

ELECTROREDUCTION OF SUBSTITUTED 2-(5-PHENYL-2-FURFURYLIDENE)-1,3-INDANDIONES

D. ZACHAROVÁ-KALAVSKÁ^a, A. PERJÉSSY^b and P. HRNČIAR^b

^a Department of Analytical Chemistry and

^b Department of Organic Chemistry,
Komenský University, 801 00 Bratislava

Dedicated to Professor S. Stankovianský on the occasion of his 65th birthday.

Received March 3rd, 1972

Analogous polarographic behaviour of substituted 2-(5-phenyl-2-furfurylidene)- and 2-benzylidene-1,3-indandiones was found in basic medium, the compounds of both types giving one four-electron cathodic wave. The preparative electroreduction in these media was carried out with six 2-(5-phenyl-2-furfurylidene)-1,3-indandione derivatives at the potential chosen from the beginning of limiting current of the cathodic wave. It was confirmed that under these conditions the electroreduction of the compounds proceeds via reduction of the >CO-CH=CH- grouping to the $\text{>CH(OH)-CH}_2\text{-CH}_2\text{-}$ grouping, substituted 2-(5-phenyl-2-furfuryl)-3-hydroxy-1-indanones being isolated as reduction products. The structure of the reduction products was confirmed by infrared spectroscopy.

The present work is a continuation of our previous studies^{1,2} dealing with the electroreduction of 2-benzylidene-1,3-indandiones and the structure of the reduction products, *cis*-2-benzyl-3-hydroxyl-1-indanones, containing intramolecular hydrogen bonds between the OH group and π -electrons of the benzyl group. With 2-(5-phenyl-2-furfurylidene)-1,3-indandiones, it was of interest to investigate the effect of the furan ring on the properties of these compounds and their reduction products as well as to study the character of the hydrogen bond formed. These problems will be discussed in a subsequent communication³.

EXPERIMENTAL

Preparation of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones was reported elsewhere⁴. Their melting points agreed well with already recorded data. *Polarographic measurements* were carried out on a polarograph, Model OH-102 (Radelkis, Budapest) in Kalousek cell equipped with saturated calomel electrode (s.c.e.), using glycine buffers or 0.01M-NaOH with the addition of 50% ethanol. *Preparative electroreduction* was effected with high-surface mercury cathode, the reduction potential being stabilized by hand^{1,5}. The electroreduction was carried out with c. $8 \cdot 10^{-5}$ – $1 \cdot 10^{-4}$ M solutions of the compounds in c. 0.01M-NaOH with the addition of 50% ethanol. The reduction potential was chosen from the region of the beginning of limiting current

of the cathodic wave. Products of the electroreduction were isolated by the earlier described method^{1,5} and were purified by crystallization from tetrachloromethane. In addition to polarographic measurements and elemental analyses, the results of infrared spectroscopy were also used in identification of the products. The infrared spectra were recorded with Zeiss, Model UR 20, spectrophotometer in the 3800—800 cm^{-1} region, using 0.2M chloroform solutions in 0.01 cm thick cells.

RESULTS AND DISCUSSION

In the present work we were concerned with basic polarographic investigation of 2-(5-phenyl-2-furfurylidene)-1,3-indandione and several derivatives thereof. Comparison of the results obtained for 2-benzylidene-1,3-indandiones¹ with polarographic behaviour of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones revealed an analogy in the behaviour of these compounds. The solubility of 2-(5-phenyl-2-furfurylidene) derivatives in the aqueous-ethanolic media generally used in polarographic measurements is considerably reduced, relative to the solubility of 2-benzylidene-1,3-indandiones, which is the reason of experimental limitation to the solutions of $\text{pH} \geq 10.5$. In these solutions the solubility of the compounds of both types is greatly increased. 2-(5-Phenyl-2-furfurylidene)-1,3-indandiones exhibit in these solutions only one cathodic

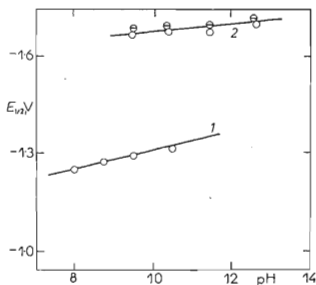


FIG. 1

Dependence of Half-Wave Potentials of Cathodic Waves on pH of Glycine Buffers

1 The wave of undissociated form; 2 the wave of dissociated form; full points 2-(5-phenyl-2-furfurylidene)-1,3-indandione; circles 2-benzylidene-1,3-indandione; 50 per cent of ethanol, conc. $8 \cdot 10^{-5}\text{M}$.

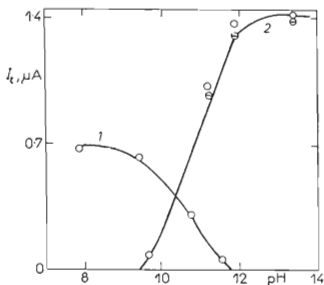


FIG. 2

Dependence of Limiting Current on pH of Glycine Buffers

For legend and denotation see Fig. 1.

wave, the limiting current of which attains maximum in the media of $\text{pH} \geq 11$. On the basis of comparison of the limiting current of this wave with limiting currents of other 1,3-indandione derivatives^{1,5,6}, the wave corresponds to a four-electron process. The half-wave potential of this wave is little dependent on pH and does not depend on the kind of substituent (Fig. 1). In the solutions of 2-benzylidene-1,3-indandiones the pH of which is greater than 10, the first, more positive wave decreases, this being accompanied by simultaneous increase of the more negative wave, which has similar character as the already mentioned electron wave (Figs 1 and 2). This fact is due to the acid-base equilibrium between the yellow, undissociated and insoluble form and the nearly colourless, dissociated form, which is highly soluble in polar solvents. The equilibrium is characterized by $\text{p}K_a \sim 11$, in harmony with the fact that 2-benzylidene- and 2-(5-phenyl-2-furfurylidene)-1,3-indandione, when compared with 2-phenyl-1,3-indandione ($\text{p}K_a \sim 4.7$) (ref.⁶) and 2-benzoyl-1,3-indandione ($\text{p}K_a \sim 4.3$) (ref.⁶) show lesser tendency to dissociate.

