

ELECTROREDUCTION OF THE ENOLATE-ANIONS OF SOME 5,7-DIOXO-6,7-DIHYDRO-5H-DIBENZO[*a,c*]CYCLOHEPTENE DERIVATIVES. THE INFRARED SPECTRA AND STRUCTURES OF 5-OXO-7-HYDROXY-6,7-DIHYDRO-5H-DIBENZO[*a,c*]CYCLOHEPTENES

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

^a Department of Analytical Chemistry,

^b Department of Organic Chemistry, Comenius University, 801 00 Bratislava, and

^c Research Institute of Medicaments, 800 00 Bratislava

Received February 14th, 1974

Basic polarographic investigation of 5,7-dioxo-6,7-dihydro-5H-dibenzo[*a,c*] cycloheptene and its 6-phenyl and 6-benzylidene derivatives was performed. The enolate-anions of these compounds were reduced on a mercury pool cathode. The structure of the products, 5-oxo-7-hydroxy-6,7-dihydro-5H-dibenzo[*a,c*]cycloheptenes, was determined by elemental analysis and IR spectroscopy. The formation of hydrogen bonds between the hydroxy groups and π -electrons of the diphenyl system was confirmed.

This work concerns with the electroreduction of seven-membered β -diketones derived from diphenyl and with the structure of the reduction products. The electrochemical properties of 5,7-dioxo-6,7-dihydro-5H-dibenzo[*a,c*]cycloheptene and its 6-phenyl and 6-benzylidene derivatives and the products of their electroreduction, the derivatives of 5-oxo-7-hydroxy-6,7-dihydro-5H-dibenzo[*a,c*]cycloheptene (*I*), were studied. The present study is a continuation of our previous studies¹⁻³ on the electroreduction of 1,3-indandiones and the structure of their reduction products.

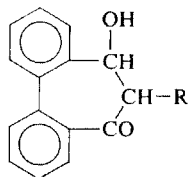
EXPERIMENTAL

5,7-Dioxo-6,7-dihydro-5H-dibenzo[*a,c*]cycloheptene was prepared by reported procedure⁴. Its 6-phenyl derivative was obtained according to ref.⁵. The synthesis and properties of the *p*-benzylidene derivative were reported elsewhere⁶.

Polarographic measurements were carried out on a OH-102 polarograph (Radelkis, Budapest). The solutions contained $5 \cdot 10^{-5}$ M depolarisator; 30 v.% of ethanol was added to Britton-Robinson buffers and their ionic strength was adjusted to a value of $I = 1$.

Preparative electroreduction was performed similarly as in works¹⁻³; 10^{-3} M-NaOH solutions were used and 30 v.% of ethanol was added. The concentration of the compound studied was $5 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ M. The ionic strength of the solutions was adjusted by KCl to a value of $I = 1$. The electroreduction was carried out under nitrogen. Its course was followed polaro-

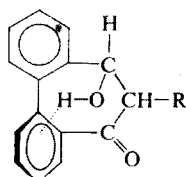
graphically. The decrease of the cathodic wave was only observed. After completion of the reduction, the solutions were made neutral with hydrochloric acid, the ethanol was removed by distillation under reduced pressure at a temperature not exceeding 50°C. The reduction products were extracted with ether and purified by crystallisation from a $\text{CCl}_4\text{-CHCl}_3$ (7 : 3) mixture. The unsubstituted derivative was purified by column chromatography, using Silpear (Kavalier, Votice) and a $\text{CHCl}_3\text{-CCl}_4$ (4 : 1) mixture as an eluent.



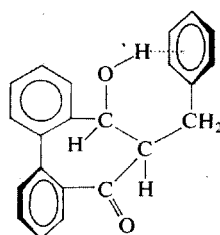
Ia, R = H

Ib, R = C_6H_5

Ic, R = $\text{CH}_2\text{C}_6\text{H}_5$



II



III

Infrared spectra were recorded with a Zeiss, Model UR-20, spectrophotometer (Zeiss, Jena). Approx. 0.2M solutions of the compounds in chloroform (0.01 cm cells) were used for the measurements in the $700\text{--}3800\text{ cm}^{-1}$ region. For the measurements in the $3200\text{--}3800\text{ cm}^{-1}$ region $5 \cdot 10^{-4}\text{M}$ solutions of the compounds in tetrachloromethane were used (4 cm cells). The wave-numbers of absorption band maxima were read with an accuracy of $\pm 2\text{ cm}^{-1}$. The measurements were carried out at $20 \pm 0.5^\circ\text{C}$. The elemental analyses for the reduction products are presented in Table I.

