

TRANSMISSION OF ELECTRONIC EFFECTS IN  
 3-[5-(4-X-PHENYLTHIO)-2-FURYL]- AND  
 3-[5-(4-X-PHENYLSULPHONYL)-2-FURYL]ACRYLIC ACIDS\*

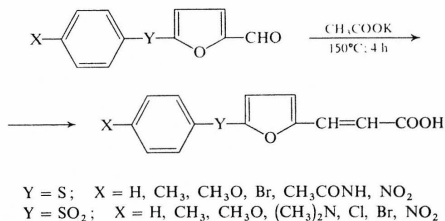
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Received March 1st, 1977

Thirteen 5-arylthio- and 5-arylsulphonylfurylacrylic acids were prepared by Perkin synthesis from the corresponding aldehydes and acetic anhydride. The transmission of polar substituent effects through the S atom or the SO<sub>2</sub> group in these systems was studied by determination of pK values of the title acids by potentiometric titration.

Within the framework of our investigations on sulphur-containing furan derivatives we studied the synthesis and properties of 5-arylthio-2-furaldehydes<sup>1</sup> and 5-arylsulphonyl-2-furaldehydes<sup>2</sup> as well as of the corresponding 2-furancarboxylic acids<sup>3</sup> arising from them by oxidation. In this paper we describe the preparation of 5-arylthio- and 5-arylsulphonylfurylacrylic acids by Perkin synthesis from the corresponding aldehydes and acetic anhydride (Scheme 1).



SCHEME 1

Physical constants and analytical data of the synthesized furylacrylic acids are listed in Table I. In spite of relatively low yields, we have chosen Perkin synthesis for the preparation of these compounds because of its stereospecificity. It leads exclusi-

\* Part CXII in the series Furan Derivatives; Part CXI: This Journal 43, 463 (1978).

vely to the *E* isomers as evidenced by the presence of an infrared absorption band at about  $970\text{ cm}^{-1}$  and by the coupling constant of the ethylenic protons  $J_{AB} = 15\text{ Hz}$  in the  $^1\text{H-NMR}$  spectrum. We synthesized these acids also by the reaction of the corresponding aldehydes with malonic acid in pyridine which afforded the desired acids in 35–40% yields; however, the products melted over a substantially wider

TABLE I  
Properties of the Synthesized 3-[5-(4-X-Phenyl-Y)-2-furyl]acrylic Acids

No	X Y	Formula (mol. w.)	M.p., °C yield, % <sup>a</sup>	Calculated/Found			$\delta(\text{C-H})$ $\tilde{\nu}(\text{C=O})$ $\text{cm}^{-1}$	
				% C	% H	% S		
I	H	$\text{C}_{13}\text{H}_{10}\text{O}_3\text{S}$ (246.1)	142–146	63.40	4.06	13.00	965	1 695
	S		14.6	63.25	4.05	12.98		
II	$\text{CH}_3$	$\text{C}_{14}\text{H}_{12}\text{O}_3\text{S}$ (260.2)	156–160	64.65	4.62	12.30	967	1 694
	S		24.3	64.70	4.80	12.35		
III	$\text{CH}_3\text{O}$	$\text{C}_{14}\text{H}_{12}\text{O}_4\text{S}$ (276.1)	134–138	60.80	4.34	11.59	970	1 693
	S		27.5	60.44	4.72	11.42		
IV	Br	$\text{C}_{13}\text{H}_9\text{BrO}_3\text{S}$ (325.1)	141–144	48.00	2.77	9.84	970	1 694
	S		24.3	47.60	2.52	9.72		
V	$\text{CH}_3\text{CONH}$	$\text{C}_{15}\text{H}_{13}\text{NO}_4\text{S}$ (303.2)	216–220	59.50	4.33	10.56	967	1 693
	S		31.7	59.49	4.38	10.49		
VI	$\text{NO}_2$	$\text{C}_{13}\text{H}_9\text{NO}_5\text{S}$ (291.1)	163–166	53.60	3.10	10.99	965	1 692
	S		25	53.25	3.04	10.98		
VII	H	$\text{C}_{13}\text{H}_{10}\text{O}_5\text{S}$ (278.1)	148–151	56.20	3.63	11.50	974	1 714
	$\text{SO}_2$		31.4	55.82	3.45	11.68		
VIII	$\text{CH}_3$	$\text{C}_{14}\text{H}_{12}\text{O}_5\text{S}$ (292.2)	181–185	57.55	4.11	10.96	973	1 713
	$\text{SO}_2$		29.0	57.45	4.23	10.94		
IX	$\text{CH}_3\text{O}$	$\text{C}_{14}\text{H}_{12}\text{O}_6\text{S}$ (308.2)	149–153	54.50	3.90	10.38	965	1 696
	$\text{SO}_2$		31.6	54.53	3.85	10.35		
X	$(\text{CH}_3)_2\text{N}$	$\text{C}_{15}\text{H}_{15}\text{NO}_5\text{S}$ (321.2)	204–208	55.90	4.66	9.97	966	1 695
	$\text{SO}_2$		25.2	55.37	4.68	9.91		
XI	Cl	$\text{C}_{13}\text{H}_9\text{ClO}_5\text{S}$ (312.6)	178–181	49.90	2.88	10.22	970	1 696
	$\text{SO}_2$		25.2	49.92	2.78	10.27		
XII	Br	$\text{C}_{13}\text{H}_9\text{BrO}_5\text{S}$ (357.1)	214–217	43.75	2.60	8.95	969	1 697
	$\text{SO}_2$		29.4	43.56	2.42	9.09		
XIII	$\text{NO}_2$	$\text{C}_{13}\text{H}_9\text{NO}_7\text{S}$ (323.1)	216–220	48.30	2.79	9.97	971	1 692
	$\text{SO}_2$		31.2	47.87	2.81	9.91		

