Furan derivatives. LI.
Synthesis and some properties of α,β-unsaturated sulfones of the 5-nitrofuran series

[a]A. JURÁŠEK, [a]J. KOVÁČ, and [b]J. ABRAHÁM

[a]*Department of Organic Chemistry, Slovak Technical University,*
880 37 Bratislava

[b]*Research Department, Chemical Works of J. Dimitrov,*
*810 01 Bratislava*

Derivatives of 1-(5-nitro-2-furyl)-1-methylsulfonyl-2-(4-X-phenyl)ethylene (*A*), where X is H, $N(CH_3)_2$, I, CN, and NO_2 were synthesized by the condensation of 5-nitrofurfuryl methyl sulfone (S_m) with 4-substituted benzaldehydes. Similar condensation of S_m with 5-substituted 2-furaldehydes gave the derivatives of 1-(5-nitro-2-furyl)-1-methylsulfonyl-2-(5-X-furyl)-ethylene (*B*), where X is H, CH_3, Br, I, and $COOCH_3$. Condensation of 5-nitrofurfuryl phenyl sulfone (S_p) with 5-X-2-furaldehydes afforded the derivatives of 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-(5-X-furyl)ethylene (*C*), where X is H, CH_3, SCH_3, Br, I, $COOCH_3$, and NO_2. Based on their i.r. and u.v. spectra the structure of the synthesized substances is discussed.

In our previous papers we have described the use of 5-nitrofurfuryl nitrate in the preparation of substances of the 5-nitrofuran series [1] including 5-nitrofurfuryl sulfones having an active methylene group [1, 2] located between the 5-nitrofuran electron-withdrawing residue and the SO_2-R group, where R is an alkyl or an aryl group or a heterocycle. We showed that S_p reacts readily with substituted benzaldehydes and 5-aryl-2-furaldehydes to give, in one step, 1,1,2-trisubstituted derivatives of ethylene *i.e.* the corresponding 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-(X-phenyl)ethylenes (*D*) [3] or 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-[5-(X-phenyl)-2-furyl]ethylenes (*E*) [4]. These compounds, as can be deduced from their u.v. spectra and models, do not possess planar structure and thus they can exist in different conformations depending upon the mode of attachment of the bulky substituents to the ethylene carbon atoms [3, 4].

It appeared interesting to examine whether S_m, having a methyl radical, which through its $+I$ effect decreases the reactivity of methylene hydrogens bonded to the SO_2 group, would also be amenable to the condensation reaction and, in addition, what would be the structure of the formed products like. With the aim to examine the structure of *C* sulfones S_p were also submitted to the condensation reaction with furaldehydes. Compounds *C* are of interest because they have furan residues attached directly to the ethylene carbon atoms. The compounds described herein were prepared according to the Scheme 1.

Experimental

The starting S_m, S_p, and 1-(5-nitro-2-furyl)-2-phenylethylene (*XVIII*), used in the interpretation of spectra, were prepared as described respectively in [1, 2, and 5].
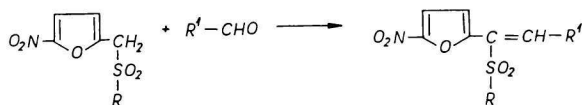
$$R = CH_3, \ C_6H_5; \quad R^1 = \text{residue of aldehyde}$$

Scheme 1

Infrared spectra in alcohol-free chloroform (anal. grade) were measured with an UR-20 (Zeiss, Jena) spectrometer. The instrument was calibrated against a polystyrene foil. Concentration of compounds A was 0.0125 M and of other substances 0.01 M; the thickness of the sodium chloride cell was 1.02 mm.

Electron spectra were obtained with a Specord UV VIS (Zeiss, Jena) spectrometer. The measurements were done in ethanol using a 10-mm cell at the concentration $1 \times 10^{-5} - 6 \times 10^{-5}$ M. The accuracy of the measurements was ± 1 nm. For comparison, the spectra of standard S_m and $XVIII$ were also taken.

Compounds I—XVII

A mixture of 5-nitrofurfuryl methyl sulfone (2 g; 0.01 mole), 4-substituted benzaldehyde, or 5-substituted 2-furaldehyde (0.01 mole), ammonium acetate (1.5 g; 0.02 mole) and benzylamine or piperidine (0.2 ml) in acetic acid (25—40 ml) was refluxed with stirring for 30 min—12 hrs (see Table 1). After this time the reaction mixture was poured onto crushed ice (100 g), the separated dark precipitate was filtered, dried, and extracted with ethanol or chloroform. The extract was decolourized with charcoal, concentrated to a small volume, and the product was allowed to crystallize. Sometimes, repeated crystallization or purification by chromatography (a column of alumina, Brockmann activity grade II, 20 × 2 cm) was necessary.

