Furan derivatives. LXXXIX. Synthesis and properties of α, β-unsaturated sulfones of the arylfuran series

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Received 20 August 1975

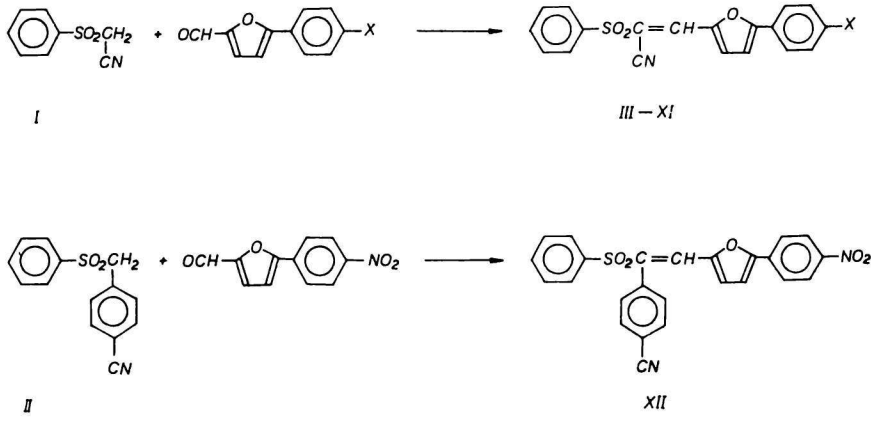
Paper published on the occasion of the 35th anniversary of the foundation of the Department of Organic Chemistry, Slovak Technical University, Bratislava

1-Phenylsulfonyl-1-cyano-2-[5-(4-X-phenyl)-2-furyl]ethylenes (X = H, CH_3, OCH_3, $NHCOCH_3$, Cl, Br, I, $COOC_2H_5$, NO_2) were prepared by condensation of phenylsulfonylacetonitrile with the corresponding 5-(4-X-phenyl)-2-furaldehydes. 1-Phenylsulfonyl-1-(4-cyanophenyl)-2-[5-(4-nitrophenyl)-2-furyl]ethylene was synthesized from 4-cyanobenzyl phenyl sulfone and 5-(4-nitrophenyl)-2-furaldehyde. The infrared and electronic spectra of the new compounds are discussed.

При помощи конденсации фенилсульфонилацетонитрила с 5-(4-X-фенил)-2-фуральдегидами были синтезированы соответствующие 1-фенилсульфонил-1-циано-2-[5-(4-X-фенил)-2-фурил]этилены, где X = H, CH_3, OCH_3, $NHCOCH_3$, Cl, Br, I, $COOC_2H_5$, NO_2. Реакцией 4-цианобензилфенилсульфона с 5-(4-нитрофенил)-2-фуральдегидом был приготовлен также 1-фенилсульфонил-1-(4-цианофенил)-2-[5-(4-нитрофенил)-2-фурил]этилен. Обсуждаются инфракрасные и электронные спектры впервые синтезированных веществ.

Our previous paper [1] dealt with the synthesis of saturated 5-nitrofuran sulfones. The condensation of these sulfones having an active methylene group with variously substituted benzaldehydes [2], furaldehydes [3], and arylfuraldehydes [4] presents a new one-step synthesis of trisubstituted derivatives of ethylene. We suggested a reaction mechanism [4] and investigated the kinetics of respective reactions [5].

In this paper we wish to report on the synthesis of 1-phenylsulfonyl-1-cyano-2-[5-(4-X-phenyl)-2-furyl]ethylenes *III—XI* starting from phenylsulfonylacetonitrile (*I*) and 4-substituted 5-aryl-2-furaldehydes in ethanol in the presence of piperidine as a catalyst. We also synthesized sulfone *XII* bearing a CN group in position 4 of the benzene ring for a comparison of the u.v. spectra (Scheme 1).



Scheme 1

Experimental

Infrared absorption spectra were measured with a UR-20 spectrophotometer (Zeiss, Jena) in spectral grade chloroform passed twice through a column packed with blue silica gel in order to remove ethanol. The apparatus was calibrated against a polystyrene foil. The concentration of substances was 0.02 M, the thickness of the NaCl cell 1.02 mm. Electronic spectra were taken with a Specord UV VIS spectrophotometer (Zeiss, Jena) in 10 mm cells in ethanol. The concentration was 3 to 5×10^{-5} M. Reading accuracy was ± 1 nm.