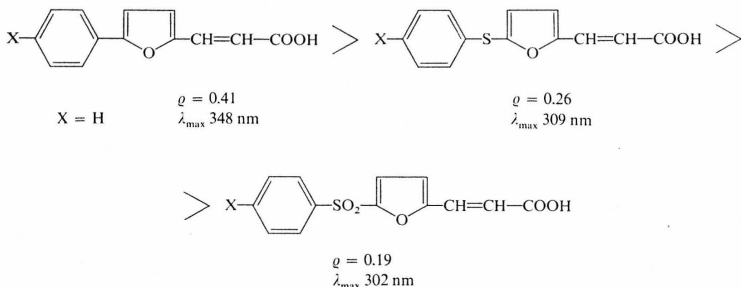
<sup>a</sup> Crystallized from aqueous ethanol.

range (8–12°C); this behaviour indicates contamination with the Z-isomer. Both methods failed in the attempted synthesis of 3-[5-(4-nitrophenylsulphonyl)-2-furyl]-acrylic acid even when the reaction conditions were varied. This acid was prepared by oxidation of 3-[5-(4-nitrophenylthio)-2-furyl]acrylic acid by hydrogen peroxide in glacial acetic acid.

The UV spectral parameters of the synthesized furylacrylic acids are given in Table II. Spectra of the compounds exhibit three absorption maxima, for the thio derivatives (I–VI) in the regions 206–207 nm, 234–267 nm and 296–315 nm, for the sulphonyl derivatives (VII–XIII) in the regions 205–207 nm, 227–282 nm and 291–330 nm. Previously we described<sup>4</sup> the preparation and UV spectra of a series of 3-[5-(4-X-phenyl)-2-furyl]acrylic acids, *i.e.* compounds in which the 4-X-phenyl substituent is attached immediately to the position 5 of the furylacrylic acid. Comparison of the positions of the highest wavelength absorption maxima in the spectra of these compounds (340–360 nm) with those of the acids prepared in our recent study shows that the presence of a sulphide bridge causes a significant hypsochromic shift of this band.

TABLE II  
UV Spectral Data ( $\lambda_{\max}$ , nm) and pK Values of the Synthesized Compounds

No	X	Y	$\lambda_{\max}$	log $\epsilon$	$\lambda_{\max}$	log $\epsilon$	$\lambda_{\max}$	log $\epsilon$	pK
I	H	S	206	4.24	243	4.06	309	4.13	6.45
II	CH <sub>3</sub>	S	206	4.31	245	4.04	313	4.13	6.48
III	CH <sub>3</sub> O	S	206	4.35	234	4.13	314	4.23	6.52
IV	Br	S	206	4.27	240	4.03	296	4.19	6.44
V	CH <sub>3</sub> CONH	S	207	4.45	267	4.35	305	4.29	6.43
VI	NO <sub>2</sub>	S	206	4.25	—	—	315	4.36	6.23
VII	H	SO <sub>2</sub>	206	4.13	227	4.05	302	4.38	5.95
VIII	CH <sub>3</sub>	SO <sub>2</sub>	207	4.16	237	4.13	302	4.36	5.90
IX	CH <sub>3</sub> O	SO <sub>2</sub>	206	4.24	252	4.25	304	4.38	6.01
X	(CH <sub>3</sub> ) <sub>2</sub> N	SO <sub>2</sub>	206	4.26	282	4.46	330	4.26	6.18
XI	Cl	SO <sub>2</sub>	206	4.25	238	4.24	304	4.41	5.89
XII	Br	SO <sub>2</sub>	206	4.24	243	4.26	305	4.39	5.98
XIII	NO <sub>2</sub>	SO <sub>2</sub>	205	4.23	281	4.21	291	4.26	5.85



