

PHENYLSULPHONYL DERIVATIVES OF CHALCONES
DERIVED FROM 5-NITROFURAN*

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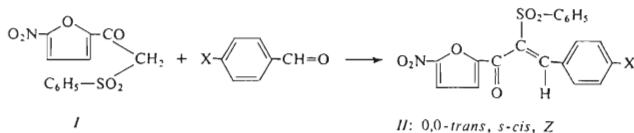
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1-(5-Nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes *II* were synthesized by condensation of phenyl-2-(5-nitro-2-furyl)-2-oxoethyl sulfone (*I*) with 4-substituted benzaldehydes ($X = \text{H}, \text{CH}_3, \text{CH}_3\text{O}, \text{N}(\text{CH}_3)_2, \text{F}, \text{Cl}, \text{NO}_2, \text{CN}$) in tetrahydrofuran or dioxane under catalysis of titanium-IV chloride and pyridine. As evidenced by spectral data (^1H NMR, IR, UV) the stereospecific condensation afforded exclusively *Z* isomers of ethylenes *II*; these exist in an *0,0-trans, s-cis* conformation.

Condensation reactions of 5-nitrofurfuryl sulfones with aromatic and heterocyclic aldehydes are known to be stereospecific¹⁻⁴, the α,β -unsaturated sulfones with an *E*-configuration being the products. β -Ketosulfides derived from 5-nitrofurane, having the active methylene group separated from the ring by a $-\text{CO}-$ group, afforded α,β -unsaturated sulfides of a *Z*-configuration⁵ with aromatic aldehydes.

This paper refers to the preparation, structure assignment and properties of 1-(5-nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes *II* obtained by condensation of phenyl-2-(5-nitro-2-furyl)-2-oxoethylsulfone (*I*) with aromatic aldehydes. The reaction course shown in Scheme 1 is in line with⁶.



SCHEME 1

Although sulfones *I* are very strong CH-acids derived from 5-nitrofurane⁷ (pK_a 7.82–5.23), they do not condense with aromatic aldehydes under conditions reported for 5-nitrofurfuryl sulfones¹⁻⁴. The unsaturated sulfones *II* were successfully pre-

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pared by a Knoevenagel condensation modified by Lehnert⁶ in 58–90% yields. Physical constants and spectral data of substances prepared in this way are listed in Tables I to III. Sharp melting points, thin-layer chromatography and ¹H NMR data of crude products evidence that this reaction leads to pure isomers, which can exist in an *E*, or a *Z*-arrangement at the ethylenic bond, and *s-cis*, or *s-trans* conformation at the —CO—C=CH— grouping. Chemical shifts of the ethylene proton of all products appear at 8.02–8.41 ppm, and correlate with ρ_p Hammett constants of substituents X ($\rho = 0.267$, $r = 0.97$). Since the additive increment of substituents⁸ cannot be unequivocally employed (the calculated chemical shift value of the ethylenic bond proton for both *E* and *Z* isomers is close to the determined one: δ C=C—H calculated for *E* = 8.52, for *Z* = 8.47 ppm), the coupling constant through three bonds J ($C_{(3)}H$) in the ¹³C NMR spectra was employed; it depends on the *cis*, or the *trans* arrangement of the ethylene derivatives⁹. The NOE ¹³C NMR measurement of derivative *Iic* (X = OCH₃) showed the $J(C_{(3)}H)$ to be 9.8 Hz thus evidencing

