

SYNTHESIS AND PROPERTIES OF 5-STYRYL-2-FURANCARBOXYLIC ACIDS*

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5-(4-X-Styryl)-2-furancarboxylic acids (X = H, Br, NO₂, COOCH₃, (CH₃)₂N) were prepared by oxidation of the appropriate 5-(4-X-styryl)-2-furaldehydes, or alternatively by alkaline hydrolysis of the corresponding methyl esters. The latter were obtained by reacting the 4-substituted benzaldehydes with 5-methoxycarbonylfuryltriphenylphosphonium chloride. The UV and IR spectra of products are commented. The apparent pK values of the synthesized acids were employed for calculation of the transmission coefficient π' through the benzene-furan system bridged by a —CH=CH— group.

As already found^{1,2} series of substituted phenoxy- and benzoyl-2-furancarboxylic acids having the reaction constant $\rho = 0.472 \pm 0.02$, and $0.52 \pm$ respectively, reveal a transmission of polar effects through a bridged system —O— and —CO—. An analogous series of 5-phenylthio-2-furancarboxylic acids exhibited³ transmission through atom of sulfur and the value of reaction constant ρ (0.400 ± 0.025) is a little lower than that of phenoxy derivatives. Substantially higher values of dissociation constants were measured with 5-phenylsulfonyl-2-furancarboxylic acids³; this indicates a stronger acidifying effect of arylsulfonyl group, but transmission of polar effects through the —SO₂— group is the lowest in the series of bridged derivatives of furan ($\rho = 0.260 \pm 0.015$).

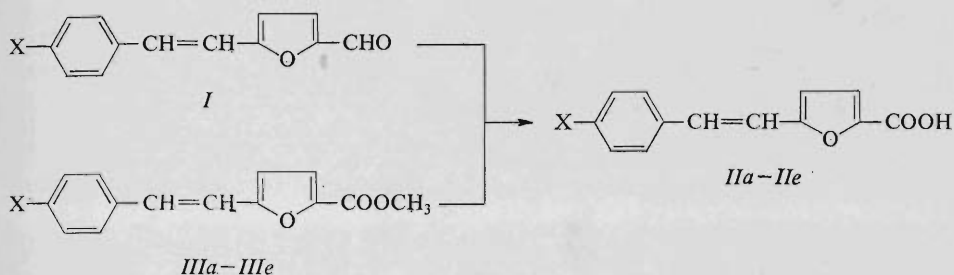
The measure of influencing the acidity of carboxylic acids by the substituent at the benzene ring through a CH=CH bridge was examined in the series of 5-(4-X-styryl)-2-furan-carboxylic acids *II*, which were prepared either by oxidation of the corresponding 5-(3-X-styryl)-2-furaldehydes *I*, or by alkaline hydrolysis of methyl esters 5-(4-X-styryl)-2-furancarboxylic acids *III*.

Methyl esters *III* were synthesized by Wittig reaction from 4-substituted benzaldehydes and 5-methoxycarbonylfuryltriphenylphosphonium chloride (*V*) in the presence of sodium methanolate as catalyst. The phosphonium salt was obtained

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by chloromethylation of methyl ester 2-furancarboxylic acid⁴ followed by reaction with triphenylphosphine.

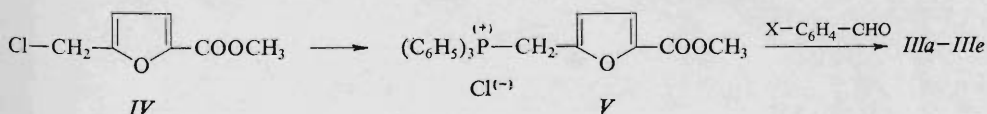
Chromatographic behaviour and analysis of ¹H-NMR spectra showed that both *II* and *III* exist exclusively as (*E*)-isomers (Scheme 1). Similarly as with 5-(4-X-styryl)-2-fural-dehydes⁵, protons H_A and H_B at the double bond were seen in the spectrum as two doublets ($J = 15.3$ Hz) the coupling constant being in agreement with the structure of an (*E*)-isomer.