The  $pK$  values for the thio derivatives (Table II) are within the range 6.23–6.52, the extreme values corresponding to compounds with the  $\text{NO}_2$  and  $\text{CH}_3\text{O}$  group, respectively. The interval  $\Delta pK = 0.29$  shows that the strength of these acids is affected by the substituent  $X$  in the *para* position of the benzene ring, across the thio bridge and the furylvinyl grouping. This is confirmed also by linear dependence of the  $pK$  values on the Hammett  $\sigma_p$  constants,  $r = 0.97$  and  $\rho = 0.26$  (Fig. 1). The  $pK$  values obtained for the sulphonyl acids (VII–XIII, Table II) are lower which indicates that an arylsulphonyl group in the position 5 enhances the acidity more than does the arylsulphide group. Also in this case the substituents  $X$  affect the acid strength as seen from the  $pK$  values of compounds VII–XIII and from the linear plot of  $pK$  against  $\sigma_p$  ( $r = 0.90$  and  $\rho = 0.19$ ) (Fig. 1). For the series of 3-[5-(4- $X$ -phenyl)-2-furyl]acrylic acids the relationship  $pK$  vs  $\sigma_p$  was found previously<sup>4</sup> to have

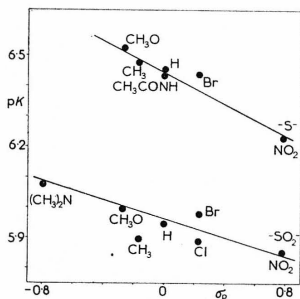


FIG. 1  
Plot of  $pK$  against  $\sigma_p$  for 3-[5-(4- $X$ -Phenylthio)-2-furyl]- and 3-[5-(4- $X$ -Phenylsulphonyl)-2-furyl]acrylic Acids

$\rho = 0.41$ ; for the series of 5-arylthio- and 5-arylsulphonylpyromucic acids  $\rho$  was found to be 0.40 and 0.26, respectively<sup>3</sup>. Thus, the transmission of electronic effects of substituents X decreases in the order 5-aryl, 5-arylthio, 5-arylsulphonyl derivatives (Scheme 2).

## EXPERIMENTAL

### 3-[5-(4-X-Phenylthio)-2-furyl]- and 3-[5-(4-X-Phenylsulphonyl)-2-furyl]acrylic Acids

A mixture of 5-(4-X-phenylthio)-2-furaldehyde or 5-(4-X-phenylsulphonyl)-2-furaldehyde (0.1 mol) (ref.<sup>1,2</sup>), anhydrous potassium acetate (0.1 mol) and acetic anhydride (150 ml) was refluxed under exclusion of moisture for 4 h, poured into water (400 ml) under stirring and set aside for 12 h. The aqueous layer was neutralized with saturated sodium carbonate solution which caused partial separation of sodium salt of the desired acid. The organic layer was briefly boiled with a 10% sodium carbonate solution. The hot solution was filtered, the filtrate cooled and the precipitated salt collected. Both parts of the sodium salt were combined, dissolved in water, the acid was liberated by acidification with 10% hydrochloric acid and purified by crystallization.

3-[5-(4-Nitrophenylsulphonyl)-2-furyl]acrylic acid was obtained by oxidation of the corresponding sulphide<sup>5</sup>.

### Measurements

The IR spectra were taken in  $1 \cdot 10^{-2}$  M chloroform solutions on a double-beam UR 20 (Zeiss) spectrophotometer in 1 mm NaCl cells. The instrument was calibrated with a polystyrene foil. Electronic absorption spectra were taken on a Specord UV VIS (Zeiss, Jena) recording spectrophotometer in the region 200–500 nm. Measurements were done on  $4 \cdot 10^{-5}$  M ethanolic solutions, cell thickness 1 cm. The apparent pK values of the synthesized acids were determined by potentiometric titration in 80% methyl cellosolve<sup>4</sup>.

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Translated by M. Tichý.