Furan derivatives. LXXXVII. The synthesis and ultraviolet spectra of 5-(4-X-phenylsulfonyl)-2-furaldehydes and 2-cyano-3-[5-(4-X-phenylsulfonyl)-2-furyl]acrylonitriles

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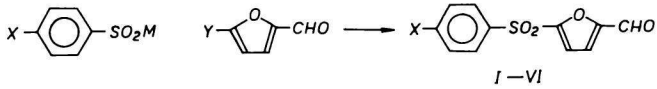
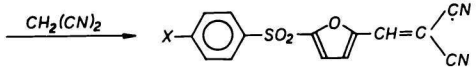
5-(4-X-Phenylsulfonyl)-2-furaldehydes, obtained from alkaline salts of 4-X-substituted benzenesulfinic acids (X = H, CH_3, CH_3CONH, Cl, Br, $(CH_3)_2N$) and 5-halide-2-furaldehydes in dimethylformamide, were reacted with malonic acid dinitrile under conditions of Knoevenagel condensation to yield the corresponding 2-cyano-3-[5-(4-X-phenylsulfonyl)-2-furyl]acrylonitriles. Ultraviolet spectra of the synthesized compounds are interpreted.

При помощи реакции щелочных солей 4-X-замещенных бензолсульфиновых кислот (X = H, CH_3, CH_3CONH, Cl, Br, $(CH_3)_2N$) с 5-галоген-2-фуральдегидами в диметилформамиде получены 5-(4-X-фенилсульфонил)-2-фуральдегиды, из которых при воздействии динитрила малоновой кислоты были приготовлены, в условиях конденсации по Кневенагелю, соответствующие 2-циано-3-[5-(4-X-фенилсульфонил)-2-фурил]акрилонитрилы. Приводится интерпретация УФ спектров синтезированных веществ.

In the frame of the program dealing with the study of the synthesis, physicochemical and biological properties of sulfides and sulfones of the furan



I — VI



VII — XII

M = Na, Li.
X = H (*I*, *VII*); CH_3 (*II*, *VIII*); CH_3CONH (*III*, *IX*); Cl (*IV*, *X*); Br (*V*, *XI*); $(CH_3)_2N$ (*VI*, *XII*).
Y = Br, I.

Scheme 1

series 5-(4-X-phenylsulfonyl)-2-furaldehydes were prepared from the corresponding alkaline salts of benzenesulfinic acids and 5-bromo- or 5-iodo-2-furaldehydes in dimethylformamide. Substances of this type were synthesized also by other authors. Thus 5-methylsulfonyl-2-furaldehyde was obtained from sodium methanesulfinate and 5-bromo-2-furaldehyde [1], 5-phenylsulfonyl- and 5-(4-acetamidobenzylsulfonyl)-2-furaldehydes from the respective sodium benzenesulfinates and 5-bromo-2-furaldehydes in methyl cellosolve [2, 3]. *Lieb* and *Eiter* [4] ascertained that 5-nitro-2-furaldehyde is also involved in the S_N reaction with various nucleophiles; its reaction with sodium benzenesulfinate resulted in the formation of 5-phenylsulfonyl-2-furaldehyde.

In this paper we wish to report on the preparation of 2-cyano-3-[5-(4-X-phenylsulfonyl)-2-furyl]acrylonitriles by the Knoevenagel reaction of 5-(4-X-phenylsulfonyl)-2-furaldehydes with malonic acid dinitrile. The compounds were prepared according to reactions shown in Scheme 1.

Experimental

Sodium benzenesulfinate and 4-methylbenzene sulfinate were commercial products; further alkaline salts of 4-substituted benzenesulfinic acids were prepared according to [5—7].

Infrared spectra were measured with a UR-20 spectrophotometer (Zeiss, Jena) in NaCl cells (1.04 mm, concentration 0.025 M) in chloroform, polystyrene foil being used for the calibration. Reading accuracy ± 1 cm^{-1}

Ultraviolet spectra were taken with a Specord UV VIS apparatus in the 200—400 nm region; concentration $2—5 \times 10^{-5}$ M in methanol. The measured data are listed in Table 3.

