

# SYNTHESIS AND ULTRAVIOLET SPECTRA OF 1-(5-NITRO-2-FURYL)-3-(5-(4-X-PHENYLTHIO)-2-FURYL)- -1-PROPENONES\*

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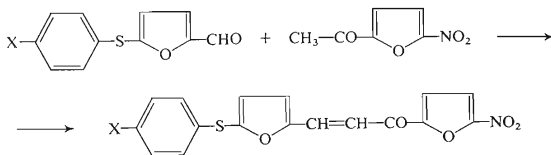
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Received February 4th, 1977

5-(4-X-Phenylthio)-, 5-phenylsulphonyl- and 5-phenyl-2-furaldehydes were reacted with 5-nitro-2-acetylfuran in ethanol in the presence of piperidine, pyridine or concentrated sulphuric acid as catalyst to give the respective  $\alpha,\beta$ -unsaturated ketones of 5-nitrofuran series. The ultraviolet spectra of the prepared substances were interpreted.

Several authors synthesized and studied properties of  $\alpha,\beta$ -unsaturated ketones of the furan series. Many papers dealt with their spectral characteristics, in others nitro-furan derivatives were subjected to biological tests<sup>1-5</sup>. So far, no  $\alpha,\beta$ -unsaturated ketones were described having, besides of 5-nitrofuran ring, another furan ring with a sulphur containing substituent in position 5. These substances might be of biological interest.

This paper deals with the preparation of 1-(5-nitro-2-furyl)-3-(5-(4-X-phenylthio)-2-furyl)-1-propenones and interpretation of their UV spectra. These compounds were prepared by condensation of 5-(4-X-phenylthio)-2-furaldehydes with 5-nitro-2-acetylfuran in ethanol under catalysis of piperidine, pyridine, or concentrated sulphuric acid (Scheme 1). Under the same conditions 1-(5-nitro-2-furyl)-3-(4-phenyl-



X = H, CH<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>CONH, Cl, Br, NO<sub>2</sub>

SCHEME 1

\* Part CVII in the series Furan Derivatives; Part CVI: This Journal 42, 3333 (1977).

-2-furyl)- and 1-(5-nitro-2-furyl)-3-(5-phenylsulphonyl-2-furyl)-1-propenones were prepared starting from 5-phenyl-2-furaldehyde and 5-phenylsulphonyl-2-furaldehyde, respectively.

Physical constants and elemental analyses of products are listed in Table I. The best yields were obtained with basic catalysts (60–87%), whereas concentrated sulphuric acid as catalyst lowers the yields to 20–40%. A 10% solution of sodium hydroxide used in the condensation reaction as catalyst produces tarry products from which the desired 1,3-disubstituted propenones were obtained in a 3–5% yield by separation of their chloroform solutions on an  $\text{Al}_2\text{O}_3$  column.

