SYNTHESIS AND PROPERTIES OF 5-PHENOXYFURANCARBOXYLIC ACIDS*

Viera KNOPPOVÁ[a], Anton BEŇO[b] 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 50 Bratislava*

Received May 16th, 1979

Furancarboxylic acids were prepared by oxidation with Ag_2O of the corresponding 5-(X-phenoxy)-2-furaldehydes (X = 4-OCH_3, 4-SCH_3, 3-$NHCOCH_3$, 4-Cl, 4-Br, 4-$COOC_2H_5$, 3-NO_2, and 4-NO_2). The appearing pK_a values of the synthesized acids were determined by potentiometric titration. The transfer effect of the substituents through the oxygen bridge is discussed and the transfer coefficient is compared with π' values of other linking groups in the furan series.

In connection with studies of transfer effects of substituents to the reaction center through an oxygen bridge and a furan ring some types of 5-substituted furancarboxylic acids have already been studied. Functional groups they bore at the position 5 of the furan ring were arylthio-[1], arylsulphonyl-[1], aryl-[2], and benzoyl-[3]. 5-Phenoxy-2-furancarboxylic acids are another class of derivatives suitable for studies aimed at the clasification of the transfer of electronic effects of substituents.

5-Phenoxy-2-furancarboxylic acids described herein were prepared by oxidation of the corresponding aldehydes with Ag_2O under alkaline conditions. Physical constants observed for the prepared substances are summarized in Table I. The starting 5-phenoxy-2-furaldehydes were prepared by a nucleophilic substitution reaction from 5-bromo-2-furaldehyde and substituted sodium phenolates in dimethylsulphoxide[4]. When freshly prepared Ag_2O was used oxidation of aldehydes under alkaline conditions at room temperature gave high yields of the corresponding acids.

The electron spectra of 5-phenoxy-2-furancarboxylic acids show two absorption bands. The one at $\lambda = 214-223$ nm can be assigned to the transfer of electrons in the benzene ring and the other is at ~ 270 nm (Table I). Compared with the band in the spectra of the corresponding aldehyde ($\lambda = 308-293$ nm) the λ observed for the second band is shifted by ~ 30 nm to the lower values, confirming the conclusions arrived at previously[5]. As far as the IR spectra are concerned (Table I) we have focussed our attention mainly at the band corresponding to the carbonyl group. In the spectra of 5-phenoxy-2-furancarboxylic acids the absorption band

---

* Part CXLVII in the series Furan Derivatives; Part CXLVI: This Journal *45*, 906 (1980).

TABLE I

Physico-Chemical Constants and Spectral Data for 5-(4- and 3-X-Phenoxy)-2-furancarboxylic Acids

Compound X	Formula (mol.w.)	M.p. yield, %	Calculated/Found			λ_{max}, log ε nm		$\tilde{\nu}_{C=O}$ cm^{-1}	pK_a
			% C	% H	% Het				
I	$C_{12}H_{10}O_5$	144—146	61·54	4·30	—	222	270	1 680	4·70
4-OCH_3	(234·2)	72·7	61·40	4·38		(3·81)	(4·10)	1 700 s	
II	$C_{12}H_{10}O_4$	143—144	66·05	4·62	—	220	270—3	1 675	4·58
4-CH_3	(218·2)	70·0	66·20	4·58		(3·84)	(4·22)	1 700 s	
III	$C_{12}H_{10}O_4S$	156—158	57·60	4·02	12·80^a	205	266	1 685	4·50
4-SCH_3	(250·2)	48·0	57·45	3·98	12·72	(4·25)	(4·34)	1 705 s	
IV	$C_{13}H_{11}NO_5$	157—158	59·77	4·24	5·36^b	249	284 s	1 680	4·45
3-$NHCOCH_3$	(261·2)	58·5	59·60	4·18	5·08	(4·34)	(3·97)	1 718 s	
V	$C_{11}H_7ClO_4$	164—165	55·37	2·96	14·86^c	223	265	1 670	4·42
4-Cl	(238·6)	63·5	55·30	2·85	15·17	(3·83)	(4·16)	1 690 s	
VI	$C_{11}H_7BrO_4$	166—168	46·66	2·49	28·22	222	265	1 670	4·38
4-Br	(283·1)	71·4	46·48	2·52	28·27	(3·91)	(4·20)	1 680 s	
VII	$C_{14}H_{12}O_5$	238—240	64·62	4·65	—	—	262	1 695	4·30
4-$COOC_2H_5$	(260·2)	65·5	64·45	4·55	—	—	(4·33)	1 680 s	
VIII	$C_{11}H_7NO_6$	179—181	53·01	2·83	5·62^b	—	262	1 693	4·22
3-NO_2	(249·2)	68·5	52·90	2·78	5·75	—	(4·42)	1 680 s	
IX	$C_{11}H_7NO_6$	189—191	53·01	2·83	5·62^b	214	267	1 705	4·15
4-NO_2	(249·2)	66·6	52·90	2·75	5·70	(4·05)	(4·26)	1 680 s	

^{a} % S; ^{b} % N; ^{c} % Cl; ^{d} % Br; s shoulder.

of the C=O valency vibrations is located at 1705 – 1670 cm^{-1} and shows a shoulder, as does the one present in the spectra of 5-benzoyl-2-furancarboxylic acids[3]. The non-symmetry of the band may be attributed to the existence of *s-cis* and *s-trans* arrangement of the carbonyl group and the system of multiple bonds of the furan ring.

