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Übersetzt von M. Wichsová.

PREPARATIVE ELECTROREDUCTION OF 1,3-INDANDIONE AND 2-PHENYL-1,3-INDANDIONE

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Received June 22nd, 1970

Among the derivatives of 1,3-indandione 2-phenyl-1,3-indandione¹⁻³ and some of its derivatives⁴⁻⁸ have been studied polarographically. In the paper by Tutane and Stradyň³ it was demonstrated that the intermediary product of the two-electron reduction of 2-phenyl-1,3-indandione is an dienediol the life-time of which is 0.1 seconds. However, in the mentioned papers the isolation and the identification of the final products of the reduction has not been described.

In this paper we investigated the preparative electroreduction of 1,3-indandione and 2-phenyl-1,3-indandione, the isolation, and the identification of the final products of their two-electron electroreduction.

EXPERIMENTAL

We carried out the electroreduction on a mercury-pool cathode in the manner described in papers^{9,10}, using $1.2 \cdot 10^{-3} - 10^{-3}$ mol/l solutions of the investigated substances, or using

an arrangement with a Ple potentiostat of the SVÚOM enterprise and $2 \cdot 10^{-4} - 10^{-4}$ mol/l in 0.1–0.01N-HCl or in acetate or Britton–Robinson buffers, using KCl for the adjustment of the ionic strength to a value of $\mu = 0.1$.

When the preparative electroreduction was finished the reduction products were isolated by extraction with ether, after previous neutralisation and elimination of acetone used for better solubility during the operation. Ether was evaporated and the residue dried and then crystallised from cyclohexane and purified by column chromatography on alumina (Brockmann II, neutral). Benzene-chloroform mixture was used for elution.

The infrared spectra of the reduction products were measured on a Zeiss UR-20 spectrophotometer in the $800-3800 \text{ cm}^{-1}$ region in chloroform solutions of approx. $6 \cdot 10^{-2}$ mol/l concentration. The cell thickness was 0.08 mm. In order to prove the presence of intramolecular hydrogen bonds spectra were measured of approx. $1 \cdot 10^{-3} - 2 \cdot 10^{-4}$ molar solutions in carbon tetrachloride, in the $2800-3800 \text{ cm}^{-1}$ region, using cells of 2–10 cm thickness. Polarographic measurements were carried out on a LP-60 polarograph provided with an EZ-2 recorder.

The isolated reduction products were submitted to elemental analysis, spectral measurements in the IR region, polarographic analysis, and molecular weight determination by Rast's method, which was necessary to make sure that dimerisation did not take place.

RESULTS AND DISCUSSION

During the careful polarographic control of the course of the preparative two-electron reduction in acidic solutions it was observed that the second (more negative) cathodic wave, which is lower before the reduction than the first two-electron wave, steadily increases in the course of the reduction until it is as high as the first wave. The increase of the second wave is evident in acid media. At higher pH values this effect is less pronounced. The observed fact can be explained in accordance with the paper³, by the supposition that the intermediate of the two-electron electroreduction is a polarographically unreducible dienediol which rearranges to the corresponding hydroxy ketone at a rate which is less than that of the diffusion. The rate of this transformation increases with increasing pH. This fact was observed in both compounds studied.

When the electroreduction of 1,3-indandione and 2-phenyl-1,3-indandione was carried out in more dilute or more concentrated solutions, either in inert atmosphere or in the presence of air, we isolated one reaction product exclusively.

The reduction of 1,3-indandione was carried out in acid or weakly acid solutions. In neutral or basic solutions 1,3-indandione could not be reduced because it was too unstable; the instability was probably caused by its easy oxidation^{3,4} or autocondensation¹¹. The reduction of 2-phenyl-1,3-indandione was carried out in the whole pH range.

1,3-Indandione

The product of two-electron reduction of 1,3-indandione makes itself apparent by a cathodic wave the half-wave potential of which is in the range of half-wave potentials of 1-indandione derivatives⁹. The results of elemental analysis for the supposed 3-hydroxy-1-indanone $\text{C}_9\text{H}_8\text{O}_2$ ($M \neq 148.16$) are: calculated: 73.00% C, 5.40% H; found: 73.13% C, 5.56% H. In the IR spectrum of a chloroform solution of the supposed 3-hydroxy-1-indanone a single absorption band approx. at 1720 cm^{-1} was observed, belonging to the stretching vibration of the $\text{C}=\text{O}$ group in the 1-indanone skeleton¹². In the $3250-3550 \text{ cm}^{-1}$ region there is a broad band of the O—H stretching vibration of bonded hydroxyls. In this band, at approx. 3590 cm^{-1} , the O—H stretching band of the free hydroxy groups can be observed as a shoulder (Fig. 1a). After the breaking of the

intermolecular bonds (by diluting the solutions in carbon tetrachloride to an approx. $2 \cdot 10^{-4}$ molar concentration) the spectrum consists solely of one narrow band at 3610 cm^{-1} , due to the O—H stretching vibration of free hydroxy groups (Fig. 1b). The weaker absorption band at approx. 3440 cm^{-1} can be assigned to the first overtone of the C=O stretching vibration.