TABLE I  
1-(5-Nitro-2-furyl)-3-(5-R-2-furyl)-1-propenones

No	R (catalyst) <sup>a</sup>	Molecular formula (mol.wt.)	M.p., °C yield, %	Calculated/Found			
				% C	% H	% N	% S
1	$\text{C}_6\text{H}_5\text{—S}$ (B)	$\text{C}_{17}\text{H}_{11}\text{NO}_5\text{S}$ (341.3)	165–167 80	59.82 59.78	3.24 3.17	4.18 4.21	9.39 9.43
2	$4\text{—CH}_3\text{—C}_6\text{H}_4\text{—S}$ (B)	$\text{C}_{18}\text{H}_{13}\text{NO}_5\text{S}$ (355.3)	163–165 85	60.84 60.71	3.68 3.67	3.94 3.97	9.02 8.88
3	$4\text{—CH}_3\text{O—C}_6\text{H}_4\text{—S}$ (A)	$\text{C}_{18}\text{H}_{13}\text{NO}_6\text{S}$ (371.3)	138–140 60	58.22 58.06	3.52 3.47	3.77 3.71	8.63 8.62
4	$4\text{—CH}_3\text{CONH—C}_6\text{H}_4\text{—S}$ (A)	$\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_6\text{S}$ (398.3)	199–201 55	57.29 57.18	3.54 3.46	7.03 6.95	8.05 7.98
5	$4\text{—Cl—C}_6\text{H}_4\text{—S}$ (A)	$\text{C}_{17}\text{H}_{10}\text{ClNO}_5\text{S}$ (375.7)	198–200 68	54.34 54.27	2.68 2.62	3.72 3.75	8.53 8.58
6	$4\text{—Br—C}_6\text{H}_4\text{—S}$ (B)	$\text{C}_{17}\text{H}_{10}\text{BrNO}_5\text{S}$ (421.2)	179–181 87	48.47 48.44	2.39 2.32	3.32 3.19	7.81 7.69
7	$4\text{—NO}_2\text{—C}_6\text{H}_4\text{—S}$ (A)	$\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_7\text{S}$ (386.3)	186–188 65	52.85 52.84	2.60 2.54	7.25 7.16	8.30 8.35
8	H (A)	$\text{C}_{11}\text{H}_7\text{NO}_5$ (233.1)	174–175 68	56.67 56.48	3.02 2.91	6.00 5.88	— —
9	$\text{C}_6\text{H}_5$ (A)	$\text{C}_{17}\text{H}_{11}\text{NO}_5$ (309.2)	220–222 62	66.03 65.86	3.58 3.53	4.52 4.44	— —
10	$\text{C}_6\text{H}_5\text{—SO}_2$ (A)	$\text{C}_{17}\text{H}_{11}\text{NO}_7\text{S}$ (373.3)	188–190 72	54.69 54.61	2.97 2.96	3.75 3.69	8.58 8.47

<sup>a</sup> A pyridine, B piperidine.

Stretching vibrations  $\nu(\text{NO}_2)_{\text{as}}$  appear in the  $1560\text{--}1554\text{ cm}^{-1}$  range and the symmetric stretching vibrations of the  $\text{NO}_2$  group at  $1356\text{--}1347\text{ cm}^{-1}$  (very strong) (Table II). In the  $1610\text{--}1597\text{ cm}^{-1}$  range very strong absorption bands  $\nu(\text{C}=\text{C})$  are present. The position of these absorption bands is influenced by substituents in position 5 of the furan ring; electron donating substituents shift it toward lower wave number, electron accepting ones in the opposite direction. Stretching vibrations of the carbonyl group are complex and appear at  $1673\text{--}1663\text{ cm}^{-1}$ . The band at a lower wave number is less intense. It could be, therefore, presumed that the compounds under investigation exist in *s-cis* and *s-trans* conformations.

A comparison of UV spectra of the starting 5-(4-X-phenylthio)-2-furaldehydes<sup>6</sup> with those of 1,3-disubstituted propenones shows that the latter reveal an additional absorption band at  $373\text{--}400\text{ nm}$  (K-band) corresponding to an oscillation of electrons over the entire  $\pi$ -electron system of the molecule. This band is bathochromically shifted by electron donating substituents in position 4 of the phenylthio group by  $8\text{--}14\text{ nm}$ , whilst the electron accepting nitro group exerts a hypsochromic shift by  $12\text{ nm}$ . Compounds 8–10 (Table II) also reveal 3 absorption bands the position of which, and especially of the K-band, is considerably affected by the substituent at  $\text{C}_{(5)}$ . The 5-phenyl-2-furyl derivative (compound 9, Table II) has this band extended to the visible region of the spectrum due to the extension of the conjugated system of the molecule. On the other hand, K-band of 5-phenylsulphonyl-2-furyl derivative (compound 10, Table II) is markedly hypsochromically shifted. Comparison of K-bands of 5-phenyl-2-furyl- ( $\lambda_{\text{max}}$  427 nm) and 5-phenylthio-2-furyl

TABLE II  
UV ( $\lambda_{\text{max}}$  nm) and IR ( $\text{cm}^{-1}$ ) Spectral Bands