The pK_a values of the synthesized acids (Table I) lie within 4·70 (for 4-OCH_3) and 4·15 (for 4-NO_2). The observed $\Delta pK_a = 0{\cdot}55$ indicates that, as a result of a transfer of electronic effects through the atom of oxygen and the furan ring, the substituent X at the position 4 and 3 of the benzene ring causes a decrease or an increase of the acidity of the carboxyl group. From the found pK_a values the reaction constants $\varrho = 0{\cdot}472 \pm 0{\cdot}0299$ ($r = 0{\cdot}986$), $s = 0{\cdot}03$ and $q = 4{\cdot}53 \pm 0{\cdot}02$ for the linear function $pK_a = f(\sigma_p)$ were calculated. The higher ϱ value (0·560) found[2] for a series of 5-aryl-2-furancarboxylic acids suggests that an oxygen atom introduced into the basic arylfuran system decreases the transfer coefficient π'. Table II shows values found for systems studied so far. They were calculated using the equation $\pi' = \varrho/\varrho_0$, where ϱ are reaction constants of the individual series of furan derivatives given by a function $pK_a = f(\sigma_p)$, and σ_0 is the reaction constant of benzoic acids[6] (1·522). As a result of the introduction of the furan ring into the benzoic system the reaction constant ϱ decreases ($\varrho = 1{\cdot}522 \rightarrow$, $\varrho = 0{\cdot}560$), and the transfer coefficient π', as a result of the introduction of a linking group, decreases in the order -CO-furan < > -O-furan ≅ -S-furan > -SO_2furan, which is basically in agreement with the order found for similar series of aldehydes[4].

EXPERIMENTAL

The electron absorption spectra (200—800 nm) for solutions (1—5 . 10^{-5}M) in methanol were recorded with a Specord UV VIS (Zeiss) spectrometer using 1 cm cells. The IR spectra (3600 to 600 cm^{-1}) were measured applying KBr technique (2 mg of a substance/g KBr) with a double beam UR 20 (Zeiss) spectrometer using sodium chloride cells.

TABLE II
The Transfer Coefficients π' for the Systems

Series	*Z*	ϱ	π'	Ref.
1	-furan-	0·560	0·367	2
2	-S-furan-	0·400	0·262	1
3	-SO_2-furan-	0·26	0·170	1
4	-CO-furan-	0·519	0·341	3
5	-O-furan-	0·472	0·310	this work
6	—	1·522	—	6

The starting 5-phenoxy-2-furaldehydes were prepared from 5-bromo-2-furaldehyde and substituted phenols as described[4].

5-(4- or 3-X-Phenoxy)-2-furancarboxylic Acids

5-Phenoxy-2-furaldehyde (0·1 mol) was added slowly (during 20 min) at 0—5°C to a mixture of silver nitrate (7·5 g) and sodium hydroxide (3·5 g) in water (30 ml). The mixture was stirred for 0·5—3 h during which time silver mirror formed on the walls of the reaction flask. The precipitated silver was filtered off, washed with water and the filtrate was acidified with hydrochloric acid (1 : 1). After 1 h, the separated acid was filtered off, wasshed with water, dried and recrystallized from water.

Determination of Dissociation Constants

The pK_a values were determined at 25 ± 0·02°C by potentiometric titrations of solutions ($5 \cdot 10^{-3}$M, 20 ml) of the acids in aqueous ethanol (1 : 1, *v*/*v*) with 0·1M sodium hydroxide. The measurements were performed with the accuracy of 0·01 pH using a PHM 64 pH meter equipped with a G 202 B glass, and a K 401 calomel electrodes, and an automatic ABU 1 C (Radiometer, Copenhagen) burette. The linear correlation parameters were calculated from pK_a = f(σ_p) values using a Hewlett-Packard calculator, Model 9100 B.

REFERENCES

1. Kada R., Surá J., Kováč J., Jurášek A., Arvay A.: This Journal *41*, 2571 (1976).
2. Krutošíková A., Surá J., Kováč J., Kalfus K.: This Journal *40*, 3357 (1975).
3. Knoppová V., Jurášek A., Vörös V.: This Journal *42*, 3175 (1977).
4. Knoppová V., Beňo A., Kováč J., Kada R.: This Journal, in press.
5. Borisova N. N., Kuľnevich V. G.: Khim. Geterotsikl. Soedin. *1973*, 590.
6. McDaniel D. H., Brown H. C.: J. Org. Chem. *23*, 420 (1958).

Translated by P. Kováč.