TABLE I

1-(5-Nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes *Iia*–*Iih*

Compound X	Formula (<i>Mr</i>)	M.p., °C (yield, %)	Calculated/Found			
			% C	% H	% N	% S
<i>Iia</i> H	C ₁₉ H ₁₃ NO ₆ S (383.3)	130–131 ^a (75)	59.52 59.21	3.42 3.38	3.65 3.61	8.36 8.31
<i>Iib</i> CH ₃	C ₂₀ H ₁₅ NO ₆ S (397.3)	190–192 ^b (67)	60.46 60.55	3.81 3.85	3.52 3.38	8.07 8.09
<i>Iic</i> CH ₃ O	C ₂₀ H ₁₅ NO ₇ S (413.3)	157–159 ^c (67)	58.12 57.88	3.66 3.62	3.39 3.36	7.76 7.67
<i>Iid</i> (CH ₃) ₂ N	C ₂₁ H ₁₈ N ₂ O ₆ S (426.4)	192–194 ^a (58)	59.15 58.73	4.25 4.19	6.57 6.50	7.52 7.28
<i>Iie</i> F	C ₁₉ H ₁₂ FNO ₆ S (401.3)	163–165 ^b (89)	58.86 58.15	3.02 3.25	3.49 3.36	7.99 7.85
<i>Iif</i> Cl	C ₁₉ H ₁₂ ClNO ₆ S (417.7)	194–195 ^b (87)	54.62 54.50	2.90 2.84	3.35 3.18	7.66 7.60
<i>Iig</i> NO ₂	C ₁₉ H ₁₂ N ₂ O ₈ S (428.3)	223–225 ^b (92)	53.28 53.21	2.82 2.84	6.54 6.29	7.49 7.39
<i>Iih</i> CN	C ₂₀ H ₁₂ N ₂ O ₆ S (408.3)	146–148 ^b (90)	58.83 58.47	2.96 2.87	6.86 6.80	7.85 7.74

^a From ethanol; ^b from acetic acid.

the *Z* configuration. This coupling constant of the analogous sulfide related to 5-nitrofurane was measured just for comparison purposes; this sulfide has a *Z* configuration⁵. The measured value $J(C_{(3)}H) = 5.5$ Hz is the argument entitling the assignment of *Z*-configuration to the ethylenes under study. The IR data and Raman spectra referring to the position and integrated intensity of bands corresponding to >C=O and >C=C< groups¹⁰ were used for the conformation determination of chalcones. The IR spectra of derivatives *Ila–Ili* display one unsplit band of the >C=O group at $1678\text{--}1671\text{ cm}^{-1}$, and a band associated with (C=C) at 1621 to 1604 cm^{-1} (Table III). Bands corresponding to the same groups in Raman spectra have the same wave number, but a reverse intensity. The low ratio of the integrated intensities $A(\text{C=O})/A(\text{C=C})$, ranging within $0.64\text{--}2.07$, and the fact that the wave numbers $\tilde{\nu}(\text{CO})$ do not correlate with σ_p Hammett constants of substituents ($r = 0.78$, what evidences the deteriorated conjugation of the system) prove that these compounds appear in *0,0-trans, s-cis* conformation as *Z* isomers^{11,12}. These conforma-

TABLE II
UV and ¹H NMR spectral data of compounds *Ila–Ili*

Compound	λ_{max} , nm (log ϵ)	C=C--H (δ , ppm) ^a
<i>Ila</i>	— 221 (4.35)	308 (4.27)
<i>Ilb</i>	212 (4.43)	224 (4.37)
<i>Ilc</i>	210 (4.41)	294 (4.50)
<i>Ild</i>	210 (4.45)	309 (4.55)
<i>Ile</i>	210 (4.42)	310 (4.52)
<i>Ilf</i>	211 (4.42)	295 (4.31)
<i>Ilg</i>	212 (4.49)	288 (4.45)
<i>Ili</i>	212 (4.49)	299 (4.45)
<i>IIIh</i>	213 (4.55)	286 (4.51)

^a Singlet.

tional conclusions are in line with data obtained with europium shift reagent¹³. In addition to those already mentioned bands other vibrations appeared. $\tilde{\nu}(\text{NO}_2)_{\text{as}}$ at 1 554–1 552 cm^{-1} , $\tilde{\nu}(\text{NO}_2)_{\text{s}}$ at 1 349–1 347 cm^{-1} , $\tilde{\nu}(\text{SO}_2)_{\text{as}}$ at 1 326–1 320 cm^{-1} , $\tilde{\nu}(\text{SO}_2)_{\text{s}}$ at 1 155–1 153 cm^{-1} , and ring skeletal vibrations of furan at 1 027 to 1 023 cm^{-1} .

The UV spectral data (Table II) when compared with those of reference substances show that the compounds under investigation are not planar due to the bulky substituents attached to the ethylene bond; a similar feature was encountered with other trisubstituted α,β -unsaturated sulfones¹⁴. This fact is supported by the position of the K-band, appearing at 310–286 nm. This band in the fundamental representative of these compounds is hypsochromically shifted by 79 nm when contrasted with 1-(5-nitro-2-furoyl)-1-phenylthio-2-phenylethylene⁵ (λ_{max} 387 nm).