Results and discussion

The physical constants of the synthesized compounds and their analytical figures are summarized in Table 1, i.r. and u.v. spectral data in Table 2. From Table 1 it can be seen that the yields of the unsaturated sulfones A and B (5—41%) are markedly lower than those of C, obtained by the condensation of S_p with furaldehydes, or D and E given rise to by similar condensation of aromatic aldehydes [3] and aldehydes of the phenylfuran series [4], respectively. Attempts to increase the yields by varying the reaction conditions (prolonged reaction time, the use of a catalyst, and different reaction medium [3]) were met with little success. The formation of a considerable amount of resinous material, probably by polymerization of the final products, was observed. In some cases, e.g. the reaction of 5-nitro-2-furaldehyde with S_m was not successful at all. 4-Nitrobenzaldehyde also reacted in a peculiar manner; its condensation resulted in a low yield of the corresponding sulfone IV. As this compound has a very wide range of m.p. we suppose that compound IV is a mixture of geometric isomers. It follows from the low yields of A and B that the methylsulfonyl group, due to its $+I$ effect, decreases the acidity of the methylene hydrogens and thus also the reactivity of the starting sulfone. However, the possibility of the formation of resins as the primary reason for the low yields of the sulfones cannot be excluded. In spite of this the work

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Table 1

Characterization of the synthesized compounds

No.	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C]	Reaction time [hrs]
				% C	% H	% N	% S			
1-(5-Nitro-2-furyl)-1-methysulfonyl-2-(4-X-phenyl)ethylenes (*A*)									
I	H	$C_{13}H_{11}NO_5S$	293.3	53.23	3.75	4.77	10.93	41	159 — 160	8
				52.98	3.59	4.92	10.70			
II	I	$C_{13}H_{10}NO_5SI$	419.2	37.24	2.41	3.34	7.64	34.5	63 — 65	4
				37.40	2.52	3.38	7.52			
III	CN	$C_{14}H_{10}N_2O_5S$	318.3	52.80	3.16	8.79	10.05	14.5	115 — 117	2.5
				52.19	2.97	8.87	10.10			
IV	NO₂	$C_{13}H_{10}N_2O_7S$	338.3	46.15	2.98	8.28	9.47	5.0	125 — 145	4
				45.79	2.88	8.40	9.51			
V	N(CH₃)₂	$C_{15}H_{16}N_2O_5S$	336.4	53.55	4.79	8.32	9.53	6.0	208 — 210	12
				54.05	4.60	8.41	9.67			
1-(5-Nitro-2-furyl)-1-methylsulfonyl-2-(5-X-furyl)ethylenes (*B*)									
VI	H	$C_{11}H_9NO_6S$	283.3	46.63	3.19	5.94	11.28	11	129 — 131	1
				46.52	3.08	5.39	11.23			
VII	CH₃	$C_{12}H_{11}NO_6S$	297.3	48.47	3.72	4.73	10.78	18	126 — 127	5
				48.28	3.54	5.02	10.76			
VIII	Br	$C_{11}H_8NO_6SBr$	362.2	36.47	2.22	3.86	8.85	11.5	130 — 133	0.5
				36.28	2.09	3.90	8.94			

Table 1 (Continued)

No.	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C]	Reaction time [hrs]
				% C	% H	% N	% S			
IX	I	$C_{11}H_8NO_6SI$	408.2	32.36	1.97	3.43	7.84	5.0	152 — 153	2.5
				32.42	2.06	3.48	7.67			
X	COOCH₃	$C_{13}H_{11}NO_8S$	341.3	45.64	3.24	4.09	9.43	6.0	162 — 164	5
				45.60	3.18	4.30	9.48			

1-(5-Nitro-2-furyl)-1-phenylsulfonyl-2-(5-X-furyl)ethylenes (*C*)

