Furan derivatives. LV. Preparation of 5-aryl-2-furfuryl phenyl and 5-aryl-2-furfuryl 4-tolyl sulfones

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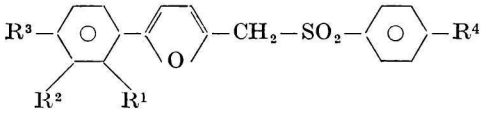
The preparation of 5-(X-phenyl)-2-furfuryl phenyl sulfones (X = 4-NO_2, 3-NO_2, 2-NO_2, 4-Br, 4-Cl, 3-Cl, 2-Cl, 4,3-diCl, H, 4-CH_3) and 5-(X-phenyl)-2-furfuryl 4-tolyl sulfones (X = 4-NO_2, 3-NO_2, 2-NO_2, 4-Br, 4-Cl, 3-Cl, 2-Cl, 4,3-diCl) is described. Sulfones were prepared by reaction of 5-aryl-2-furfuryl bromides with sodium arenesulfinate.

In a series of 5-aryl-2-furfuryl derivatives there has been described the preparation of some 5-aryl-2-furfuryl alcohols [1], sulfides [2], thiocyanates and isothiocyanates [3, 4], esters and ethers [5, 6]. Substituted 5-phenyl-2-furylacetic acids are active as antiinflammatory [7, 8] and ethers of 5-aryl-2-furfuryl type as antiviral agents [5]. Biological activity of sulfones of furfuryl type [9] was taken as the basis for the synthesis of 5-aryl-2-furfuryl type in order to study their biological activity.

Continuing the investigation into the nucleophilic substitution of bromide ion in bromides of 5-aryl-2-furfuryl type [2, 4] we prepared the sulfones outlined in Scheme 1.



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
I	H	H	NO_2	H	*X*	H	H	CH_3	H
II	H	NO_2	H	H	*XI*	H	N	NO_2	CH_3
III	NO_2	H	H	H	*XII*	H	NO_2	H	CH_3
IV	H	H	Br	H	*XIII*	NO_2	H	H	CH_3
V	H	H	Cl	H	*XIV*	H	H	Br	CH_3
VI	H	Cl	H	H	*XV*	H	H	Cl	CH_3
VII	Cl	H	H	H	*XVI*	H	Cl	H	CH_3
VIII	H	Cl	Cl	H	*XVII*	Cl	H	H	CH_3
IX	H	H	H	H	*XVIII*	H	Cl	Cl	CH_3

Scheme 1

Bromides of 5-aryl-2-furfuryl type [4] and commercial sodium arenesulfinates were used as starting compounds for the preparation of sulfones. 5-(3,4-Dichlorophenyl)-2-furfuryl bromide was prepared from the respective alcohol synthesized from newly prepared 5-(3,4-dichlorophenyl)-2-furancarbaldehyde [10] by the method previously

described [1]. In an attempt to synthesize sulfones from 5-(nitrophenyl)-2-furfuryl bromides in ethanol we obtained ethers, as pointed out in paper [2]. In this study we used acetone as solvent; the desired products were formed by the S_N2 mechanism.

The substituent on the benzene ring affects the yield, what is connected probably with the stability of the respective bromides [3, 4]. If there is a substituent with electron-donating properties on the benzene ring, the yields become lower as a result of resinification. In case the methoxy group was a substituent, our attempt to obtain sulfone failed. 4-Substituted derivatives have the highest and 2-substituted ones the lowest melting points (compounds *I—III*, *V—VII*, *XI—XIII*, *XV—XVII*; Table 1).

Infrared spectra (Table 2) of the synthesized compounds show intensive absorption bands of the $>SO_2$ group. The effect of the position and character of substituent upon the u.v. spectra is similar to that discussed in our previous papers [3, 11, 12].

Table 1

Characterization of the synthesized compounds

No.	Formula	*M*	Calculated/found					Yield	M.p.
			% C	% H	% Hal	% N	% S	[%]	[°C]
I	$C_{17}H_{13}NO_5S$	343.36	59.47	3.82	—	4.08	9.34	86	220—221
			59.44	3.76		4.11	9.39		
II	$C_{17}H_{13}NO_5S$	343.36	59.47	3.82	—	4.08	9.34	82	150—151
			59.40	3.74		4.21	9.01		
III	$C_{17}H_{13}NO_5S$	343.36	59.47	3.82	—	4.08	9.34	80	91—92
			59.38	3.70		4.21	9.41		
IV	$C_{17}H_{13}BrO_3S$	377.26	54.12	3.47	21.18	—	8.50	80	165—166
			54.06	3.36	21.46		8.61		
V	$C_{17}H_{13}ClO_3S$	332.80	61.35	3.94	10.65	—	9.63	78	187—188.5
			61.26	3.86	10.77		9.57		
VI	$C_{17}H_{13}ClO_3S$	332.80	61.35	3.94	10.65	—	9.63	76	169—170
			61.28	3.92	10.75		9.89		
VII	$C_{17}H_{13}ClO_3S$	332.80	61.35	3.94	10.65	—	9.63	76	111—112
			61.42	3.90	10.81		9.72		
VIII	$C_{17}H_{12}Cl_2O_3S$	367.25	55.60	3.29	19.31	—	8.71	84	216—217
			55.52	3.18	19.43		8.90		
IX	$C_{17}H_{14}O_3S$	298.36	68.44	4.73	—	—	10.75	68	136—137.5
			68.40	4.76			10.55		
X	$C_{18}H_{16}O_3S$	312.39	69.21	4.98	—	—	10.26	62	116—117
			69.30	4.90			10.25		
XI	$C_{18}H_{15}NO_5S$	357.39	60.49	4.23	—	3.92	8.97	88	226—227
			60.40	4.16		4.01	8.92		
XII	$C_{18}H_{15}NO_5S$	357.39	60.49	4.23	—	3.92	8.97	86	157—158
			60.38	4.10		4.05	8.91		
XIII	$C_{18}H_{15}NO_5S$	357.39	60.49	4.23	—	3.92	8.97	82	100—101
			60.42	4.20		3.75	9.02		
XIV	$C_{18}H_{15}BrO_3S$	391.29	55.25	3.86	20.42		8.19	83	186—188
			55.20	3.80	20.62		8.32		
XV	$C_{18}H_{15}ClO_3S$	343.86	62.87	4.39	10.31		9.32	81	190—191
			62.92	4.32	10.34		9.32		
XVI	$C_{18}H_{15}ClO_3S$	343.85	62.87	4.39	10.31		9.32	77	152—153
			62.93	4.40	10.33		9.42		
XVII	$C_{18}H_{15}ClO_3S$	343.85	62.87	4.39	10.31		9.32	79	102
			62.86	4.46	10.40		9.27		
XVIII	$C_{18}H_{14}Cl_2O_3S$	381.28	56.70	3.70	18.59		8.41	86	205—206
			56.72	3.82	18.76				

