

ELECTROREDUCTION OF 2-CINNAMOYL-1,3-INDANDIONE AND THE STRUCTURE OF REDUCTION PRODUCT

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Polarographic properties of 2-cinnamoyl-1,3-indandione are in the first approximation the superposition of polarographic properties of 2-acetyl- and 2-benzylidene-1,3-indandione. Polarographic reduction of 2-cinnamoyl-1,3-indandione in an acidic and an alkaline medium proceeds in one six-electron wave. The product of the preparative electroreduction of 2-cinnamoyl-1,3-indandione in the alkaline medium is 2-(3-phenyl-1-hydroxypropyl)-3-hydroxy-1-indanone. The structure of the product was determined by IR and ¹H-NMR spectroscopy. On the basis of the IR spectra, hydrogen bonding in the molecule of the reduction product is discussed.

In previous works^{1,2} we have studied the preparative electroreduction of 2-benzylidene-1,3-indandiones and 2-acyl-1,3-indandiones. In the present communication we deal with the preparative electroreduction of 2-cinnamoyl-1,3-indandione and the structure of the reduction product determined by means of the IR and NMR spectroscopy. The electroreduction was performed with 2-cinnamoyl-1,3-indandione and 2-(4-methoxycinnamoyl)-1,3-indandione.

EXPERIMENTAL

Compounds studied. 2-Cinnamoyl- and 2-(4-methoxycinnamoyl)-1,3-indandione were prepared by condensation of stoichiometric amounts of 2-acetyl-1,3-indandione and benzaldehyde or 4-methoxybenzaldehyde in pyridine. The reaction mixture was heated to the boiling point of pyridine for 4 h. After the pyridine had been removed by distillation under reduced pressure, the reaction product was crystallized from ethanol. The melting points of the obtained products agreed with literature data³. Prior to use in polarographic measurements and in preparative electroreduction, the compounds were recrystallized from ethanol.

Polarographic measurements and preparative electroreduction. Polarographic measurements were carried out with a Polarograph, Model OH-102 (Radelkis, Budapest), using a modified, temperature-controlled Kalousek cell equipped with standard calomel electrode (s.c.e.) and $1 \cdot 10^{-4}$ M solutions of 2-cinnamoyl-1,3-indandione in Britton-Robinson buffers with the addition of 40 v.% ethanol. The pH values of the buffers were determined with pH-meter, Model PH M-26 (Radiometer, Copenhagen), using a glass G 202 B and a calomel K 401 electrode.

The preparative electroreduction was accomplished with high-surface mercury electrode with the aid of QTK compensator (Metra, Blansko, Czechoslovakia), with manual stabilisation of the reduction potential (measured against s.c.e.). The reduction was carried out with $1 \cdot 10^{-4}$ – $5 \cdot 10^{-4}$ M solutions of 2-cinnamoyl- and 2-(4-methoxycinnamoyl)-1,3-indandione in 0.03 M-NaOH with the addition of 35 v.% ethanol. The reduction potential was chosen from the initial region of the limit current and was kept with the accuracy ± 15 mV. All the measurements were carried out at $20 \pm 0.1^\circ\text{C}$ using the solutions with ionic strength 0.1, which was adjusted by potassium chloride. The isolation of reduction products was achieved by the already reported procedure^{1,2}. The products are light-yellow substances, stable in air and in acidic and alkaline media. For $\text{C}_{18}\text{H}_{18}\text{O}_3$ calculated: 76.57% C, 6.43% H; found: 76.90% C, 6.25% H. For $\text{C}_{19}\text{H}_{20}\text{O}_4$ calculated: 73.06% C, 6.45% H; found: 73.27% C, 6.60% H.

Spectroscopic measurements. The infrared spectra were recorded with Zeiss, Model UR 20 spectrophotometer (Jena) in the 2000 – 700 cm^{-1} and 3800 – 2800 cm^{-1} regions. The wave-number scale of the instrument was calibrated with polystyrene foil and water vapour. The $6 \cdot 10^{-2}$ M chloroform solutions of the compounds were measured in 0.008 cm thick cells, and the $2 \cdot 10^{-4}$ M solutions of the compounds in tetrachloromethane in 10 cm thick cells. Prior to the application, the analytical grade solvents were purified and dried in the usual way.

The $^1\text{H-NMR}$ spectra were taken with Tesla, Model BS 487, spectrometer equipped with proton stabilisation and working at 80 MHz. The measurements were carried out by the frequency sweep method. The solvent, deuteriochloroform (99.3% purity), was supplied by Isocomerz (USSR). The concentration of the measured compounds was about 1 w.%. Hexamethylsiloxane (3 v.%) served as the internal standard.