No.	X	Formula	M	% C	% H	% N	% S	Yield [%]	M.p. [°C]	Reaction time [hrs]
XI	H	$C_{16}H_{11}NO_6S$	345.3	55.65	3.19	4.06	9.28	26	115 — 116	5
				55.60	2.95	4.34	9.19			
XII	CH₃	$C_{17}H_{13}NO_6S$	259.4	56.82	3.62	3.89	8.91	61	113 — 115	5
				56.84	3.76	4.05	9.04			
XIII	SCH₃	$C_{17}H_{13}NO_6S_2$	391.4	52.16	3.32	3.58	16.36	51	124 — 125	5
				52.30	3.04	3.44	16.36			
XIV	Br	$C_{16}H_{10}BrNO_6S$	424.2	45.33	2.36	3.32	7.61	24	115 — 117	5
				45.43	2.55	3.37	7.45			
XV	I	$C_{16}H_{10}INO_6S$	471.2	40.75	2.13	3.00	6.79	27	131 — 132	5
				40.82	2.25	3.06	6.90			
XVI	COOCH₃	$C_{18}H_{13}NO_8S$	403.4	53.72	3.23	3.51	7.94	25.6	140 — 142	5
				53.54	3.17	3.61	7.94			
XVII	NO₂	$C_{16}H_{10}N_2O_8S$	390.3	49.25	2.56	7.18	8.25	35	165 — 167	5
				49.11	2.78	7.27	8.49			

Table 2

Ultraviolet and infrared data of the synthesized compounds

No.	λ_{max} [nm] $\log \varepsilon$			$\nu_{aliph}(C=C)$	$\nu_{as}(NO_2)$	$\nu_{s}(NO_2)$ [cm^{-1}]	$\nu_{s}(SO_2)$	$\nu_{s}(SO_2)$	$\nu(C-O-C)$	$\nu_{def}(C-H)$
						A				
I	212 4.86	219 i 4.83	279 4.88	1638	1545 1508	1360	1327	1147	1027	895
II	212 4.80	236 4.93	274 4.49	1632	1532	1363	1340	1157	1022	883
III	210 4.30	233 sh 3.30	282 4.25 307 4.27	1640	1555 1512	1360	1337	1150	1026	855
IV	210 4.12	—	263 4.03 370 3.76	1642	1509	1358	1335	1162	1026	867
V	210 4.24	243 4.14	319 4.29 366 4.42	1610	1506	1359	1317	1137	1027	902
						B				
VI	212 4.10	244 i 3.99	297 4.40	1637	1510	1360	1330	1147	1035	897
VII	210 3.99	219 i 3.86	304 4.28	1636	1525	1363	1326	1146	1060	890
VIII	211 4.10	222 i 3.95	303 4.37	1636	1530	1360	1331	1150	1030	895
IX	211 4.25	244 i 3.97	308 4.40	1634	1535	1360	1328	1149	1028	898
X	210 4.29	218 i 4.20	298 4.46	1635	1546	1360	1331	1147	1034	896
						C				
XI	209 4.42 222 i 4.35	244 i 4.25	307 4.66 385 i 4.08	1628	1540	1352 1380	1326	1156	1030	900 890

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Table 2 (Continued)

| No.	λ_{max} [nm] log ε			$\nu_{aliph}(C=C)$	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$ [cm^{-1}]	$\nu_s(SO_2)$	$\nu_s(SO_2)$	$\nu(C-O-C)$	$\nu_{def}(C-H)$
XII	208 4.44	245 i 4.18	312 4.60	1635	1550	1358	1328	1157	1032	898
	222 i 4.35		412 i 4.09			1382				
XIII	208 4.55	244 i 4.25	323 4.52	1632	1545	1358	1328	1158	1033	898
	218 sh 4.51		422 i 4.08			1384				
XIV	208 4.44	243 i 4.20	310 4.60	1626	1540	1352	1327	1158	1030	898
	220 i 4.35		403 i 4.01			1380				
XV	210 4.51	250 i 4.26	317 4.65	1635	1540	1358	1330	1160	1030	898
	222 i 4.45		412 i 4.10			1387				
XVI	209 4.47	244 i 4.15	306 4.55	1648	1548	1358	1334	1160	1030	900
	221 i 4.39		376 i 4.00		1520	1388				
XVII	208 4.43	248 i 4.28	313 4.50	1645	1550	1358	1336	1163	1030	900
	221 i 4.41		357 4.14			1390				
				Standards						
S_m	208 3.86	236 i 3.60	308 3.83		1512	1360	1336	1155	1026	877
XVIII	205 i 4.15	241 4.09	281 4.30	1639	1520	1365			1027	967
	214 4.22		395 4.49							

i — inflex, sh — shoulder.

confirmed that 5-nitrofurfuryl alkyl sulfones can be used for the synthesis of 1,1,2-tri-substituted ethylenes (unsaturated sulfones). The unsaturated sulfone $XVII$ was prepared from 5-nitro-2-furaldehyde and S_p by the condensation in acetic anhydride according to [3].