SCHEME 1

Electronic spectra of *II* (Table I) displayed three maxima. The principal absorption band of a high intensity ($\log \epsilon > 4$) lay in the 345–380 nm region and resulted from the oscillation of π -electrons throughout the whole conjugated system. The UV spectra of methyl esters *III* (Table I) also exhibited three maxima the last of which was between 350 and 390 nm. The strong conjugation transmission of the benzene and furan rings through the vinylidene group was recognized from comparing the UV spectrum of methyl ester 5-benzyl-2-furancarboxylic acid, where two absorption bands appeared at 208 and 260 nm (Table II). Assignment of the long-wave band was also backed by comparison with the spectrum of methyl 2-furancarboxylate, having the absorption maximum at 250 nm.

The effect of substituent X to COOH group through a vinylidene grouping of substances *IIa-IIe* was investigated by measurement of p*K* values of acids (Table I). Dissociation constant values are a linear function of Hammett σ constants of substituents with a reaction constant $\rho = 0.527 \pm 0.064$ ($\rho = 4.53 \pm 0.02$; $r = 0.978$; $s = 0.064$). Constant ρ was employed for calculation of the transmission coefficient $\pi = \rho/\rho_0$, where for ρ_0 the reaction constant $\rho_0 = 1.522$ (ref.⁶), obtained from



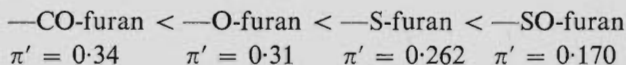
SCHEME 2

TABLE I
5-(4-X-Styryl)-2-furancarboxylic acids and their methyl esters

Compound	X R	Formula (mol.w.)	M.p., °C yield, %	Calculated/Found, %			λ_{\max} , nm log ϵ	$\tilde{\nu}(\text{C}=\text{O}), \text{cm}^{-1}$ pK		
				C	H	N				
<i>IIa</i>	Br	$\text{C}_{13}\text{H}_9\text{BrO}_3$	186–190	53.26	3.07	—	218	328 r	345	1 682
	H	(292.9)	60	53.05	2.95	—	4.05	4.05	4.42	4.43
<i>IIb</i>	NO_2	$\text{C}_{13}\text{H}_9\text{NO}_5$	140–144	60.21	3.47	5.40	224	260	369	1 694
	H	(259.1)	52	60.10	3.35	5.25	4.00	3.98	4.05	4.18
<i>IIc</i>	H	$\text{C}_{13}\text{H}_{10}\text{O}_3$	164–166	72.86	4.67	—	230	334	350 r	1 680
	H	(214.1)	50.5	72.55	4.60	—	3.98	4.09	4.10	4.54
<i>IIId</i>	COOCH_3	$\text{C}_{15}\text{H}_{12}\text{O}_5$	264–266	66.12	4.41	—	225	338 r	350	1 685
	H	(272.2)	58.5	65.95	4.31	—	4.10	4.20	4.45	4.28
<i>IIe</i>	$(\text{CH}_3)_2\text{N}$	$\text{C}_{15}\text{H}_{15}\text{NO}_3$	195–197	70.03	5.83	5.45	220	300	380	1 665
	H	(257.0)	60.0	69.85	5.70	5.35	4.05	4.0	4.48	4.83
<i>IIIa</i>	Br	$\text{C}_{14}\text{H}_{11}\text{BrO}_3$	147–149	54.75	4.61	—	218	2180	360	1 721
	CH_3	(307.1)	65.0	54.65	3.55	—	4.25	4.00	4.48	—
<i>IIIb</i>	NO_2	$\text{C}_{14}\text{H}_{11}\text{NO}_5$	173–175	61.54	4.05	5.12	221	—	368	1 727
	CH_3	(273.2)	96.6	61.70	4.10	5.28	4.25	—	4.51	—
<i>IIIc</i>	$(\text{CH}_3)_2\text{N}$	$\text{C}_{16}\text{H}_{17}\text{NO}_3$	166–167	70.82	6.31	5.16	218	290	390	1 720
	CH_3	(271.3)	68.6	70.68	6.20	5.04	4.20	4.04	4.56	—
<i>IIId</i>	CN	$\text{C}_{15}\text{H}_{11}\text{NO}_3$	135–137	71.14	4.37	5.53	236	248	346	1 728
	CH_3	(253.2)	78.5	71.30	4.45	5.48	4.05	4.04	4.46	—
<i>IIIe</i>	I	$\text{C}_{14}\text{H}_{11}\text{IO}_3$	138–140	47.48	3.13	—	218	280	352	1 718
	CH_3	(354.1)	71.4	47.40	3.10	—	4.18	3.98	4.50	—

measurement of dissociation constants of 4-substituted benzoic acids, was substituted. The value $\pi' = 0.346$. This value is very close to that of π' (0.32) for transmission through CH=CH group of 5-(4-X-styryl)-2-furaldehydes⁵ (Scheme 2).