The starting saturated sulfone *I* was synthesized from chloroacetonitrile and sodium benzenesulfinate; m.p. 112—113°C. (Ref. [6] 114°C.) Sulfone *II* was prepared from 4-cyanobenzyl bromide and sodium benzenesulfinate in a 54% yield; m.p. 210—211°C. (Ref. [7] 204.5°C.)

1-Phenylsulfonyl-1-cyano-2-[5-(4-X-phenyl)-2-furyl]ethylenes (III—XI) and 1-phenylsulfonyl-1-(4-cyanophenyl)-2-[5-(4-nitrophenyl)-2-furyl]ethylene (XII)

A solution of phenylsulfonylacetonitrile (5.1 g; 0.3 mole), 5-(4-X-phenyl)-2-furaldehyde (0.3 mole), and piperidine (0.5—1.0 ml) in ethanol (100 ml) was stirred for 2 hrs. The separated products *III—XI* were filtered off and crystallized from ethanol. The product *XII* was synthesized and isolated similarly as sulfones *III—XI* except that the reaction mixture was heated under a reflux condenser for 2 hrs.

Results and discussion

Products *III—XI* listed in Table 1 were obtained by condensation of arylfuraldehydes with sulfone *I*, the active methylene group of which is localized between the electron withdrawing groups —CN and —SO_2—; their —I effect results in

Table 1

Characteristic data of α,β-unsaturated sulfones derived from arylfuran

Compound	X	Formula	*M*	Calculated/found				Yield %	M.p., °C
				% C	% H	% N	% S		
III	H	$C_{19}H_{13}NO_3S$	335.4	67.94	3.91	4.18	9.55	68.7	168—169
				67.73	3.87	4.29	9.37		
IV	CH_3	$C_{20}H_{15}NO_3S$	349.4	68.86	4.33	4.01	9.17	71.5	175—176
				68.67	4.39	4.19	8.89		
V	OCH_3	$C_{20}H_{15}NO_4S$	365.4	65.74	4.11	3.83	8.77	69.5	170—171
				65.49	4.15	3.92	8.71		
VI	NHAc	$C_{21}H_{16}N_2O_4S$	392.4	61.92	4.21	7.14	8.14	55.2	259—260
				61.91	4.36	7.22	7.78		
VII	Cl	$C_{19}H_{12}ClNO_3S$	369.8	61.81	3.27	3.78	8.67	85.7	211—212
				61.72	3.33	3.80	8.67		
VIII	Br	$C_{19}H_{12}BrNO_3S$	414.3	55.12	2.92	3.38	7.74	82	213—214
				55.29	2.81	3.50	7.47		
IX	I	$C_{19}H_{12}INO_3S$	461.3	49.43	2.61	3.04	6.96	71	201—202
				49.50	2.69	3.19	7.05		
X	$COOC_2H_5$	$C_{23}H_{17}NO_5S$	407.5	65.18	3.93	3.43	7.87	82	221—223
				65.01	4.00	3.60	7.78		
XI	NO_2	$C_{19}H_{12}N_2O_5S$	380.4	60.12	3.18	7.36	8.42	68	214—215
				60.43	3.32	7.11	8.30		
XII		$C_{25}H_{16}N_2O_5S$	456.5	65.71	3.53	6.13	7.02	32	175—176
				66.09	3.65	5.92	7.43		

acidification of hydrogens of the —CH_2— group. The condensation in this case was carried out in ethanol under the catalytic influence of piperidine. The reactive carbanion generated from sulfone *I* had a markedly localized negative charge between the —SO_2— and —CN groups and is, therefore, more favourable from the sterical point of view than the bulkier carbanion formed during the synthesis of the unsaturated sulfone *XII*; here the delocalization of the negative charge to the directly bound aromatic system occured. This fact was reflected by a lower reactivity and, consequently, by a lower yield (32%) of the unsaturated sulfone, even if the reaction was carried out in dry boiling ethanol with a catalytic amount of piperidine.

