NEW SUBSTITUTED DIFURYLCHALCONES

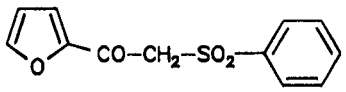
Katarína ŠPIRKOVÁ and Štefan STANKOVSKÝ

Department of Organic Chemistry, Slovak Technical University, 812 37 Bratislava

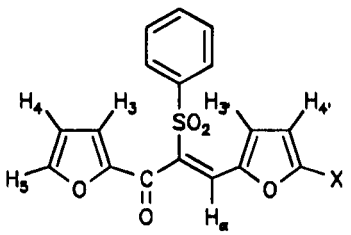
Received January 31, 1992
Accepted March 10, 1992

Preparation of 1-(5-substituted-2-furyl)-2-phenylsulfonyl-2-furoyl ethylenes (*IIa – IId*) using the Lehnert modification of Knoevenagel condensation, as well as substitution nucleophilic reactions of the 1-(5-bromo-2-furyl)-2-phenylsulfonyl-2-furoyl derivative (*IIa*) with the corresponding phenolate, thiophenolate and secondary amines are described[1,2].

IR, UV and ^{1}H NMR spectra of final products are presented.



I



II

II	X	*II*	X
a	Br	*g*	3-NO_2-PhO
b	NO_2	*h*	4-NO_2-PhO
c	PhS	*i*	4-Cl-PhS
d	$PhSO_2$	*j*	4-CH_3CONH-PhS
e	PhO	*k*	piperidinyl
f	2-NO_2-PhO	*l*	morpholinyl

EXPERIMENTAL

IR spectra were measured in KBr pellets. UV absorption spectra were measured in methanolic solutions, concentration of $1 \cdot 10^{-4}$ l^{-1}. ^1H NMR spectra of deuteriochloroform solutions containing tetramethylsilane as an internal standard were recorded with a JEOL FX 100 (100 MHz) spectrometer.

TABLE I
Characteristic data for prepared compounds *IIa – IIl*

Compound X	Formula (M. w.)	M. p., °C Yield, %	Calculated / Found		
			% C	% H	% S
IIa	$C_{17}H_{11}O_5BrS$	161 – 162	50.14	2.72	7.87
	(407.2)	60	49.98	2.63	7.67
IIb	$C_{17}H_{11}NO_7S$	164 – 166	54.69	2.96	8.58
	(373.3)	49	54.57	2.83	8.29
IIc	$C_{23}H_{16}O_5S_2$	165 – 167	63.29	3.69	14.68
	(436.5)	39	63.11	3.62	14.42
IId	$C_{23}H_{16}O_7S_2$	171 – 172	58.96	3.44	13.68
	(468.5)	51	58.83	3.40	13.50
IIe	$C_{23}H_{16}O_6S$	110 – 112	65.70	3.83	7.62
	(420.5)	48	65.61	3.79	7.47
IIf	$C_{23}H_{15}NO_8S$	163 – 165	59.35	3.25	6.88
	(465.5)	48	59.20	3.20	6.59
IIg	$C_{23}H_{15}NO_8S$	165 – 167	59.35	3.25	6.88
	(465.5)	46	59.23	3.21	6.62
IIh	$C_{23}H_{15}NO_8S$	144 – 146	59.35	3.25	6.88
	(465.5)	51	59.19	3.17	6.61
IIi	$C_{23}H_{15}ClO_5S_2$	109 – 111	58.65	3.21	13.61
	(471.0)	56	58.43	3.16	13.47
IIj	$C_{25}H_{19}NO_6S_2$	175 – 177	60.83	3.88	12.99
	(493.6)	55	60.59	3.77	12.83
IIk	$C_{22}H_{21}NO_5S$	154 – 156	64.21	5.14	7.79
	(411.5)	22	64.03	5.02	7.56
IIl	$C_{21}H_{19}NO_6S$	139 – 141	61.00	4.63	7.75
	(413.5)	18	60.83	4.57	7.60

2-(2-Furyl)-2-oxoethylphenylsulfone *I*

The stirred suspension of sodium benzenesulfinate (14.4 g, 100 mmol) in abs. methanol (100 ml) was treated with a solution of 2-bromoacetylfuran (18.9 g, 100 mmol) in 50 ml methanol and refluxed for 3 h. Then it was boiled with charcoal, the hot mixture was filtered and concentrated to 1/3 of the original volume. The solid separated on cooling was collected by suction and dried. Yield 18.2 g, 73%; m.p. 74 – 76 °C. For $C_{12}H_{10}O_4S$ (250.3) calculated: 57.59% C, 4.03% H, 12.81% S; found: 57.38% C, 3.97% H, 12.69% S.