RESULTS AND DISCUSSION

2-Cinnamoyl-1,3-indandione is in Britton–Robinson buffers polarographically active over the whole pH scale. As follows from the dependence of half-wave potentials of the cathodic wave and of the limit current on pH the compound is in the acid-base equilibrium: undissociated form \rightleftharpoons enolate anion + H^+ , which is characterized by the dissociation constant $\text{p}K_a$ 6.5 (Fig. 1). In the weakly acidic to acidic solutions the undissociated form (bright yellow) suffers reduction, which manifests itself in one cathodic wave. The half-wave potential of the wave strongly depends on pH: $E_{1/2}/\Delta\text{pH} \sim -50\text{ mV/pH}$. Starting from about pH 5 this wave decreases and a new, much more negative wave appears. The second wave increases almost as fast as the first, more positive wave decreases. In this medium both forms of the compound are thus reduced. In the media with pH c. 7.7 2-cinnamoyl-1,3-indandione yields only one, more negative wave, its height, when compared with the height of the waves of 2-benzoyl-1,3-indandione^{2,4} and 2-benzylidene-1,3-indandione¹, indicates a six-electron reduction. In the solutions with pH > 7.7 only the light yellow enolate anion of 2-cinnamoyl-1,3-indandione undergoes reduction. The half-wave potential of the cathodic wave of the dissociated form shifts with increasing pH to more negative values only very slowly: $E_{1/2}/\Delta\text{pH} \sim -10\text{ mV/pH}$. From the dependence of the limit current on the concentration of the compound and on the square root of the mercury column height, as well as from temperature measurements, it follows that the cathodic waves have diffusion character.

To verify the six-electron reduction and to confirm the structure of the reduction product we reduced 2-cinnamoyl-1,3-indandione and 2-(4-methoxycinnamoyl)-1,3-indandione preparatively on a high-surface mercury cathode. In the course of the reduction the cathodic wave of the compounds was gradually decreasing, without formation of another wave. The reduction was not influenced either by the air oxygen or by the nature of the organic solvent used. The structure of the isolated electroreduction products was determined by comparing the infrared and $^1\text{H-NMR}$ spectra of these compounds with the spectra of the starting compound, 2-cinnamoyl-1,3-indandione.

The molecule of 2-cinnamoyl-1,3-indandione contains four double bonds (three $\text{C}=\text{O}$ and one $\text{C}=\text{C}$) which can be reduced. In the light of current knowledge of the electroreduction and of the polarographic measurements and the results of our previous works^{1,2,4} the following three compounds should be considered as possible products of the reduction: 3-hydroxy-2-cinnamoyl-1-indanone, 2-(3-phenyl-1-hydroxypropyl)-3-hydroxy-1-indanone, and 2-(3-phenyl-1-hydroxypropyl)-1,3-indandione.

The infrared spectrum of the reduction product shows in the region of the $\text{C}=\text{O}$ stretching vibrations a strong absorption band at 1718 cm^{-1} with the shoulder at 1700 cm^{-1} and in the region of the $\text{C}=\text{C}$ vibration also the only band of medium intensity. The spectrum is very similar to that of 2-benzyl-3-hydroxy-1-indanone^{1,8}. 3-Hydroxy-2-cinnamoyl-1-indanone or 2-(3-phenyl-1-hydroxypropyl)-1,3-indandione should have^{1,2,4-9} different spectra. From the foregoing it follows that the product of the electroreduction of 2-cinnamoyl-1,3-indandione is 2-(3-phenyl-1-hydroxypropyl)-3-hydroxy-1-indanone (*I*).

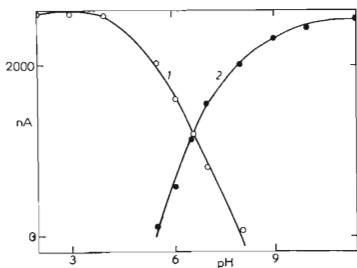


FIG. 1

Plot of Limit Current of Cathodic Waves of 2-Cinnamoyl-1,3-indandione vs pH

Wave: 1 more positive by $E_{1/2} \sim 1.0$ to 1.1 V ; 2 more negative by $E_{1/2} \sim -1.4\text{ V}$.