No	$\lambda_{\text{max}}$	(log $\epsilon$ )	$\lambda_{\text{max}}$	(log $\epsilon$ )	$\lambda_{\text{max}}$	(log $\epsilon$ )	$\nu(\text{NO}_2)_{\text{a}}$	$\nu(\text{NO}_2)_{\text{as}}$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$
1	238	(4.21)	313	(4.27)	386	(4.31)	1 355	1 555	1 603	1 664
2	233	(4.22)	313	(4.26)	392	(4.25)	1 356	1 556	1 602	1 664
3	235	(4.30)	314	(4.26)	400	(4.23)	1 354	1 554	1 597	1 659
4	263	(4.40)	313	(4.23)	398	(4.19)	1 354	1 554	1 597	1 658
5	235	(4.18)	309	(4.17)	387	(4.21)	1 352	1 555	1 601	1 659
6	238	(4.28)	311	(4.26)	384	(4.28)	1 355	1 558	1 603	1 658
7	227	(4.13)	313	(4.38)	373	(4.33)	1 347	1 555	1 607	1 659
8	233	(3.93)	304	(4.22)	373	(4.35)	1 354	1 560	1 601	1 658
9	225 267	(4.15) (4.12)	319	(4.31)	427	(4.31)	1 353	1 560	1 598	1 660
10	235	(4.10)	300	(4.12)	359	(4.31)	1 348	1 557	1 610	1 667

<sup>a</sup> Inflection.

derivatives ( $\lambda_{\max}$  386 nm) shows that the presence of a sulphide grouping in the molecule resulted in a hypsochromic shift of the K-band by 41 nm. This fact evidences an interaction of the 4-X-phenylthio grouping with the remaining moiety of the molecule as proved by compounds 1–7 (Table II) possessing a sulphide bonding, but it is, nonetheless, substantially weaker than that of 5-phenyl-2-furyl derivative. Like results were found also with UV spectra of azomethines derived from 5-(4-nitrophenyl)- and 5-(4-nitrophenylthio)-2-furaldehydes<sup>7</sup>.

## EXPERIMENTAL

5-(4-X-Phenylthio)-2-furaldehydes were obtained from sodium 4-substituted thiophenolates and 5-bromo- or 5-iodo-2-furaldehydes in ethanol or from 4-substituted thiophenols and 5-bromo-2-furaldehyde in acetone in the presence of potassium carbonate<sup>6</sup>. 5-Phenylsulphonyl-2-furaldehyde was synthesized from sodium benzenesulphinate and 5-bromo-2-furaldehyde in dimethylformamide<sup>8</sup>, 5-phenyl-2-furaldehyde by arylation of 2-furaldehyde with benzenediazonium chloride under conditions of Meerwein reaction<sup>9</sup> and 5-nitro-2-acetylfuran by nitration of 2-acetylfuran with fuming nitric acid in acetic anhydride<sup>10</sup>.

### Condensation of 5-(4-X-Phenylthio)-2-furaldehydes with 5-Nitro-2-acetylfuran

5-(4-X-Phenylthio)-2-furaldehyd (0.01 mol) was dissolved in ethanol (10 ml) at elevated temperature and added to a solution of 5-nitro-2-acetylfuran (1.55 g, 0.01 mol) in ethanol (15 ml). To this solution, cooled at 30–35°C, a catalyst (pyridine — 1 ml, or piperidine — 3 drops, or concentrated sulphuric acid — 0.5 ml) was added and shaken for 3–4 h. The separated solid was filtered off and crystallized from acetic acid.

### Spectral Measurements

Infrared spectra of substances thus synthesized were measured with a double-beam UR 20 Zeiss (Jena) spectrophotometer at a  $5 \cdot 10^{-3}$  M concentration in chloroform. The UV spectra were recorded with a Specord UV VIS spectrophotometer in the 200–500 nm region in 1 cm cells dioxane being the solvent; concentration  $5 \cdot 10^{-5}$  M. The reading accuracy  $\pm 1$  nm.

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Translated by Z. Votický.