Lithium 4-dimethylaminobenzene sulfinate

A solution of 4-bromo-*N*,*N*-dimethylaniline (21.8 g; 0.019 mole) in anhydrous ether (45 ml) was stepwise added to a stirred suspension of lithium (2 g) in anhydrous ether (45 ml) in a nitrogen atmosphere. The rate of addition should keep the solvent boiling; then the stirring was continued for another 15 min. The ethereal solution of sulfur dioxide (10—12 g) was added under external cooling with carbon dioxide to the stirred solution. Immediately after addition of the first portion the white lithium 4-dimethylaminobenzene sulfinate precipitated; this was filtered off, dried, and used directly for further synthesis. The yield of the crude product was 20—25 g.

5-(4-X-Phenylsulfonyl)-2-furaldehydes (I—VI)

A mixture of the respective alkaline 4-X-substituted-benzenesulfinate (0.01 mole), 5-bromo- or 5-iodo-2-furaldehyde (0.01 mole), and purified dimethylformamide (25—40 ml) was kept at 110 to 120°C for 3—6 hrs, cooled and poured into cold water (100 ml). The precipitate was filtered off, dried, and crystallized from ethanol. Characteristic data of substances prepared are listed in Table 1.

Table 1. Characteristic data of synthesized 5-(4-X-phenylsulfonyl)-2-furaldehydes

Compound	X	Formula	*M*	Calculated/found			Yield	M.p.	$\tilde{\nu}$(C=O)	$\tilde{\nu}_{as}(SO_2)$	$\tilde{\nu}_{s}(SO_2)$
				% C	% H	% S	%	°C		cm^{-1}	
I	H	$C_{11}H_8O_4S$	236.1					124—125	1700	1348	1145
II	CH_3	$C_{12}H_{10}O_4S$	250.2	57.61	4.03	12.82	68	115—116	1700	1345	1145
				57.49	3.89	12.84					
III	CH_3CONH	$C_{13}H_{11}NO_5S$	293.2				86.5	170—171	1700	1345	1145
IV	Cl	$C_{11}H_7ClO_4S$	270.6	48.82	2.61	11.85	42	125—126	1700	1350	1145
				48.56	2.54	11.80					
V	Br	$C_{11}H_7BrO_4S$	215.0	41.94	2.24	10.18	46.5	142—144	1700	1350	1145
				41.67	2.12	10.26					
VI	$(CH_3)_2N$	$C_{13}H_{13}NO_4S$	279.3	55.91	4.69	11.48	56.3	173—175	1700	1340	1140
				55.78	4.53	11.50					

Table 2. Characteristic data of synthesized 2-cyano-3-[5-(4-X-phenylsulfonyl)-2-furyl]acrylonitriles

Compound	X	Formula	*M*	Calculated/found				Yield	M.p.	$\tilde{\nu}$(C=N)
				% C	% H	% N	% S	%	°C	cm^{-1}
VII	H	$C_{14}H_8N_2O_3S$	284.2	59.17	2.84	9.86	11.28	71.4	126—128	2231
				58.94	2.75	9.72	11.09			
VIII	CH_3	$C_{15}H_{10}N_2O_3S$	298.3	60.40	3.38	9.39	10.75	70.5	148—150	2231
				60.29	3.22	9.31	10.68			
IX	CH_3CONH	$C_{16}H_{11}N_3O_4S$	341.3	56.31	3.25	12.31	9.40	68.7	248—250	2233
				56.28	3.12	12.21	9.24			
X	Cl	$C_{14}H_7ClN_2O_3S$	318.7	52.76	2.21	8.79	10.06	75.6	154—156	2230
				52.66	2.14	8.58	9.87			
XI	Br	$C_{14}H_7BrN_2$	363.1	46.31	1.94	7.71	8.83	77.3	157—159	2232
				46.23	1.86	7.61	8.68			
XII	$(CH_3)_2N$	$C_{16}H_{13}N_3O_3S$	327.3	58.72	4.00	12.84	9.80	68.4	195—197	2234
				58.65	3.87	12.58	9.86			

2-Cyano-3-[5-(4-X-phenylsulfonyl)-2-furyl]acrylonitriles (VII—XII)

A solution of malonic acid dinitrile (0.66 g; 0.01 mole) was added to corresponding aldehyde (0.01 mole) dissolved in absolute ethanol (20 ml). Five drops of 10% sodium ethoxide were added to the well stirred solution as a catalyst. The mixture was stirred for an additional hour after which the separated crystals of the condensation product were filtered off and dried. Further product, obtained by addition of water to the filtrate, was combined with the main product and crystallized from ethanol. Characteristic data of substances prepared are listed in Table 2.

