

ELECTROREDUCTION OF THE ENOLATE-ANIONS OF SOME 2-ARYLTHIO- AND 2-AROXY-1,3-INDANDIONES. INFRARED SPECTRA AND STRUCTURE OF REDUCTION PRODUCTS

A. PERJÉSSY^a, D. ZACHAROVÁ-KALAVSKÁ^b and M. LÁCOVÁ^a

^aDepartment of Organic Chemistry and

^bDepartment of Analytical Chemistry, Komenský University, Bratislava

Received February 9th, 1971

It has been found that polarographic behaviour of 2-arylthio- and 2-aroxy-1,3-indandiones is similar to that of 2-aryl-1,3-indandiones. New derivatives of *cis*-3-hydroxy-2-phenylthio-1-indanone were isolated as the products of preparative two-electron electroreduction of the enolate-anions of some 2-arylthio-1,3-indandiones. The structure and isomerism of these compounds is discussed on the basis of their IR spectra in the region of the C=O and O—H stretching vibrations. In the preparative electroreduction of the enolate-anions of 2-aroxy-1,3-indandiones it has been observed that the reduction products, 3-hydroxy-2-aroxy-1-indanones, are oxidised on isolation to the starting 2-aroxy-1,3-indandiones.

We have recently studied¹⁻⁴ a preparative electroreduction of 2-phenyl-1,3-indandione, 2-arylmethylene- and 2-acyl-1,3-indandiones, along with the infrared spectra and structure of the reduction products. In the present work, which continues our previous studies, we deal with the preparative electroreduction of the enolate-anions of 2-arylthio- and 2-aroxy-1,3-indandiones and with the structure of reduction products studied by IR spectroscopy. The electroreduction of sodium salts of the following compounds was examined: 2-phenylthio-1,3-indandione, 2-(4-methylphenylthio)-1,3-indandione, 2-(2-methylphenylthio)-1,3-indandione, 2-(2,5-dichlorophenylthio)-1,3-indandione, 2-phenoxy 1,3-indandione, 2-(4-methylphenoxy)-1,3-indandione, and 2-(4-chlorophenoxy)-1,3-indandione.

EXPERIMENTAL

The preparation of 2-arylthio- and 2-aroxy-1,3-indandiones was already reported⁵⁻⁷. Sodium salts of these compounds were prepared by heating 3-arylthiomethylene- and 3-aroxy-methylene-phthalides in 1% methanolic sodium methoxide to about 50°C for half an hour. Then the salts were freed from methanol by evaporation *in vacuo*, washed by ether and isolated. Their purity was checked by IR spectroscopy.

Polarographic measurements were carried out on LP 60 instrument at $20 \pm 0.5^\circ\text{C}$, using a polarographic cell designed by Kalousek with reference saturated calomel electrode (S.C.E.). The preparative electroreduction on a high-surface mercury cathode was described elsewhere^{8,9}. The electroreduction was carried out with freshly prepared $5 \cdot 10^{-5} - 5 \cdot 10^{-4}\text{M}$ aqueous solutions

of the compounds in c. $5 \cdot 10^{-3}$ — $5 \cdot 10^{-2}$ N sodium hydroxide. Before commencing the reduction the solutions were freed from oxygen by introduction of a stream of nitrogen into the reduction vessel. The reduction itself was carried out with the exclusion of air. In the electrochemical measurements the ionic strength of the solutions 0.1 was maintained by KCl. After the electroreduction was completed, the solutions were made neutral and extracted with ether. After evaporation of the ether, the products were crystallized from tetrachloromethane. Melting points and analytical data of several new 3-hydroxy-2-arylthio-1-indanones are presented in Table I.