TABLE II
IR and UV spectra of compounds *IIa – III*

Compound	IR Spectrum, cm^{-1}			UV Spectrum		
	ν(CO)	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	λ_{max}, nm / log ε		
IIa	1 653	1 327	1 160	223	287	320
				3.11	3.29	3.14
IIb	1 643	1 340	1 154	217	289	–
				3.18	3.27	–
IIc	1 644	1 320	1 153	236	288	333
				3.10	3.26	3.11
IId	1 654	1 341[a]	1 174[a]	217	255	289
		1 329[b]	1 155[b]	3.32	3.26	3.29
IIe	1 654	1 327	1 155	217	285	299
				3.28	3.20	3.41
IIf	1 652	1 328	1 154	218	288	301
				3.26	3.27	3.42
IIg	1 650	1 326	1 154	216	255	289
				3.30	3.13	3.15
IIh	1 648	1 323	1 155	222	287	322
				3.23	3.37	3.17
IIi	1 648	1 322	1 155	232	287	320
				2.98	3.09	2.99
IIj	1 658[c]	1 320	1 145	–	263	319
	1 670[d]			–	3.42	3.26
IIk	1 650	1 327	1 154	217	283	–
				3.15	2.81	–
III	1 653	1 326	1 155	216	273	–
				3.13	2.80	–

[a] SO_2 on ethylenic bond; [b] SO_2 on furan; [c] CO on furan; [d] CO (CH_3CONH).

IR (ν, cm^{-1}): 1 650 (C=O), 1 323 (as SO_2), 1 155 (s SO_2). UV (λ, nm, (log ε)): 216 (3.36), 285 (3.23), 296 (3.27). ^1H NMR (δ, ppm): 7.29 dd, 1 H (H-3); 6.53 dd, 1 H (H-4); 7.89 dd, 1 H (H-5); 7.43 – 7.68 m, 5 H (phenyl); 4.60 s, 2 H (CH_2).

1-(5-X-2-Furyl)-2-phenylsulfonyl-2-furoyl ethylenes

A) Trisubstituted ethylenes prepared by the condensation (IIa – IId): A solution of 18.9 g (0.1 mol) $TiCl_4$ in 25 ml CCl_4 was added dropwise to 200 ml of abs. THF and the mixture was treated successively with 0.04 mol 5-X-2-furaldehyde in 20 ml THF and 0.04 mol of compound *I*. Within further 2 h, 15.8 g of pyridine (16.1 ml, 0.2 mol) in 30 ml THF was added dropwise under stirring and cooling at 0 – (–5) °C. The stirring was continued at 0 °C for further 24 h, then the mixture was decomposed with 50 ml water. The aqueous layer was extracted with ether, dried, concentrated, and left to crystallize. The raw product was recrystallized from ethanol. Prepared compounds are characterized in Tables I – III.

B) Trisubstituted ethylenes (IIe – III) prepared by nucleophilic substitution of *IIa*: A solution of 12.2 g (0.03 mol) *IIa* in 20 ml acetonitrile was treated with 0.09 mol of the corresponding sodium phenolate, sodium thiophenolate and secondary amine, respectively. The mixture was stirred at room temperature and the end of the reaction was detected by TLC (10 – 48 h).

The solvent was removed under reduced pressure, the products were isolated by column chromatography (silica gel, benzene–ethyl acetate 2 : 1) and crystallized from ethanol. Prepared compounds are characterized in Tables I – III.

TABLE III
^1H NMR data of compounds *IIa – III* (δ, ppm)

Compound	H-α, s	H-3', d	H-4', d	H-3, dd	H-4, dd	H-5, d	H-phenyl, m
IIa	7.80	7.15	6.68	7.15	6.58	7.95	7.54 – 7.79
IIb	8.35	7.56	8.01	7.43	6.75	8.14	7.62 – 7.96
IIc	7.72	6.47	6.70	*d*	6.33	7.96	7.62 – 7.72
IId	7.91	7.35	7.50	7.27	6.62	8.03	7.50 – 7.75
IIe	7.85	7.20	7.35	7.21	6.58	7.93	7.50 – 7.75
IIf	7.90	7.25	7.41	7.19	6.56	7.96	7.50 – 7.90
IIg	7.82	7.15	7.30	7.18	6.57	7.91	7.50 – 7.77
IIh	7.81	7.05	7.17	7.05	6.60	7.92	7.52 – 7.80
IIi	7.90	6.68	7.15	*d*	6.62	7.95	7.42 – 7.81
IIj[a]	7.77	7.02	6.78	*d*	7.02	7.95	7.20 – 7.68
IIk[b]	7.82	7.01	5.38	7.27	6.70	8.02	7.55 – 7.77
III[c]	7.72	6.95	5.42	7.10	6.57	7.83	7.50 – 7.70

[a] 2.06 s (CH_3); [b] 1.42 – 1.72 m, 3.50 – 3.71 m (piperidine); [c] 3.00 t, 3.52 t (morpholine); [d] in aromatic multiplet, unresolved $J(3',4')$ = 3.5 – 3.8 Hz, $J(3,4)$ = 3.5 – 3.8 Hz, $J(4,5)$ = 1.0 – 1.8 Hz, $J(3,5)$ = 0.3 – 0.7 Hz, $J(3',\alpha)$ = 0.6 Hz.

REFERENCES

1. Lehnert W.: Tetrahedron *28*, 663 (1972).
2. Lehnert W.: Tetrahedron *30*, 301 (1974).

Translation revised by H. P. Mašková.