dec.	$C_{15}H_{12}O_4S$	Calcd.	62.49	4.20	11.12	----
			Found	61.90	4.27	10.67	----
IIc	210 dec.	$C_{14}H_{10}O_5$	Calcd.	65.13	3.91	----	----
			Found	65.07	3.88	----	----
IIIa	232	$C_{14}H_8O_3S$	Calcd.	65.61	3.15	12.51	----
			Found	65.76	2.86	12.67	----
IIIb	205	$C_{15}H_{10}O_3S$	Calcd.	66.66	3.73	11.87	----
			Found	66.49	3.74	11.80	----
IIIc	212	$C_{14}H_8O_4$	Calcd.	70.05	3.36	----	----
			Found	70.57	3.56	----	----
VIIa	145	$C_{13}H_{10}O_2S$	Calcd.	67.81	4.38	13.93	----
			Found	67.65	4.25	13.70	----
VIIb	207 dec.	$C_{14}H_{12}O_2S$	Calcd.	68.85	4.96	13.13	----
			Found	68.78	4.96	12.93	----
VIIIa	66	$C_{13}H_{10}O_2S$	Calcd.	67.81	4.38	13.93	----
			Found	67.99	4.32	13.97	----

Table III

Compd.	M.p., °C	Formula	Anal.	C, %	H, %	N, %	OCH₃ %
Id	158-160	$C_{16}H_{15}NO_4$	Calcd.	67.37	5.31	4.91	10.88
			Found	67.54	5.55	4.63	10.44
Ie	210 dec.	$C_{19}H_{15}NO_4$	Calcd.	71.02	4.71	4.35	9.66
			Found	71.28	4.42	4.53	9.55
IId	204	$C_{15}H_{13}NO_3$	Calcd.	66.41	4.84	5.17	----
			Found	66.36	4.92	5.21	----
IIe	205° dec.	$C_{18}H_{13}NO_4$	Calcd.	70.36	4.27	4.56	----
			Found	70.88	4.35	4.44	----
IIId	175	$C_{15}H_{11}O_3N$	Calcd.	71.14	4.38	5.54	----
			Found	71.06	4.45	5.43	----
IIIe	205 dec.	$C_{18}H_{11}O_3N$	Calcd.	74.71	3.84	4.85	----
			Found	75.15	3.97	5.36	----
IVd	128	$C_{16}H_{15}O_4N$	Calcd.	67.37	5.31	4.91	10.88
			Found	67.55	5.27	4.93	10.73
IVe	155 dec.	$C_{19}H_{15}O_4N$	Calcd.	71.02	4.71	----	9.66
			Found	71.01	4.74	----	9.86
V	165	$C_{16}H_{13}O_3N$	Calcd.	71.90	4.91	5.25	11.62
			Found	71.40	4.91	4.72	11.19
VI	206 dec.	$C_{19}H_{13}O_3N$	Calcd.	75.24	4.32	4.61	10.23
			Found	74.90	4.23	4.23	9.91

(Z)-Methyl o-Carboxyphenyl-3-(1'-methyl-2'-pyrrolyl)prop-2-enoate (Id).

The condensation of 1-methylpyrrolyl-2-carboxaldehyde yielded Id, crystallised from acetone-benzene in white crystals, (yield, 80%); nmr: δ 3.74 (s, 6, CO₂CH₃ and N-CH₃), 7.85 (s, 1, olefinic) and 10.15 (s, 1, COOH).

(Z)-Methyl o-Carboxphenyl-3-(3'-indolyl)prop-2-enoate (Ie).

The condensation of indolyl-3-carboxaldehyde gave Ie, crys-

tallised from benzene in yellow crystals (yield, 87%); nmr: δ 3.68 (s, 3, CO₂CH₃), 4.51 (broad singlet, 1, NH), 8.06 (s, 1, olefinic) and 10.16 (s, 1, COOH).

Hydrolysis of the Half-esters (Ia-c).

The half-ester was refluxed with 15% aqueous alcoholic potassium hydroxide solution (20 ml./1 g.) for a period of 2 hours, to give the corresponding dibasic acid.

(E)-o-Carboxyphenyl-3-(2'-thienyl)prop-2-enoic Acid (IIa).

The acid IIa, obtained from Ia, was crystallised from dilute acetic acid in white crystals (yield, 90%); nmr: δ 7.95 (s, 1, olefinic). Esterification of this acid with dimethyl sulphate gave the corresponding ester, crystallised from n-hexane in white crystals, m.p. 90°; ir (potassium bromide): 1720, 1708 cm⁻¹ ($C=O$ α,β-unsaturated and aromatic esters); nmr: δ 3.38 (s, 6, $2CO_2CH_3$).

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.54; H, 4.67; S, 10.61; OCH_3, 20.53. Found: C, 63.62; H, 4.70; S, 10.66; OCH_3, 20.27.

(E)-o-Carboxyphenyl-3-(5'-methyl-2'-thienyl)prop-2-enoic Acid (IIb).

The acid IIb was crystallised from dilute acetic acid in yellow needles (yield, 80%).

(E)-o-Carboxyphenyl-3-(2'-furyl)prop-2-enoic Acid (IIc).

This acid was crystallised from dilute acetic acid in yellow crystals (yield, 90%). Esterification of this acid with dimethyl sulphate gave the corresponding ester crystallised from n-hexane, m.p. 78°; ir (potassium bromide): 1723 cm⁻¹ ($C=O$ α,β-unsaturated and aromatic esters).