TABLE I

Melting Points and Elemental Analyses of New 3-Hydroxy-2-arylthio-1-indanones I

Aryl group	M. p., °C	Formula (M.w.)	Calculated/Found		
			% C	% H	% S
Phenyl	140—141	C ₁₅ H ₁₂ O ₂ S (256.3)	70.24	4.72	12.51
			70.38	4.81	12.35
2-Methylphenyl	103—105	C ₁₆ H ₁₄ O ₂ S (270.4)	71.09	5.23	11.84
			70.88	5.37	11.61
2,5-Dichlorophenyl	115—117	C ₁₅ H ₁₀ O ₂ SCl (325.2)	55.39	3.09	21.81
			55.21	3.20	21.69
4-Methylphenyl	145—146	C ₁₆ H ₁₄ O ₂ S (270.4)	71.09	5.23	11.84
			71.18	5.17	11.65

Infrared spectra of electroreduction products were measured on a Zeiss UR 20 spectrophotometer, in the 2000—700 cm⁻¹ and 3800—2800 cm⁻¹ regions. The wavenumber scale of the instrument was calibrated with the standard spectrum of polystyrene foil and water vapour. The measurements were carried out with $6 \cdot 10^{-2}$ M chloroform solutions (cell 0.008 cm thick) and 10^{-3} M, $5 \cdot 10^{-4}$ M, and $2 \cdot 10^{-4}$ M tetrachloromethane solutions of the compounds (cells thick 2 cm, 4 cm, and 10 cm, respectively). The solvents, analytical purity, were dried and purified prior to use in the usual manner.

RESULTS AND DISCUSSION

It has been reported that 2-arylthio-1,3-indandiones⁵, and especially 2-aroxy-1,3-indandiones¹⁰, undergo decomposition, both in acidic solutions and in solid state. This led us to use in the electroreduction sodium salts of 2-aroxy- and 2-arylthio-1,3-indandiones, in place of the parent compounds, since these salts are much more stable.

Polarographic behaviour of 2-arylthio- and 2-aroxy-1,3-indandiones is similar to that of 2-aryl-1,3-indandiones². Depending on pH and a buffer used, these compounds are reduced in one or two two-electron polarographic waves. In basic media, *i.e.* in the form of enolate-anions, the reduction proceeds in one two-electron cathodic wave, the limit current of which is diffusion current.

2-Arylthio-1,3-indandiones

During electroreduction of the enolate-anions of 2-arylthio-1,3-indandiones at the reduction potential of about 1620 mV/SCE, the solution progressively decolourizes, which indicates a decrease in concentration of the reduced compound. In the polarographic check of the course of the reduction, a new polarographic wave has not been detected; only decrease of limit current of the original wave was observed. The products of the electroreduction are stable and do not undergo oxidation upon introduction of air oxygen into the solution of the reduced compound. After the electroreduction of 2-arylthio-1,3-indandiones, homogeneous reduction products were always isolated.

The infrared spectra of the products of reduction of the enolate-anions of 2-arylthio-1,3-indandiones (in chloroform) show only one strong absorption band of the C=O stretching vibration at 1718–1710 cm^{-1} , unlike 2-arylthio-1,3-indandiones¹¹, the spectra of which exhibit characteristic doublet of the assymmetric and symmetric vibration of the 1,3-dicarbonyl system, located at 1762–1752 cm^{-1} and 1725 to 1720 cm^{-1} . In the spectra of $6 \cdot 10^{-2}\text{M}$ solutions of these compounds in chloroform

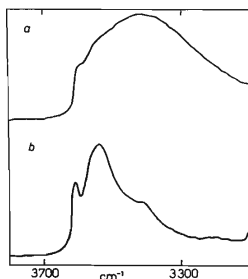


FIG. 1

IR Spectrum of 3-Hydroxy-2-phenylthioindanone

a $6 \cdot 10^{-1}\text{M-CHCl}_3$ (cell 0.008 cm thick),
b $2 \cdot 10^{-4}\text{M-CCl}_4$ (cell ~ 10 cm thick).

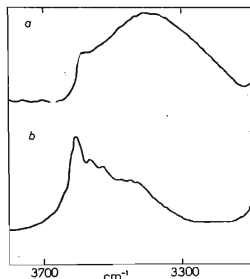


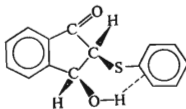
FIG. 2

IR Spectrum of 3-Hydroxy-2-(2,5-dichlorophenylthio)indanone

a $6 \cdot 10^{-1}\text{M-CHCl}_3$ (cell 0.008 cm thick),
b $2 \cdot 10^{-4}\text{M-CCl}_4$ (cell ~ 10 cm thick).

at about 3400 cm^{-1} one can observe a broad band of the stretching vibration of associated O—H groups, and at 3600 cm^{-1} , as a shoulder, the band corresponding to the stretching vibrations of free O—H groups (Figs 1a and 2a). From the foregoing as well as from the results of elemental analysis (Table I) and polarographic measurements it follows that the isolated product of the electroreduction of the enolate-anions of 2-arylthio-1,3-indandiones are the corresponding 3-hydroxy-2-arylthio-1-indanones.