EXPERIMENTAL

Spectral Measurements

The IR spectra were taken with a UR-20 (Zeiss, Jena) spectrophotometer in chloroform solution in 0.02–1 mm-cells and a $2 \cdot 10^{-2} \text{ mol l}^{-1}$ concentration. Raman spectra were measured with an SPX 100 spectrophotometer in a thick-wall capillary tube of a 0.2 mm diameter as solids. The helium-argon laser was the radiation source. The electron absorption spectra were recorded with a Specord UV VIS apparatus in dioxane at a $2.5\text{--}5 \cdot 10 \text{ mol l}^{-1}$ concentration in a 100 mm-cell; the reading accuracy was $\pm 1 \text{ nm}$. The ^1H NMR spectra were run with a BS-487C Tesla (Czechoslovakia) instrument operating at 80 MHz in deuteriated chloroform containing tetramethylsilane as an internal standard.

TABLE III
IR spectra of compounds IIa–IIh ($\tilde{\nu}$, cm^{-1} ; A m mol^{-1})

Compound	$\tilde{\nu}(\text{C=O})$	$\tilde{\nu}(\text{C=C})$	$A(\text{C=O})$	$A(\text{C=C})$	$A(\text{C=O})/A(\text{C=C})$
IIa	1 678	1 618	1 708	885	1.93
IIb	1 677	1 610	2 113	1 573	1.34
IIc	1 675	1 612	1 932	3 017	0.64
IId	1 671	1 618	1 887	2 370	0.77
IIe	1 677	1 610	1 558	933	1.67
IIf	1 678	1 614	2 178	1 050	2.07
IIg	1 678	1 604	1 969	1 023	1.92
IIh	1 677	1 621	1 558	834	1.85

1-(5-Nitro-2-furoyl)-1-phenylsulfonyl-2-(4-X-phenyl)ethylenes *Ila*–*IIIh*

To tetrahydrofuran or dioxane (200 ml) (compounds *Ilg*, *IIIh*) titanium-IV chloride (0.1 mol, 11 ml) in tetrachloromethane (25 ml) was dropwise added with stirring and exclusion of the air moisture. The yellow flocculous precipitate was then stirred for 30 min, after which following solutions were stepwise added: the particular aldehyde (50 mmol) and phenyl-2-(5-nitro-2-furyl)-2-oxoethylsulfone (*I*, 14.7 g, 50 mmol) in tetrahydrofuran (25 ml). Pyridine (0.2 mol, 16 ml) in tetrahydrofuran (30 ml) was added after additional 30 min and stirring was continued at 0°C for 6–10 h. Water (50 ml) were added; the ethereal layer was separated and the aqueous one extracted with ether (3 × 50 ml). The combined ethereal extracts were gradually washed with a saturated sodium chloride solution (50 ml) and water and dried with MgSO₄. The solvent was removed under diminished pressure and the crude product either crystallized from a suitable solvent, or purified on an alumina (neutral, activity grade III) column with benzene-ethyl acetate 5 : 1 as solvent. The purity of final products was verified by thin-layer chromatography using Silufol (Kavalier, Czechoslovakia) sheets; the solvent system employed was benzene-ethyl acetate 3 : 1.

The respective oximes *III* were obtained by a process according to¹⁵ from sulfones *Ilc*, *Ile*, *Ilg*. For compound *IIIc*, C₂₀H₁₆N₂O₇S (428.4), calculated: 56.0% C, 3.76% H, 6.54% N; found: 55.95% C, 3.70% H, 6.50% N; m.p. 163–164°C, yield 55%. For *IIIe* C₁₉H₁₃FN₂O₆S (416.4), calculated: 54.80% C, 3.15% H, 6.72% N; found: 54.65% C, 3.14% H, 6.28% N; m.p. 175–176°C, yield 58%. For *IIIg* C₁₉H₁₃N₃O₈S (443.4), calculated: 51.46% C, 2.95% H, 9.48% N; m.p. 177 to 178°C, yield 62%. All oximes were crystallized from ethanol.

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