The successful condensation of this sulfone confirms that not only 5-nitrofurfuryl sulfones [1—4] and their benzene analogs [2, 8], but also sulfones bearing an electron withdrawing cyano group can be the starting material for synthesis of trisubstituted ethylenes possessing a sulfonyl group.

The infrared spectra of substances *III—XI* showed a medium intense $\tilde{\nu}$(CN) band at 2220 cm^{-1}, which is not influenced by substituents bound to the arylfuran moiety of the molecule. Absorption bands associated with the $\tilde{\nu}$(C=C) are in the 1608—1618 cm^{-1} region, those of $\tilde{\nu}_s(SO_2)$ and $\tilde{\nu}_{as}(SO_2)$ in the 1160—1165 and 1338—1320 cm^{-1} regions, respectively. The absorption band of the $\tilde{\nu}_{as}(SO_2)$ is shifted by electron withdrawing substituents towards higher wavenumbers. In addition to the band at ~1040 cm^{-1} two other bands are seen at 978—975 and 868—840 cm^{-1}

Ultraviolet absorption data of the synthesized compounds are listed in Table 2; the region above 300 nm is important for their structural features. As seen,

Table 2

Ultraviolet spectral data of α,β-unsaturated sulfones derived from arylfuran

Compound	λ_{max}, nm (log ε)			
III	205 (4.11)	226 sh (4.09)	275 (4.08)	403 (4.43)
IV	207 (4.25)	243 i (4.25)	259 (4.33)	415 (4.55)
V	206 (4.29)	244 (4.19)	274 (4.31)	429 (4.55)
VI	206 (4.39)	249 (4.19)	284 (4.39)	429 (4.57)
VII	207 (4.18)	241 i (4.20)	257 (4.30)	403 (4.53)
VIII	206 (4.29)	245 i (4.23)	266 (4.36)	405 (4.55)
IX	205 (4.32)	246 (4.19)	276 i (4.15)	408 (4.48)
X	206 (4.10)		265 (4.25)	400 (4.48)
XI	206 (4.27)	223 (4.08)	279 sh (3.87)	403 (4.52)
XII	205 (4.57)	236 (4.56)	289 sh (3.63)	345 (4.38)
		223 sh (4.48)		

i — inflection; sh — shoulder.

substances *III—XI* have the last intense absorption band in the 400—429 nm range, whereas that of *XII* is at 345 nm. This absorption band (the K band) corresponds to electronic transitions of the whole conjugated system of the

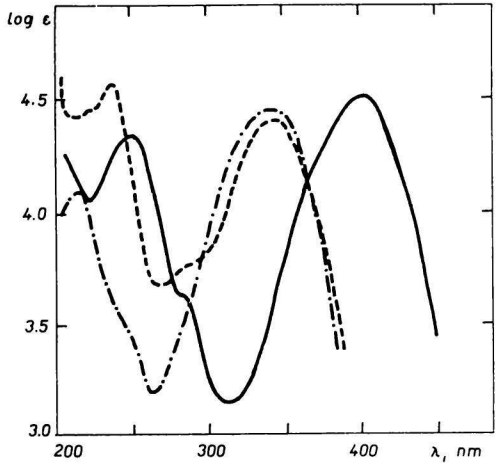


Fig. 1. Ultraviolet spectra of sulfones.
——— 1-Phenylsulfonyl-1-cyano-2-[5-(4-nitrophenyl)-2-furyl]ethylene; – – – – 1-phenylsulfonyl-1-(4-cyanophenyl)-2-[5-(4-nitrophenyl-2-furyl)]ethylene; –·–·– 5-(4-nitrophenyl)-2-furaldehyde.

molecule and therefore it is associated with the stereochemical arrangement. Fig. 1 shows absorption curves of the representative of sulfones *III—XI*, sulfone *XII* and the reference aldehyde. The last absorption band of the reference aldehyde, corresponding to the electronic transitions of the whole conjugated system, lay in the same range as that of sulfone *XII*. Hence it follows that the conjugation of substance *XII* is discontinued, due to the bulky $—SO_2C_6H_5$ group attached to carbon atom and therefore, the molecule is not planar. The 5-(4-nitrophenyl)-2-furyl or the 4-cyanophenyl group have to be oriented under an angle close to 90° towards the ethylene bond.

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Translated by Z. Votický