RESULTS AND DISCUSSION

In contradistinction to 1,3-indandiones, the derivatives under study are representatives of seven-membered cyclic systems. The enolate-anions of these compounds are pale yellow due to nonplanar arrangement, unlike the enolate-anions or enol forms of 1,3-indandiones which form planar associates of intense colouration⁷. 5,7-Dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene, its 6-phenyl and 6-benzylidene derivative are polarographically active in the whole pH region of aqueous-ethanolic solutions. With the first two compounds, acid-base equilibrium is observed. In acidic or neutral media the reduction of these compounds occurs in one or two cathodic waves of comparable height. The more positive wave begins to decrease from pH 6, due to the formation of the dissociated form. The positive wave disappears at pH 10, and both compounds are reduced in one two-electron cathodic wave, similarly as the enolate-anion of 2-phenyl-1,3-indandione¹. The 6-benzylidene derivative was studied only in basic solutions, since it was poorly soluble in acid solutions. The reduction

of this compound takes place in one cathodic wave ($\text{pH} > 9$), the limiting current of which is two times higher than in the case of the 6-phenyl derivative. The half-wave potentials of studied compounds are in the range of the half-wave potentials of 1,3-indandione derivatives. Polarographic behaviour of these compounds is analogous to the behaviour of the corresponding 1,3-indandione derivatives¹⁻³. The preparative electroreduction of the three compounds mentioned above was carried out at the potential of the cathodic wave of the enolate-anion of these compounds (c. -1400 mV/s.c.e.). No anomaly was observed during polarographic test. The pale yellow solution turned colourless as the wave decreased.

TABLE I

The Elemental Analyses and Characteristic IR Bands (cm^{-1}) for the Reduction Products, 5-Oxo-7-hydroxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene Derivatives (*I*)

No	Formula (m.v.)	Calculated/Found		$\nu(\text{C}=\text{O})^a$	$\nu_1(\nu_2)^b$	$\Delta \nu_{1,2}(\text{OH})^c$
		% C	% H			
<i>Ia</i>	$\text{C}_{15}\text{H}_{12}\text{O}_2$ (224.3)	80.26	5.39	1 708 s	3 623 s	28
		80.00	5.23			
<i>Ib</i>	$\text{C}_{21}\text{H}_{16}\text{O}_2$ (300.4)	83.98	5.37	1 707 s	3 611 s	35
		83.20	5.54			
<i>Ic</i>	$\text{C}_{22}\text{H}_{18}\text{O}_2$ (314.4)	84.05	5.77	1 701 s	3 618 s	26
		83.80	5.64			

^a In chloroform, 0.2 M; ^b in tetrachloromethane, $5 \cdot 10^{-4} \text{ M}$; ^c $\Delta \nu_{1,2}(\text{OH}) = \nu_1 - \nu_2$; ^d ν_3 3 540 s, $\nu_1 - \nu_3 = 78 \text{ cm}^{-1}$.

The infrared data in Table I show that the products of the preparative electroreduction of the enolate-anions of 5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene and its 6-phenyl and 6-benzylidene derivatives are the 5-oxo-7-hydroxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene derivatives *Ia-c*. The spectra of concentrated solutions of these compounds in chloroform show in the region of the $\text{C}=\text{O}$ stretching vibrations a single band at $1708-1701 \text{ cm}^{-1}$ which is due to the stretching vibration of the carbonyl group, instead of the doublet of symmetrical and asymmetrical vibration of the β -dicarbonyl system (in the case of the 6-phenyl derivative instead of the strong bands of the enol form⁸). Furthermore, the spectrum exhibits the broad band at approx. 3440 cm^{-1} which can be assigned to the stretching vibration of the hydroxy groups bonded by intermolecular hydrogen bridge, and a shoulder at approx. 3600 cm^{-1} which originates from the vibrations of free hydroxy groups. From the

foregoing it follows that only one carbonyl group of the dicarbonyl system of these compounds undergoes reduction. With the 6-benzylidene derivative, the C=C bond of the benzylidene group is also reduced, in addition to the carbonyl group. This is indicated by the absence of the strong absorption band of the C=C stretch at approx. 1600 cm^{-1} , which band appears in the spectrum of the starting compound⁸.