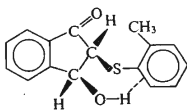
In the spectra of 3-hydroxy-2-arylthio-1-indanones the intensity of a broad band of the stretching vibration of associated O—H group decreases when concentration of measured solutions (in tetrachloromethane) is progressively decreased, indicating the break of intermolecular hydrogen bonds between the hydroxyl groups. At the lowest concentration used ($2 \cdot 10^{-4}\text{ M}$), both the spectrum of 3-hydroxy-2-phenylthio-1-indanone and that of 3-hydroxy-2-(4-methylphenyl)-1-indanone, besides the shoulder at about 3400 cm^{-1} , show only two narrow absorption bands at about 3605 cm^{-1} and 3535 cm^{-1} (Fig. 1b). The shoulder at about 3400 cm^{-1} can be assigned to the first overtone of the C=O stretching vibration. The absorption band at about 3605 cm^{-1} corresponds to the free O—H stretching vibrations, while the more intense band at about 3535 cm^{-1} arises from the stretching vibrations of the O—H groups bonded by intramolecular hydrogen bond. Like in 3-hydroxy-2-phenyl-1-indanone¹ and derivatives of 3-hydroxy-2-benzyl-1-indanone³, also here we deal with intramolecular hydrogen bonding between the hydroxylic hydrogen atom and π -electrons of the benzene ring of the arylthio group (I), the frequency shift in 3-hydroxy-2-phenylthio-1-indanone being $\Delta\nu(\text{OH}) = 69\text{ cm}^{-1}$ ($\Delta\nu(\text{OH}) = \nu(\text{O—H})_{\text{free}} - \nu(\text{O—H})_{\text{assoc.}}$). The formation of intramolecular hydrogen bond of this type in 3-hydroxy-2-arylthio-1-indanones requires *cis*-orientation of the hydroxyl and arylthio groups with respect to the plane of the 1-indanone ring. From the foregoing it follows that, similarly as with other 2-substituted derivatives of 1,3-indandione^{1,3,4}, with 2-arylthio-1,3-indandiones, too, the two-electron reduction of the carbonyl group is stereospecific, the products of the reduction being *cis*-3-hydroxy-2-arylthio-1-indanones.



I

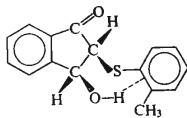
When in the case of 3-hydroxy-2-(2-methylphenylthio)-1-indanone and 3-hydroxy-2-(2,5-dichlorophenylthio)-1-indanone the intermolecular hydrogen bonds are broken

(by decreasing the concentration of tetrachloromethane solutions of these compounds to $2 \cdot 10^{-4}M$), the spectra in the region of the O—H stretching vibrations show different patterns (Fig. 2b), compared to the analogous spectra of 3-hydroxy-2-phenylthio-1-indanone and 3-hydroxy-2-(4-methylphenylthio)-1-indanone. The spectra, besides the band of the stretching vibration of free O—H groups near 3615 cm^{-1} , show in the region of the stretching vibrations of the associated O—H groups, two less intense bands, as shoulders, occurring at about 3570 cm^{-1} and 3535 cm^{-1} . Since these bands appear also in the spectra of the 2-methyl and the 2,5-dichloro derivative, it seems possible to attribute the formation of both bands to intramolecular hydrogen bonds of the type O—H $\cdots\pi$. These compounds, because of hindered rotation around the single bond between sulphur atom and substituted benzene ring, may exist, however, in two conformations (*II* and *III*), which both are able to form π -hydrogen bonds. The band at about 3535 cm^{-1} in the spectrum of 3-hydroxy-(2-substituted phenylthio)-1-indanones can be then assigned to the stretching vibration of the associated O—H groups of the isomers of type *II*, and the band at about 3570 cm^{-1} to the analogous vibrations in the isomers of type *III*.



