

SYNTHESIS AND POLAROGRAPHIC INVESTIGATION OF 5-PHENOXY-2-FURALDEHYDES*

Viera KNOPPOVÁ^a, Anton BEŇO^b, Rudolf KADA^a and Jaroslav KOVÁČ^a

^a Department of Organic Chemistry,

Slovak Institute of Technology, 880 37 Bratislava and

^b Department of Analytical Chemistry,

Comenius University, 816 00 Bratislava

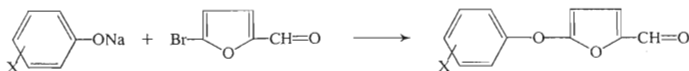
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5-(4- Or 3-X-phenoxy)-2-furaldehydes were prepared from 5-bromo-2-furaldehyde and the respective sodium 4- or 3-X-phenolates (X = 4-Cl, 4-Br, 4-NO₂, 4-CH₃, 3-NO₂, 4-CH₃O, 4-COOC₂H₅, 4-SCH₃, 3-NHCOCH₃ in dimethyl sulfoxide. The transmission effect of a substituent on the reaction centre through oxygen is discussed on the basis of polarographic study of the CHO group.

Our preceding papers concerning the study of furan derivatives with incorporated benzoyl¹, phenylthio and phenylsulfonyl² systems showed the possibility to transmit the polar effects of substituents on the reaction centre in the molecule through the furan ring. Further suitable compounds for such a study are phenoxy derivatives of 2-furaldehyde. 5-(4-Methylphenoxy)-2-furaldehyde, the intermediate in the synthesis of biologically active thiosemicarbazides, was prepared³ by formylation of 4-tolyl-2-furyl ether; the 4-nitro and 4-chloro derivatives were obtained by reacting 5-bromo-2-furaldehyde with the corresponding phenolates⁴ under conditions applied also in this project.

The aim of this paper was to prepare a series of 5-(4- or 3-X-phenoxy)-2-furaldehydes serving as model substances for the examination of the substituent effect through oxygen atom and furan ring on the reaction centre — the aldehyde group *via* the half-wave potentials of the aldehyde group.

5-Bromo-2-furaldehyde was the starting material for the preparation of 5-phenoxy-2-furaldehydes. The course of this S_N reaction is close to that of thiolates⁵, or alkali metal salts of benzenesulfinic acids⁶, which afford the corresponding 5-arylthio or 5-arylsulfonyl-2-furaldehydes.



X = 4-Cl, 4-Br, 4-NO₂, 3-NO₂, 4-CH₃, 4-CH₃O, 4-COOC₂H₅, 4-SCH₃, 3-NHCOCH₃.

* Part CXLIII in the series Furan Derivatives; Part CXLII: This Journal 45, 155 (1980).

TABLE I
Characteristic Data of 5-(4- or 3-X-Phenoxy)-2-furaldehydes

Number X	Molecular formula (M)	M.p., °C yield, %	Calculated/Found		λ_{\max} , nm $\log \epsilon$	$\tilde{\nu}(\text{C}=\text{O})$ cm^{-1}	$-E_{1/2}$, V ^a (id/c)
1 4-OCH ₃	C ₁₂ H ₁₀ O ₄ (218.2)	77—78 52	66.05 65.90	4.62 4.53	222 4.43	308 3.38	1.234 (3.6)
2 4-CH ₃	C ₁₂ H ₁₀ O ₃ (202.2)	49—50 46.5	71.28 71.10	4.98 4.85	218 s 3.79	304 4.30	1.221 (3.5)
3 4-SCH ₃	C ₁₂ H ₁₀ O ₃ S (234.2)	77—78 68.5	61.54 61.40	4.30 4.35	205 4.30	304 4.36	1.209 (3.9)
4 3-NHCOCH ₃	C ₁₃ H ₁₁ NO ₄ (245.2)	121—122 42.0	63.67 63.50	4.52 4.45	205 4.33	302 4.37	1.195 (3.4)
5 4-Cl	C ₁₁ H ₇ ClO ₃ (222.6)	50—51 48.5	59.35 59.30	3.17 3.10	15.92 ^d 15.72	— 4.33	1.192 (3.7)
6 4-Br	C ₁₁ H ₇ BrO ₃ (267.1)	70—73 52.5	49.46 49.40	2.64 2.40	29.92 ^e 29.58	— 4.32	1.188 (3.2)
7 4-COOC ₂ H ₅	C ₁₄ H ₁₂ O (260.2)	28—30 50.5	64.62 64.50	4.64 4.55	223 4.00	298 4.30	1.171 (3.3)
8 3-NO ₂	C ₁₁ H ₇ NO ₅ (233.2)	72—75 42.5	56.65 56.50	3.02 3.10	6.00 ^c 6.10	293 4.42	1.340 (5.8)
9 4-NO ₂	C ₁₁ H ₇ NO ₅ (233.2)	82—84 40.0	56.65 56.28	3.02 3.10	6.00 ^c 6.08	294 4.45	1.395 (6.4)

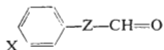
^a pH 11.6, id/c in $\mu\text{A } 1 \text{ mol}^{-1}$; ^b % S; ^c % N; ^d % Cl; ^e % Br; ^f $\tilde{\nu}(\text{C}=\text{O})$ of the ester carbonyl group; s shoulder.