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.31; H, 4.93; OCH_3, 21.68. Found: C, 66.99; H, 4.83; OCH_3, 21.92.

(Z)-o-Carboxyphenyl-3-(1'-methyl-2'-pyrrolyl)prop-2-enoic Acid (IId).

The crude acid was crystallised from acetone-benzene mixture to give IId in yellow crystals (yield, 87%).

(Z)-o-Carboxyphenyl-3-(3'-indolyl)prop-2-enoic Acid (IIe).

The crude acid IIe was crystallised from acetone-benzene mixture in white crystals (yield, 90%).

Conversion of the Dibasic Acids to the Corresponding Anhydrides.

Acetyl chloride was added to the acid (20 ml./1 g.), and left overnight by room temperature. The mixture was then refluxed for 1 hour, the excess of acetyl chloride was distilled off, and the neutral product was isolated. The yield was almost quantitative.

(E)-o-Carboxyphenyl-3-(2'-thienyl)prop-2-enoic Anhydride (IIIa).

The anhydride was crystallised from light petroleum (40-60°) in orange needles.

(E)-o-Carboxyphenyl-3-(5'-methyl-2'-thienyl)prop-2-enoic Anhydride (IIIb).

The crude anhydride was crystallised from light petroleum (40-60°) in orange needles.

(E)-o-Carboxyphenyl-3-(2'-furyl)prop-2-enoic Anhydride (IIIc).

It was crystallised from benzene in orange needles.

(Z)-o-Carboxyphenyl-3-(1'-methyl-2'-pyrrolyl)prop-2-enoic Anhydride (IIId).

It was crystallised from light petroleum (40-60°) in orange needles.

(Z)-o-Carboxyphenyl-3-(3'-indolyl)prop-2-enoic Anhydride (IIIe).

This was crystallised from light petroleum (40-60°) in grey crystals.

Cyclisation of the Half-esters.

a) A mixture of acetic acid (10 ml.), acetic anhydride (10 ml.), freshly fused zinc chloride (0.1 g.) and the half-ester (1 g.), was refluxed for 3 hours. The mixture was then poured on crushed ice and left overnight in the ice-box, and the neutral product was then isolated.

The (E)-half-esters Ia-c gave upon such treatment, the corresponding anhydrides IIIa-c, whereas the (Z)-half-esters Id,e gave the following products:

5-o-Carbomethoxyphenyl-1-oxocyclopenteno[2,3-b]-N-methyl-pyrrole (V).

This was crystallised from cyclohexane in white needles, (yield, 86%); nmr: δ 3.94 (s, 3, CO_2CH_3), 4.12 (s, 3, N-CH₃).

5-o-Carbomethoxyphenyl-1-oxocyclopenteno[2,3-b]indole (VI).

This product was crystallised from benzene in yellow crystals (yield, 85%); nmr: δ 4.06 (s, 3, CO_2CH_3), 5.43 (broad singlet, 1, N-H).

b) A mixture of the half-ester (1 mole), freshly fused sodium acetate (2 moles) and excess of acetic acid and acetic anhydride (10 ml./each 1 g. half-ester), was refluxed for 10 hours. The mixture was then poured over crushed ice and left overnight in the ice-box, and the neutral product was isolated.

The (E)-half-esters Ia-c, when subjected to this treatment, gave the corresponding anhydrides IIIa-c. The (Z)-half-esters Id,e gave the following products:

(Z)-4-Methoxycarbonyl-3-(1'-methyl-2'-pyrrolyl)-3,4-dihydroisocumarine (IVd).

The crude neutral product was crystallised from benzene in white needles (yield, 70%); nmr: δ 3.68 (s, 3, CO_2CH_3), 3.71 (s, 3, N-CH₃), 5.14 (d, 1, -CH), 5.83 (d, 1, -CH).

(Z)-4-Methoxycarbonyl-3-(3'-indolyl)-3,4-dihydroisocumarine (IVe).

This was crystallized from benzene as white crystals (yield, 62%).

c) A mixture of hydrobromic acid, acetic acid and water (6:4:2 by volume), was added to the half-ester (12 ml./ 1 g.), and warmed for 12 hours, cooled and water added. The organic material was extracted with 10% sodium carbonate solution. The acid product obtained from the carbonate solution, and the neutral product obtained from the ethereal layer were isolated and purified.

1-o-Carboxyphenyl-2-(2'-thienyl)ethylene (VIIIa) and 3,4-Dihydro-3-(2'-thienyl)isocumarine (VIIIa).

The crude acid product was crystallised from benzene-light petroleum (40-60°) to give VIIa in yellow crystals (yield, 62%). The neutral oily product, crystallised from light petroleum (60-80°) to give VIIIa in colourless crystals; nmr: δ 3.40 (d, 2, -CH₂), 5.63 (t, 1, -CH).

1-o-Carboxyphenyl-2-(5'-methyl-2'-thienyl)ethylene (VIIIb) and 3,4-Dihydro-3-(5'-methyl-2'-thienyl)isocumarine (VIIIb).

The acidic product, crystallised from benzene-light petroleum (60-80°) to give VIIb in orange crystals (yield, 90%); nmr: δ 2.43 (s, 3, Ar-CH₃), 6.45 (s, 2, olefinic protons). The neutral oily product VIIIb failed to crystallise from the available solvents.

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