PREPARATION AND PROPERTIES OF β-KETOSULPHONES OF 5-NITROFURAN SERIES. STUDY OF TRANSFER OF ELECTRONIC EFFECTS THROUGH SULPHONE GROUP*

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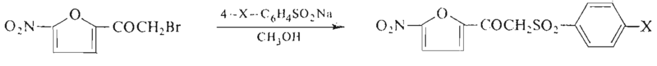
A series of 2-(5-nitro-2-furyl)-2-oxoethylarylsulphones have been synthetized by reaction of 5-nitro-2-bromoacetylfuran with sodium *p*-X-benzenesulphinates (where $X = H, CH_3, OCH_3, CH_3CONH, NH_2, N(CH_3)_2, Cl, NO_2$) and used for a study of transfer of electronic effects of the substituent through SO_2 group. The found linear dependence between the proton chemical shifts in ^1H NMR spectra (and pK_a values of the CH_2 group) and the Hammett constants of the substituents proves the existence of the transfer through SO_2 group. The results of physical measurements were compared with the data obtained by quantum-chemical calculations using the EHT method.

There exist different opinions[1-8] concerning possibility of conjugation between SO_2 group and ethylene bond and transfer of electron effects through this grouping, the investigation results depending on the systems and methods chosen. In case of arylsulphonyl derivatives a good transfer of the electronic effects was observed, which was ascribed to $d_\pi - p_\pi$ conjugation resulting from participation of *d* orbitals of sulphur in formation of S=O or S=C bonds[9-11].

Within the studies of 5-nitrofuran derivatives we synthetized a series of β-ketosulphones of general formula *II* in which we investigated (using ^1H NMR spectra and pK_a values) transfer of electronic effects of substituents through the benzene nucleus immediately connected with SO_2 group and its influence on acidity of hydrogen atoms in the grouping —CO—CH$_2$—SO$_2$—.



I

II; pK_a 5.23–7.82

Chemical shift of the methylene group signal is a function of electron-donor or -acceptor effect of the substituent at *para* position of the benzene nucleus. The

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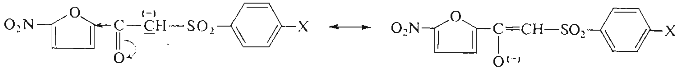
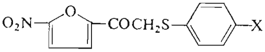
* Part CLXV in the series Furan Derivatives; Part CLXIV: This Journal *47*, 523 (1982).

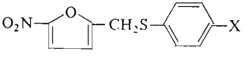
corresponding unsplit band in ^1H NMR spectra exhibits an intensity of two protons, and it varies within 4·68 to 5·39 ppm depending on the substituent (Table I). The found Hammett correlation with σ_p constants has $\varrho = 0{\cdot}37$ and $r = 0{\cdot}97$. The two electron-acceptor groups SO_2 and CO weaken the C—H bonds of the methylene group and increase acidity of the hydrogen atoms, which results in the fact that compounds of this type become relatively strong C-acids. This can be seen from comparison of pK_a values of the investigated β-ketosulphones *II* with those of analogous sulphides *III* (ref.[12]) or sulphides *IV* and sulphones *V* not containing —CO— group[13]. This fact obviously depends on different stabilization of the carbanion formed. In carbanions derived from sulphides and sulphones without —CO— group the negative charge can be delocalized preferably to the electron-acceptor 5-nitrofuran nucleus, whereas in the anions formed from the sulphur-containing β-keto derivatives the delocalization can involve the —CO— group, too. The carbanions of the types *A* and *B* tend to plane arrangement enabling a better overlap of the carbon and oxygen *p* orbitals in —CO— group, the negative charge being localized mostly at oxygen[14].



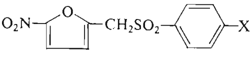
However, the strong electron-acceptor effect of SO_2 group suppresses contribution of the structure *B*, *i.e.* formation of complete double bond between α and β-carbon atoms is probably impossible. The found pK_a constants (Table I) also correlate with the Hammett σ_p constants of the substituents ($\varrho = 1{\cdot}84$; $r = 0{\cdot}99$). A similar good linear correlation applies also to chemical shifts of methylene group ($\varrho = 0{\cdot}53$; $r = 0{\cdot}97$) and its pK_a values ($\varrho = 1{\cdot}39$; $r = 0{\cdot}99$) (the both using the σ_p Hammett constants) in the case of the analogous sulphides[12]. Comparison of the ϱ constants in the two series *II* and *III* shows that substituents affect more markedly the $\delta(CH_2)$ values of the sulphides than those of the sulphones, the opposite being true with the pK_a constants. Linear dependence between these parameters was also found in the sulphur derivatives *IV* and *V*.



III; pK_a 8.81 – 10.26



IV; pK_a 8.89 – 10.15



V; pK_a 9.33 – 10.34

Thus the experimental results indicate that the substituents affect both the chemical shifts and acidities of the protons in CH_2 group, hence the sulphone group is involved in transfer of electron effects.