Table 2

Ultraviolet and infrared spectra of the synthesized compounds

No.	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	ν_s(S=O) [cm^{-1}]	ν_{as}(S=O) [cm^{-1}]	ν_{arom}(C=C) [cm^{-1}]	ν_s(NO_2) [cm^{-1}]	ν_{as}(NO_2) [cm^{-1}]
I	354	4.32	247	4.00	217	4.19	206	4.25	1157 (72)	1332 (85)	1608 (52)	1352 (80)	1560 (77)
II	294	4.38	274	4.35	217	4.29	206	4.39	1156 (72)	1328 (73)	1605 (17)	1352 (79)	1552 (24)
III	284 sh	4.06	275	4.09	267	4.10	208	4.25	1156 (72)	1324 (72)	1610 (20)	1358 (50)	1556 (17)
IV	298	4.53	—	—	216	4.32	205	4.28	1156 (71)	1324 (70)	1585 (17)		
V	297	4.46	—	—	213	4.27	—	—	1156 (71)	1323 (70)	1603 (12)		
VI	291	4.44	—	—	214	4.40	—	—	1156 (71)	1324 (70)	1610 (26)		
VII	291	4.37	235	4.01	214	4.35	—	—	1156 (71)	1323 (70)	1590 (10)		
VIII	298	4.44	238	3.81	216	4.34	206	4.38	1156 (78)	1323 (70)	1590 (12)		
IX	290	4.40	—	—	218	4.27	208	4.33	1156 (71)	1323 (70)	1596 (12)		
X	291	4.38	—	—	219	4.24	211	4.25	1156 (71)	1322 (71)	1590 (8)		
XI	357	4.22	258 sh	3.90	227	4.19	204	4.17	1156 (74)	1338 (84)	1608 (64)	1360 (78)	1560 (16)
XII	294	4.36	274 sh	4.33	227	4.29	205	4.35	1156 (71)	1327 (69)	1600 (30)	1352 (79)	1560 (25)
XIII	286 sh	4.15	268	4.20	225	4.40	206	4.35	1156 (73)	1327 (69)	1602 (38)	1360 (50)	1553 (15)
XIV	298	4.48	—	—	224	4.32	204	4.25	1156 (73)	1327 (67)	1602 (26)		
XV	297	4.40	—	—	225	4.26	204	4.15	1156 (73)	1327 (66)	1601 (26)		
XVI	291	4.38	—	—	226	4.32	205	4.29	1155 (74)	1326 (67)	1601 (44)		
XVII	290	4.36	—	—	227	4.40	206	4.25	1155 (74)	1326 (66)	1600 (36)		
XVIII	298	4.40	—	—	226	4.31	205	4.37	1153 (79)	1327 (66)	1600 (24)		

The values in brackets are % of absorption; sh — shoulder.

Experimental

The i.r. spectra were measured on a double-beam prism UR-20 (Zeiss, Jena) spectrophotometer in the 670—2000 cm^{-1} region in chloroform (1-mm NaCl cells; concentrations 2×10^{-2} mol l^{-1}). The instrument was calibrated against a polystyrene foil 25 μm thick. The reading accuracy was ± 1 cm^{-1}.

Electronic absorption spectra were taken on a recording Specord UV-VIS (Zeiss, Jena) spectrophotometer in the 200—480 nm range. The measurements were done at laboratory temperature in a 1-cm cell in spectral grade ethanol at the concentration of 4×10^{-5} mol l^{-1}.

5-(X-Phenyl)-2-furfuryl phenyl and 5-(X-phenyl)-2-furfuryl 4-tolyl sulfones (I—XVIII)

A solution of sodium benzene- or 4-methylbenzenesulfinate (0.02 mole) in acetone (40 ml) was added to a solution of substituted 5-phenyl-2-furfuryl bromide (0.02 mole) [4] in acetone (50—100 ml according to the solubility of the respective bromide). The reaction mixture was refluxed for 3 hrs. On diluting with hot water (150 ml) and cooling, the crystals were filtered off, washed with water, dried, and recrystallized from a suitable solvent: compounds *I* and *XI* from acetic acid, others from ethanol.

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