$$\Delta\nu(\text{OH}) = 77\text{ cm}^{-1}$$

II



$$\Delta\nu(\text{OH}) = 45\text{ cm}^{-1}$$

III

From the foregoing it follows that the value of $\Delta\nu(\text{OH})$ (which is directly proportional to hydrogen bond energy) for rotational isomer *II* is comparable with the $\Delta\nu(\text{OH})$ value (60 cm^{-1}) for 3-hydroxy-2-phenylthio-1-indanone (*I*). On the other hand, in rotational isomer *III*, where substituent in position 2 of the benzene ring sterically affects the formation of intramolecular hydrogen bond, the value of $\Delta\nu(\text{O—H})$, and thus also the energy of this bond, is lower, relative to the hydrogen bonds in structures *I* and *II*. The observed effect of the substituent in position 2 of the benzene ring on the formation of intramolecular hydrogen bond of the type O—H $\cdots\pi$ accords with the results of Oki and Iwamura¹², who found that in 2-arylethanols these bonds are formed between the hydroxylic hydrogen atom and π -electrons located between C_1 and C_2 atoms of the benzene ring, similarly as it is shown in structures *I—III*.

A comparison of the value of $\Delta\nu(\text{OH})$ for 3-hydroxy-2-phenylthio-1-indanone (*I*) with the corresponding values for 3-hydroxy-2-phenyl-1-indanone (34 cm^{-1}) and 3-hydroxy-2-benzyl-1-indanone³ (56 cm^{-1}) shows that these, as well as the energies

of the corresponding hydrogen bonds, increase in the order $C_6H_5 - < C_6H_5CH_2 - < C_6H_5S-$. This indicates that hydrogen bonding in these systems is affected both by geometry of the group bonded to the C_1 atom of interacting benzene ring and by the distance between this carbon atom and the C_2 atom of the 1-indandione skeleton.

2-Aroxy-1,3-indandiones

Unlike 2-arylthio-1,3-indandiones, the preparative electroreduction of the enolate-anions of 2-aroxy-1,3-indandiones proceeds without any anomalies, as checked by polarographic method. During the reduction, the solutions progressively decolourize, the height of the original polarographic wave decreases, a new polarographic wave does not appear. When isolating the products by the procedure described in Experimental, we have found that their polarographic waves, elemental analyses, melting points and infrared spectra agree with the data obtained for the starting 2-aroxy-1,3-indandiones. Furthermore, the same results were obtained, irrespective of whether the reduction was carried out in the presence or the absence of air oxygen. After the reduction had been completed, the solutions of reduction products were oxidized by a stream of air oxygen, and that both in the used basic and acidic medium; no changes in polarographic records have however been observed. From the foregoing it can be concluded that electroreduction of the enolate-anions of 2-aroxy-1,3-indandiones proceeds by the same mechanism as the reduction of the enolate-anions of 2-arylthio-1,3-indandiones, yielding the anions of corresponding 3-hydroxy-2-aroxy-1-indanones, which are, however, re-oxidized on isolation to the starting 2-aroxy-1,3-indandiones.

REFERENCES

1. Zacharová-Kalavská D., Zelenský I., Perjéssy A.: This Journal 36, 2716 (1971).
2. Zacharová-Kalavská D., Perjéssy A.: This Journal 36, 1406 (1971).
3. Perjéssy A., Zacharová-Kalavská D.: This Journal 35, 3802 (1970).
4. Zacharová-Kalavská D., Perjéssy A., Zelenský I.: This Journal 36, 2712 (1971).
5. Lácová M.: Chem. zvesti, in press.
6. Furdík M., Lácová M., Livař M.: Acta Fac. Rerum Nat. Univ. Comen. 12, Chimia, 1968, 265.
7. Lácová M.: Chem. zvesti, in press.
8. Zacharová-Kalavská D.: Thesis. Komenský University, Bratislava 1969.
9. Zelenský I., Zacharová-Kalavská D.: Acta Fac. Rerum Nat. Univ. Comen., in press.
10. Lácová M.: Chem. zvesti, in press.
11. Perjéssy A., Hrnčiar P.: Tetrahedron 27, 6159 (1971).
12. Oki M., Iwamura H.: Bull. Chem. Soc. Japan 32, 1135 (1959).

Translated by J. Hetflejš.