The spectra of these compounds were also measured using diluted solutions of the compounds in tetrachloromethane ($5 \cdot 10^{-4}\text{M}$), *i.e.* in the absence of intermolecular hydrogen bonds. The spectra of the compounds show two strong bands in the region of the O—H stretching vibrations (Table I). It is evident that the higher frequency ν_1 band ($3623\text{--}3611\text{ cm}^{-1}$) is due to the stretching vibration of the free hydroxy group. The geometry and conformation of this group is not yet clear. The lower frequency ν_2 band ($3595\text{--}3576\text{ cm}^{-1}$) can be assigned either to the O—H stretching vibration of the free hydroxy group of the second rotational isomer around the O—C bond (with respect to the above rotational isomer) or to the O—H stretching vibration of the hydroxy group bonded *via* a intramolecular hydrogen bond of the O—H... π type to one of the phenyls group of the diphenyl system *I*. As follows from the studies by Oki and Iwamura⁹⁻¹¹ who investigated the frequencies of the O—H stretching vibrations of a variety of primary, secondary and tertiary alcohols, the difference between the frequencies of the O—H stretching vibrations of the two rotational isomers is in many cases *c.* 10 cm^{-1} , however, it never exceeds 15 cm^{-1} . The $\nu_1 - \nu_2$ difference for the compounds studied equals to $35\text{--}26\text{ cm}^{-1}$. This value is too high to be ascribed to the O—H stretching vibration of free hydroxy groups of the two rotational isomers. On the other hand, the $3595\text{--}3576\text{ cm}^{-1}$ region, in which the ν_2 band occurs, is characteristic for the O—H vibrations of the associated hydroxy groups and only scarcely are the bands due to the vibrations of free O—H groups observed in this region. It can be concluded that the ν_2 band is due to the stretching vibration of the O—H group bonded *via* the intramolecular hydrogen bond to π -electrons of the aromatic ring. From nearly identical values of $\nu_1 - \nu_2$ for all the compounds *I* and Dreiding models it follows that the structure of compounds *I* can be depicted by formula *II*. The distance between the hydrogen atom and the plane of the π -electrons is approx. 0.8 \AA .

The spectrum of 6-benzyl-5-oxo-7-hydroxy-6,7-dihydro-5*H*-dibenzo²[*a*,*c*₄]cycloheptene shows an additional medium band at 3540 cm^{-1} . From examination of the Dreiding model, and in analogy with 2-benzyl-3-hydroxy-1-indandones¹², this band can be assigned to the O—H stretching vibration of the hydroxy group bonded by additional intramolecular hydrogen bond of the O—H... π type (stronger than in the previous case). This can be visualized by structure *III*. As follows from the Dreiding model, the hydroxylic hydrogen lies essentially in the plane of the π -electrons of the benzylic group (*c.* 0 \AA), which results in the greater $\nu_1 - \nu_3$ difference (78 cm^{-1}), compared to *II* ($35\text{--}26\text{ cm}^{-1}$).

REFERENCES

1. Zacharová-Kalavská D., Zelenský I., Perjéssy A.: This Journal 36, 271 (1971).
2. Zacharová-Kalavská D., Perjéssy A.: This Journal 36, 1406 (1971).
3. Perjéssy A., Zacharová - Kalavská D., Hrnčiar P.: Acta Fac. Rerum Nat. Univ. Comen., in press.
4. Ried W., Conte R.: Chem. Ber. 105, 1224 (1972).
5. Alexejev B., Milošev M.: Chem. Ber. 100, 701 (1967).
6. Szemes F., Hrnčiar P.: This Journal, in press.
7. Vanag G.: *Cikličeskije β -Diketony*, p. 54. Izd. Akad. Nauk Latvjijskoj SSR, Riga 1961.
8. Perjéssy A., Szemes F., Hrnčiar P.: Unpublished results.
9. Oki M., Iwamura H.: Bull. Chem. Soc. Japan 32, 950 (1959).
10. Oki M., Iwamura H.: Bull. Chem. Soc. Japan 32, 955 (1959).
11. Oki M., Iwamura H.: Bull. Chem. Soc. Japan 23, 955 (1959).
12. Perjéssy A., Zacharová-Kalavská D.: This Journal 35, 3802 (1970).

Translated by J. Hetflejš.