We carried out quantum-chemical calculation by the EHT method[15] for the sulphones *II*. Standard geometry[16] was used in the calculation, and the molecule was simplified in the whole series of the calculated sulphones by introduction of chlorine instead of 5-nitrofuryl residue (this substitution is justified with respect to similar electron-acceptor properties of the both substituents reflected in similar values of the Hammett σ constants[17]). The calculation results of electron population in atomic orbitals of sulphur showed within the parameters used that *d* orbitals of sulphur play a little role relatively. In all the cases the contributions of individual orbitals to the bond formed are as follows: 37·75% s, 58·80% *p*, 3·75% *d*. In spite of the little contribution of *d* orbitals of sulphur, the bond has a partial double

TABLE I
The synthetized 2-(5-nitro-2-furyl)-2-oxoethyl 4-X-phenyl sulphones

Compound X	Formula (mol. mass)	M.p., °C (yield, %)	Calculated/Found			pK_a $\delta(CH_2)$, ppm
			% C	% H	% N	
IIa	$C_{12}H_9NO_6S$	154–155[a]	48·90	3·07	4·75	6·52
H	(295·1)	(86)	48·81	2·95	4·65	5·18
IIb	$C_{13}H_{11}NO_6S$	129–131[a]	50·60	3·58	4·52	6·67
CH_3	(309·3)	(85)	50·55	3·60	4·50	5·11
IIc	$C_{13}H_{11}NO_7S$	140–143[a]	48·00	3·41	4·30	7·03
CH_3O	(325·3)	(81)	47·56	3·42	4·02	5·07
IId	$C_{14}H_{12}N_2O_7S$	215–217[a]	47·70	3·24	7·95	6·64
CH_3CONH	(352·3)	(62)	47·50	3·35	7·95	5·07
IIe	$C_{12}H_8N_2O_8S$	168–171[b]	42·40	2·36	8·24	5·23
O_2N	(340·3)	(63)	42·25	2·24	8·20	5·39
IIf	$C_{12}H_8ClNO_6S$	160–161[b]	43·15	2·44	4·25	6·08
Cl	(329·1)	(75)	43·14	2·24	3·95	5·23
IIg	$C_{14}H_{14}N_2O_6S$	178–181[c]	49·70	4·15	8·30	7·80
$(CH_3)_2N$	(338·3)	(54)	49·54	4·12	8·11	4·87
IIh	$C_{12}H_{10}N_2O_6S$	178–180[c]	46·50	3·22	9·05	7·79
NH_2	(310·3)	(60)	46·70	3·22	9·10	4·68

[a] Crystallized from methanol, [b] from ethanol, [c] from dichloromethane.

bond character due to back-donation effect of p orbitals of oxygen. This is supported by overlap populations of the bonds $\sigma_{\mathrm{pop\,S-O}} = 0{\cdot}55$ and $\pi_{\mathrm{pop\,S-O}} = 0{\cdot}21$ and by relatively low values of charges at sulphur and oxygen atoms which were calculated by iterative version[18] of the EHT method, the results being $q_S = 0{\cdot}284$, $q_O = -0{\cdot}029$. Thus the system can be considered to be considerably conjugated with good ability to transfer the substituent effects. Chemical shifts of the protons of methylene group are connected with electron densities at the respective H atom and depend on character of the substituents within the series investigated. The pK_a constants of ionisation depend on polarities of the C—H bonds (which are increased with increasing positive charge at the H atom) and on the C—H bond strengths (characterized by their overlap populations). The accidity is also increased with increasing positive charge at sulphur atom which causes weakening of C—H bond. All the calculated values could be correlated with the experimental results.

EXPERIMENTAL

The ^{1}H NMR spectra were measured with a 80 MHz apparatus Tesla BS 487 C in hexadeuteriodimethyl sulphoxide with tetramethylsilane as internal standard. The ionisation constants pK_a were obtained by spectrophotometric method[19] in buffer solutions with low ionic strength according to Perrin[20]. 2-Acetylfuran[21] was prepared by acetylation of furan and transformed into 5-nitro-2-acetylfuran by nitration[22]. Bromination of the latter in benzene gave 2-bromoacetyl-5-nitrofuran[23].

2-(5-Nitro-2-furyl)-2-oxoethyl 4-X-Phenyl Sulphones

Stirred suspension of sodium arenesulphinate (0·11—0·15 mol) in methanol (80 ml) was treated with a solution of 0·1 mol 2-bromoacetyl-5-nitrofuran in 50 ml methanol. The mixture was heated to boiling 1—3 h and concentrated to 1/3 of the original volume. The solid separated on cooling was collected by suction, washed with water, and dried. After crystallization from a suitable solvent the products were obtained as yellow or cream-coloured substances, yields 54 to 86%.

2-(5-Nitro-2-furyl)-2-oxoethyl 4-Aminophenyl Sulphone

Mixture of 3·5 g 2-(5-nitro-2-furyl)-2-oxoethyl 4-acetyl-aminophenyl sulphone (0·01 mol) and 150 ml 6M-HCl was heated to boiling 2 h. The solution was boiled with charcoal, hot filtered, cooled, and neutralized with ammonia while stirring and cooling. The solid was collected by suction, washed with water, dried, and crystallized from dichloromethane to give a red substance.

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