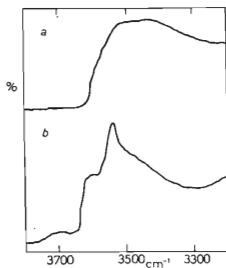
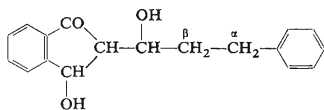


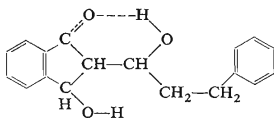
FIG. 2

IR Spectrum of 2-(3-Phenyl-1-hydroxypropyl)-3-hydroxy-1-indanone

a $6 \cdot 10^{-2}\text{ M}$ solution in CCl_3 (cell thickness 0.008 cm); b $2 \cdot 10^{-4}\text{ M}$ solution in CCl_4 (cell thickness 10 cm).



I



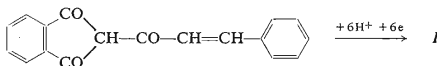
II

The IR spectrum of $6 \cdot 10^{-2}$ M chloroform solution in the $3600-3300 \text{ cm}^{-1}$ region shows a broad absorption band due to stretching vibrations of the free and associated hydroxyl groups. The bands corresponding to the symmetric and asymmetric stretching vibrations of the CH_2 groups occur in the $3000-2800 \text{ cm}^{-1}$ region. The $^1\text{H-NMR}$ spectrum of the reduction product, when compared with that of the starting 2-cinnamoyl-1,3-indandione, shows an increased absorption in the region of the signals of CH_2 and CH protons. The intense multiplet of α - and β - CH_2 protons occurs at δ 2.50–1.84. The complex multiplet of CH protons, with undeveloped structure, is located within the region δ 2.50–3.80. The signals of the aromatic protons collapse to one intense absorption band at δ 7.10–7.25. The lines at δ 7.68 and 7.79, which in the spectrum of the starting compound characterized the ethylenic protons, are absent. The overlap of the lines corresponding to the protons of the two aromatic nuclei present in the molecule renders the estimation of the change in the structure of 1,3-indandione skeleton caused by the reduction difficult. To solve this problem, we therefore examined the spectrum of the product of the reduction of 2-(4-methoxycinnamoyl)-1,3-indandione. The interaction of the 4-methoxy group with the benzene nucleus results in differentiation of chemical shifts of the protons of both aromatic nuclei. With 2-cinnamoyl-1,3-indandione, the chemical shift of the aromatic protons of the 1,3-indandione skeleton is observed at δ 7.86. In the spectrum of the product of the reduction of 2-(4-methoxycinnamoyl)-1,3-indandione these protons are characterized by complex multiplet of ABCD type with chemical shift δ 7.13–7.81. This fact can be taken as the evidence for significantly asymmetrical change in the structure of the 1,3-indandione skeleton.

The infrared spectrum of the reduction product, after cleavage of the intermolecular hydrogen bonds (by decreasing the compound concentration in tetrachloromethane to $c. 2 \cdot 10^{-4} \text{ mol/l}$) exhibits a strong absorption band at 3537 cm^{-1} and a broadened medium intensity band at about 3605 cm^{-1} (Fig. 2). The higher frequency band may be assigned only to the stretching vibration of the free hydroxyl groups. Its complex character indicates the presence of the two structurally unequal hydroxyl groups in the molecule. It is obvious that the absorption band at 3537 cm^{-1} corresponds to the O-H stretching vibrations of the hydroxyl group bonded by intramolecular hydrogen bond, the difference $\Delta\nu(\text{OH})$ being 68 cm^{-1} ($\Delta\nu(\text{OH}) = \nu(\text{OH})_{\text{free}} - \nu(\text{OH})_{\text{assoc}}$). The splitting of the band assigned to the C=O stretching vibration indicates that the carbonyl group is engaged in intramolecular hydrogen

bond of the type $>C=O \cdots H-O-$ (II). The shoulder at 1700 cm^{-1} can be assigned to the $C=O$ stretching vibration of the carbonyl group bonded to the hydroxyl group, and the band at 1718 cm^{-1} can be ascribed to the stretching vibration of the free $C=O$ group. The hydrogen bond of similar type has been observed also with 3-hydroxy-2-acetyl-1-indanone², the product of the two-electron reduction of 2-acetyl-1,3-indandione.

In conclusion it can be stated that the electroreduction of 2-cinnamoyl-1,3-indandione proceeds in such a way that the arrangement of the three conjugated double bonds $-C(=O)-CH-C(=O)-CH=CH-$ is reduced as a whole in one six-electron wave, giving 2-(3-phenyl-1-hydroxypropyl)-3-hydroxy-1-indanone as the product:



In the first approximation, the polarographic properties of 2-cinnamoyl-1,3-indandione can therefore be regarded as the superposition of the polarographic properties of 2-benzylidene-1,3-indandione¹ and 2-acetyl-1,3-indandione².

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