According to our previous results¹ the sequence of the bridged derivatives of 2-furancarboxylic acids is as follows:



The value of transmission coefficient $\pi' = 0.346$ for styryl derivatives indicated that in this series the best transmission of polar effects appeared to be through the vinylene grouping.

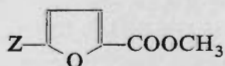
The empiric equation⁷ enabled the calculation of approximate transmission factors for some bridged systems (*e.g.* 0.45 for CH=CH). Basing upon this equation the transmission for furan ring was enumerated⁸ to be 0.47. These values and those of transmission coefficients calculated for individual bridged systems⁷ served us for calculation of the transmission coefficient for the series of styryl derivatives of furan: $\pi'(\text{Fu-CH=CH}) = 0.210$. The experimentally determined value (0.346) was a little higher than that calculated according to the equation. Like differences have also been published^{9,10}.

EXPERIMENTAL

Electron absorption spectra of methanolic solutions were measured with a Specord UV VIS (Zeiss, Jena) spectrophotometer in the 200–800 nm region at a $1-5 \cdot 10^{-5} \text{ M}$ concentration. Infrared spectra of chloroform solution were recorded with a UR-20 (Zeiss, Jena) apparatus in the $700-3800 \text{ cm}^{-1}$ region. 5-(4-X-Styryl)-2-furaldehydes (*I*) were prepared according to⁵, the corresponding acids *Ila*–*Ile* were obtained by oxidation with Ag_2O according to¹. Purity

TABLE II

Absorption maxima (λ , nm) of compounds



Z	$\lambda_{\text{max I}}$	$\lambda_{\text{max II}}$	$\lambda_{\text{max III}}$
—	205	250	—
$\text{C}_6\text{H}_5\text{---CH}_2\text{---}$	208	260	—
$4\text{-Br-C}_6\text{H}_4\text{---CH=CH---}$	218	280	350

of the synthesized compounds was monitored by thin-layer chromatography on silica gel with chloroform as solvent.

Methyl 5-(4-X-Styryl)-2-furancarboxylates *IIIa—IIIe*

A solution of 4-substituted benzaldehyde (11 mmol) in methanol (20 ml) was added to the phosphonium salt of *V* (11 mmol) dissolved in methanol (20 ml). The mixture was cooled to room temperature and, while stirred, sodium methanolate (10 mmol) was added. After a 1 h standing the mixture was poured into water (1 l) with stirring and allowed to stand overnight. The separated precipitate was filtered off, washed with water, and water extracted three times with ether. The combined extracts were dried with Na_2SO_4 and ether evaporated. The crude ester was recrystallized from ethanol and purified on a silica gel column.

5-(4-X-Styryl)-2-furancarboxylic Acids *IIa—IIe*

Methyl ester of the appropriate acid *III* (10 mmol) was heated with 10% NaOH (30 ml) on a steam bath until all material dissolved. The hydrolysis proceeded faster after addition of methanol (20 ml) and lasted about 4 h. The solvent was then removed, the solution acidified with dilute HCl (1 : 1) and the precipitated product was filtered off. The respective acids were purified *via* their sodium salts.

Determination of Dissociation Constants

The pK values were determined by a potentiometric titration of $5 \cdot 10^{-3}\text{M}$ solutions of acids *IIa—IIe* in 50% (v/v) ethanol with a 0.1M-NaOH at 25°C. The value was measured with a PHM 64 pH-meter with a glass electrode employing an automatic burette ABU 1C (Radiometer, Copenhagen). The linear correlation parameters were calculated from $\text{pK} = f(\sigma)$ values.

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