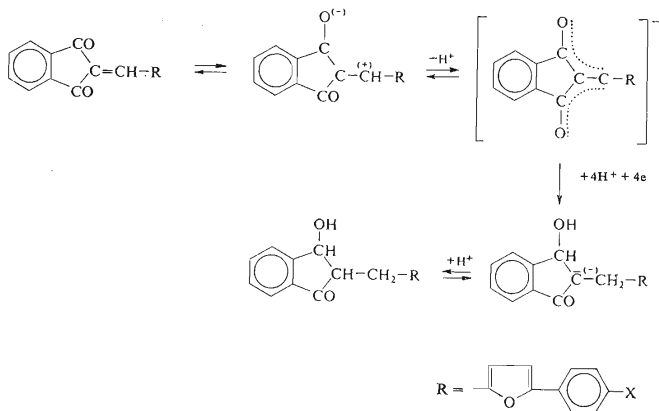
The preparative electroreduction of 2-(5-phenyl-2-furfurylidene)-1,3-indandione derivatives was effected in NaOH solutions at the potential close to the beginning of limiting current of the four-electron cathodic wave. The usual work-up^{1,5} of electroreduction products afforded the compounds whose melting points and elemental analyses are listed in Table I.

TABLE I

Melting Points (Koffler), Elemental Analyses, and Frequencies of CO Vibrations of Reduction Products of 2-(5-Phenyl 2-furfurylidene)-1,3-indandiones

Substituent	Formula	M.w.	Calculated/Found		$\nu(\text{CO}) \text{ cm}^{-1}$	M.p., °C
			% C	% H		
4-OCH ₃	C ₂₁ H ₁₈ O ₄	334-38	75.43	5.44	1 710	143—146
			75.20	5.59		
4-CH ₃	C ₂₁ H ₁₈ O ₃	318-38	79.23	5.70	1 712	160—162
			79.05	5.43		
H	C ₂₀ H ₁₆ O ₃	304-35	78.93	5.30	1 705	132—134
			78.50	5.41		
4-F	C ₂₀ H ₁₅ O ₃ F	322-34	74.52	4.69	1 710	140—142
			74.61	4.80		
4-Cl	C ₂₀ H ₁₅ O ₃ Cl	338-79	70.91	4.46	1 710	170—172
			80.05	4.26		
4-Br	C ₂₀ H ₁₅ O ₃ Br	383-25	62.68	3.95	1 710	130—132
			62.25	4.10		

The infrared spectra of the products of the electroreduction of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones show simple absorption band in the region of 1712 to 1705 cm^{-1} , which corresponds to the CO stretching vibration of 1-indanone skeleton^{1,2,6}. 2-(5-Phenyl-2-furfurylidene)-1,3-indandiones exhibit in this region the typical doublet of the 1,3-indandione system^{4,7}. Strong absorption bands of the C=C stretching vibration around 1600 cm^{-1} , which are typical for 2-(5-phenyl-2-furfurylidene)-1,3-indandiones, are absent in the spectra of reduction products. By contrast, at around 2980 and 2940 cm^{-1} there occur strong absorption bands of the symmetrical and asymmetrical C—H stretching vibrations. In the region of 3600–3200 cm^{-1} there appears a broad absorption band, corresponding to stretching vibrations of the associated and free OH groups. From the foregoing it follows that the negative cathodic wave in the basic medium represents four-electron reduction, during which, analogously to 2-benzylidene-1,3-indandiones, the >CO-C=CH- grouping of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones is reduced under the formation of 2-(5-phenyl-2-furyl)-3-hydroxy-1-indandiones according to Scheme 1.



SCHEME 1

We thank Dr R. Frim and Dr A. Krutošiková for the gift of phenylfurylaldehydes used in the preparation of phenylfurfurylpyridene indandiones.

REFERENCES

1. Zacharová-Kalavská D., Perjéssy A.: *This Journal* 36, 1406 (1971).
2. Perjéssy A., Zacharová-Kalavská D.: *This Journal* 35, 3802 (1970).
3. Perjéssy A., Zacharová-Kalavská D., Hrnčiar P.: *Acta Fac. Rerum Nat. Univ. Comen.*, in press.
4. Perjéssy A., Hrnčiar P., Krutošíková A.: *Tetrahedron* 28, 1025 (1972).
5. Zacharová-Kalavská D., Perjéssy A., Vida M.: *This Journal* 38, 892 (1973).
6. Kalavská D.: *Thesis*. Komenský University, Bratislava 1969.
7. Perjéssy A., Hrnčiar P.: *Tetrahedron* 27, 6159 (1971).

Translated by J. Hetflejš.