Results and discussion

5-(4-X-Phenylsulfonyl)-2-furaldehydes were obtained by a reaction of alkaline salts of 4-substituted benzenesulfinic acids with 5-bromo- or 5-iodo-2-furaldehyde in dimethylformamide. Dimethylformamide as solvent enabled us to achieve high yields of 5-arylsulfonyl-2-furaldehydes (Table 1) when compared with the reaction of 5-nitro-2-furaldehyde with sodium benzenesulfinate in dimethyl sulfoxide [4].

In connection with the synthesis of aldehydes under study a preparation of lithium 4-dimethylaminobenzenesulfinate has been worked out: 4-bromo-dimethylaniline, obtained from dimethylaniline and dioxan dibromide [8], was reacted with metallic lithium in absolute ether to give 4-dimethylaminobenzene lithium. An addition of ethereal solution of sulfur dioxide to this organolithium reagent furnished lithium 4-dimethylaminobenzenesulfinate in a good yield.

The condensation of 5-(4-X-phenylsulfonyl)-2-furaldehydes with malonic acid dinitrile was carried out in absolute ethanol under conditions of Knoevenagel reaction. Primary and secondary amines, as well as sodium alcoholates were tested as catalysts. Sodium ethoxide was found to be the most effective.

The values of the ultraviolet maxima of the synthesized compounds are listed in Table 3. Both series of sulfones revealed 3 or 4 absorption maxima in the 205—400 nm region. These absorption bands could be, with the exception of the long-wave band, ascribed to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electron transitions localized in the arylsulfonyl, furan or furylacrylonitrile part of the molecule [9]. The last absorption maximum (K band) corresponded to the oscillation of electrons within the entire conjugated system of the molecule. The last absorption band of 5-phenylsulfonyl-2-furaldehyde in form of an inflexion is hypsochromically shifted by 40 nm when compared with that of 5-phenyl-, 5-phenylthio-, and 5-phenylseleno-2-furaldehydes [10]. Based upon this fact one might assume that the $>SO_2$ group is an insulator of the electronic transmission. On the other hand, the substituent effect of 5-(4-X-phenylsulfonyl)-2-furaldehydes (Table 3) was found to be efficacious. The transmission of the electron effect of the substituent through the $>SO_2$ group was evidenced also when investigating the pK values of

Table 3

Ultraviolet data of synthesized compounds

Compound	λ_{max} nm	log ε	λ_{max} nm	log ε	λ_{max} nm	log ε
I	207—211	4.11	254	4.17	284 i	3.51
II	222—224	4.13	255	4.24	287 i	3.49
III	208	4.30	244	4.11	281	4.37
IV	205	4.16	227	4.13	259	4.19
V	206	4.21	233	4.12	251	4.23
VI	207	4.60	244 sh	4.39	303	4.36
VII	208	4.30	234	4.15	338	4.43
VIII	208	4.26	232	4.18	342	4.31
			253 sh	4.09		
IX	211	4.47	278	4.39	349	4.36
X	207	4.30	242	4.18	340	4.39
XI	207	4.28	239	4.16	339	4.12
			258 sh	4.12		
XII	220	4.18	301	4.52	400	3.90
			330 i	4.26		

i — inflexion; sh — shoulder.

5-nitrofurfuryl (4-X-phenyl) sulfones [11]. The hypsochromic shift of the above-mentioned band in 5-(4-X-phenylsulfonyl)-2-furaldehydes is believed to be associated with the opposite effect of the 4-X-Ar—SO_2 group towards the carbonyl group. The last absorption bands (K bands) of 2-cyano-3-[5-(4-X-phenylsulfonyl)--2-furyl]acrylonitriles (Table 3, compounds *VII—XII*) were markedly bathochromically shifted due to the extension of the conjugated system; the dimethylamino derivative has this band shifted into the vosible region. Comparison with the analogous condensation products derived from 5-aryl-2-furaldehydes showed that the K band of compounds without a sulfur containing group is substantially bathochromically shifted up into the visible region [12].

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