Electronic spectra of 5-phenoxy-2-furaldehydes reveal 2 absorption bands: that in the 211–223 nm range can be associated with transitions in the benzene ring, that in the 308–293 nm range reflects the oscillation of electrons in the whole conjugated system. The latter is influenced to a very low extent by the type of substituent (4-CH₃O λ 308 nm; 4-NO₂ λ 294 nm, Table I).

Examination of the principal polarographic characteristic data $i = f(c, h^{1/2})$ of phenoxy-2-furaldehydes showed the linear course: the lines intersect the starting position of coordinates. It could be, therefore assumed that processes at the mercury electrode are diffusion controlled. The derivatives under study behave similarly as their analogues, 5-arylthio and 5-arylsulfonyl-2-furaldehydes⁷ in relation to the pH of the medium. It can be presumed that reduction of the aldehyde group proceeds by the same mechanism as found with reduction of substituted benzaldehydes⁸. The measured $E_{1/2}$ values of the prepared 5-phenoxy-2-furaldehydes (Table I) served for statistical correlation with σ constants⁹. The $E_{1/2}$ values of nitro derivatives were substantially higher and were, therefore, not statistically evaluated. On the basis of diffuse current it can be presumed that the wave of aldehyde group compare with that of NHOH reduction to amino group. The calculated reaction constant $\rho = 0.084 \pm 0.004$ ($q = -1.21 \pm 0.001$; $r = 0.995$; $s = 0.002$) indicates a certain slowing-down effect of the substituent through oxygen atom when compared with the value $\rho = 0.179$ for 5-aryl-2-furaldehydes¹⁰. Similarly, comparison with a series of substituted benzaldehydes (Table II, $\rho = 0.298$) showed lowering of the transmission effect through O-furan grouping ($\rho = 0.084$), which equals approximately the transmission through S-furan ($\rho = 0.086$). Values of transmission coefficients π' are in favour of this finding. Numerical values of transmission coefficients π' (Table II)

TABLE II

Statistical Parameters of the Linear Relationship from Polarographic Study of Compounds of General Formula



Series ^a	Z	n	$\rho \pm s_\rho$	$-q \pm s_q$	r	s	π'
I	—	11	0.298 ± 0.015^7	1.532 ± 0.004	0.987	0.016	—
II	S-furan	7	0.086 ± 0.003^7	1.324 ± 0.00	0.996	0.002	0.29
III	SO ₂ -furan	6	0.065 ± 0.003^7	1.092 ± 0.00	0.995	0.002	0.21
IV	O-furan	9	0.084 ± 0.004	1.21 ± 0.001	0.995	0.002	0.281
V	furan	9	0.179 ± 0.005^{10}	1.42 ± 0.002	0.997	0.003	0.60

^a n Number of derivatives in a series; ρ slope and its error; q calculated $E_{1/2}$ value for the fundamental derivative and its error; r correlation coefficient; s standard deviation; π' transmission coefficient.

were calculated from equation $\pi' = \varrho/\varrho_0$, where ϱ were the reaction constants of series II, III, IV and V, ϱ_0 was the value for 4-substituted benzaldehydes.

EXPERIMENTAL

Electron absorption spectra were measured with a Specord UV VIS (Zeiss, Jena) spectrometer in the 200–800 nm region. Measured were methanolic solutions at a $1\text{--}5 \cdot 10^{-5}\text{M}$ concentration in 1 cm-cells. The IR spectra of chloroform solutions were taken on a UR-20 (Zeiss, Jena) apparatus in 0.26 mm-NaCl cell at a 0.03M concentration.

5-(4- Or 3-X-phenoxy)-2-furaldehydes

Sodium metal (2.3 g, 0.1 mol) was added to a solution of the respective phenol (0.1 mol) in dimethyl sulfoxide (125 ml) and after dissolution 5-bromo-2-furaldehyde (15.5 g, 0.1 mol) was successively added. The mixture was heated on a steam bath for 4 h, poured into water (250 ml) and steam-distilled. The residue in the flask was extracted with ether (5 · 100 ml), the combined ethereal layers washed with water, dried with Na_2SO_4 and the solvent evaporated. The solid crude aldehyde was crystallized from ethanol or ethyl acetate–light petroleum. Characteristic data of this way prepared 5-(4-phenoxy)-2-furaldehydes are listed in Table I.

Polarographic Measurements

Polarographic curves were recorded with an OH-102 polarograph (Radelkis, Budapest) in a modified Kalousek vessel with a separated calomel electrode. The mercury drop electrode had at working height of the reservoir $h = 58\text{ cm}$ the flow rate $m = 2.2\text{ mg s}^{-1}$ and drop life $t_1 = 3\text{ s}$. Values of half-wave potentials were measured by a triple-electrode system against a nonpolarized saturated calomel electrode by means of QTK-compensator (Metra, Blansko) using a glass G 202 B and K 401 calomel electrodes. Measured were aqueous-ethanolic Britton–Robinson buffer solutions at pH 2–12 at a depolarisator concentration 0.1 mM. Oxygen was removed from solutions by passing a purified nitrogen for 5 min.

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