As can be seen from the data in Table 2 the u.v. spectra of the synthesized compounds are rather simple. Three absorption bands (at $210-212$, $218-244$, and $263-319$ nm) are present in the spectra of A and B. In the case of the derivatives bearing strongly polarizable groups an additional absorption band, shifted towards the longer wavelengths, is also present. The spectra of C contain five absorption bands of which three appear as an inflex or a shoulder. Comparing the u.v. spectra of these substances with those of S_m and $XVIII$ it can be seen that in the spectra of substances A and B, except for the case of IV and V, the absorption band corresponding to the oscillation of the electrons along the conjugated system (K band), is not present. All these compounds absorb in roughly the same regions as the saturated sulfone S_m or benzene, i.e. all three bands can be attributed to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electron transitions located in the furan [6] or aryl part of the molecule [7]. The spectrum of $XVIII$, which is the *trans* isomer (967 cm^{-1}) having planar arrangement, an intense K band at 395 nm bathochromically shifted with respect to the standard sulfones A by 116 nm, is present. The absorption band of compounds C at $357-422$ nm can also be taken for a K band because it appears only as a weak inflex. The bathochromic shift observed in the case of IV and V can be probably explained by the formation of polar structures similarly as was the case with other similar derivatives [3, 4]. It follows from the u.v. spectra as well as from the models that the described 1,1,2-trisubstituted ethylenes bearing the methylsulfonyl group are, similarly as the unsaturated sulfones C and other phenylsulfonyl derivatives [3, 4], nonplanar systems. Also in the case of 1,2-difuryl derivatives B and C is this nonplanarity caused by the presence of three bulky substituents attached to the ethylene carbons. These substituents are, due to steric factors, bent out of the plane breaking thus the continuity of the conjugation. It can be at the same time presumed that the bending of the 5-nitrofuran residue out of the plane is caused mainly by the presence of the bulky SO₂ group and that these compounds exist in the E conformation (Scheme 2). The questions concerned with the geometrical isomerism and conformation of ethylenic derivatives of this type as well as the mechanism of their formation is discussed elsewhere [3, 4].

In the i.r. spectra of all the compounds under investigation (Table 2) an absorption band at $1645-1610$ cm^{-1} corresponding to the aliphatic C=C vibrations, considerably influenced by the nature of the substituent, is present.

Most important, from the point of view of the i.r. spectrometry, are the symmetric and asymmetric vibrations of NO₂ and SO₂ groups. $\nu_{as}(NO_2)$ appear between $1555-$
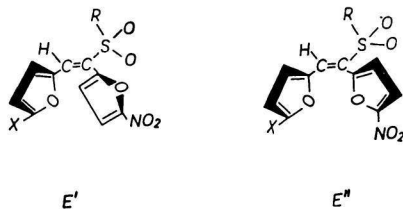
Scheme 2

-1504 cm^{-1}; in some compounds of the A series this band is split into two bands of strong and medium intensity. As in the case of other 5-nitrofuran derivatives [8] and in agreement with other authors [9], this band of A, B, and E ($1520-1486$ cm^{-1}) [4], compared to C and D ($1550-1530$ cm^{-1}) [3] is shifted strongly to the lower wavelengths. The absorption bands corresponding to $\nu_s(NO_2)$ are very intense and appear at almost constant wavelength ($1363-1358$ cm^{-1}). In the same range there is located the absorption band of $\nu_s(NO_2)$ of the standard compound $XVIII$. In the case of C, D, and E this band is again split into two bands of very strong and medium intensity appearing at $1360-1350$ and $1390-1372$ cm^{-1}, respectively [3, 4]. All the compounds show characteristic $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, the former appearing in compounds A at $1340-1317$ cm^{-1} ($\Delta\nu = 23$ cm^{-1}), in the case of B at $1331-1326$ cm^{-1} ($\Delta\nu = 5$ cm^{-1}), C at $1336-1326$ cm^{-1} ($\Delta\nu = 10$ cm^{-1}), and in the case of D at $1330-1321$ cm^{-1} ($\Delta\nu = 9$ cm^{-1}). It can be seen from the foregoing that $\nu_{as}(SO_2)$ are most influenced in the case of substances A and least in the case of B. The values $\nu_s(SO_2)$ are most affected by the nature of the substituent in the case of A ($1162-1137$ cm^{-1}; $\Delta\nu = 25$ cm^{-1}), whereas substances B, C, D, and E show $\Delta\nu_s(SO_2) = 4-8$ cm^{-1} [3, 4]. Other absorption bands correspond to the absorption of the furan cycle or to C$-$H$_{def}$. All the spectra show a narrow absorption band at $902-855$ cm^{-1}, most characteristic [10] of furan derivatives.

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