2-Phenyl-1,3-indandione

After the two-electron preparative electroreduction on the mercury pool cathode and the usual work-up we isolated a light yellow substance which on polarography gave a cathodic wave the half-wave potential of which is identical with the half-wave potential of the second (more negative) wave of 2-phenyl-1,3-indandione. Elemental analysis of the supposed 3-hydroxy-2-phenyl-1-indanone $\text{C}_{15}\text{H}_{12}\text{O}_2$ ($M \neq 224.27$) was the following: calculated :80.34% C, 5.40% H; found: 80.46% C, 5.52% H.

The IR spectrum of the supposed 3-hydroxy-2-phenyl-1-indanone, similarly to the spectrum of 3-hydroxy-1-indanone shows a single strong absorption band at 1722 cm^{-1} caused by the C=O stretching vibration. The spectrum of the concentrated chloroform solution of 3-hydroxy-2-phenyl-1-indanone in the region of O—H stretching vibrations (Fig. 2a) differs substantially from the analogous spectrum of 3-hydroxy-1-indanone (see Fig. 1a). The absorption bands of the bonded and the free hydroxy groups in the $3300\text{--}3600 \text{ cm}^{-1}$ region coalesce in one complex band with a shoulder at approx. 3565 cm^{-1} . After the breaking of the intermolecular hydrogen bonds (on dilution of the solution of the substance in tetrachloromethane to an approx. $2 \cdot 10^{-4}$ molar concentration) a spectrum was obtained again (Fig. 2b) different from the analogous spectrum of 3-hydroxy-1-indanone (Fig. 1b). In addition to the weak band of the first overtone of the C=O stretching vibration at approx. 3440 cm^{-1} we can observe in the region of the O—H vibration a complex band with a maximum at approx. 3580 cm^{-1} and a shoulder at approx. 3620 cm^{-1} . The shoulder at 3620 cm^{-1} is due to the O—H stretching vibration of free hydroxy

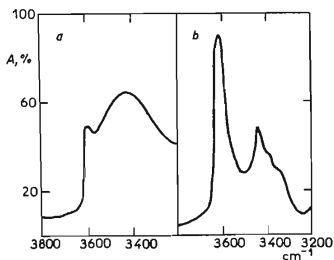


Fig. 1

Infrared Spectrum of 3-Hydroxy-1-indanone

a) In chloroform, $6 \cdot 10^{-2}$ mol/l, cell width 0.08 mm; b) in tetrachloromethane, $2 \cdot 10^{-4}$ mol/l, cell width 10 cm.

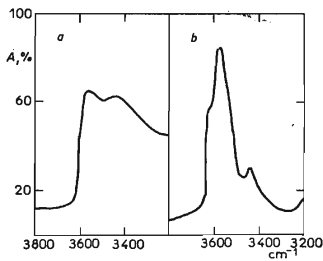
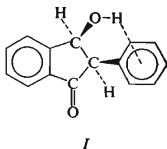


Fig. 2

Infrared Spectrum of cis-3-Hydroxy-2-phenyl-1-indanone

a) In chloroform, $6 \cdot 10^{-2}$ mol/l, cell width 0.08 mm; b) in tetrachloromethane, $2 \cdot 10^{-4}$ mol/l, cell width 10 cm.

groups, and the maximum at 3580 cm^{-1} can be assigned only to the O—H stretching vibration of the hydroxy groups bonded by intramolecular hydrogen bonds with the π -electrons of the phenyl group (*I*); $\Delta\nu(\text{OH}) = 40\text{ cm}^{-1}$. On the basis of the comparison of the $\Delta\nu(\text{OH})$ values it may be concluded that the energy of this hydrogen bond is slightly higher than the energy of the analogous hydrogen bond of the —O—H... π type in 2-phenylethanol¹³ ($\Delta\nu(\text{OH}) = 30\text{ cm}^{-1}$); on the other hand, it is lower than the energy of the —O—H... π bond in derivatives of 3-hydroxy-2-benzyl-1-indanone¹⁴ ($\Delta\nu(\text{OH}) = 50\text{--}66\text{ cm}^{-1}$).



The possibility of the formation of the hydrogen bond of the —OH... π type in 3-hydroxy-2-phenyl-1-indanone supposed a *cis*-orientation of the hydroxy and the phenyl group with respect to the plane of the 1-indanone ring. From this it follows that the electroreduction of the carbonyl group of 2-phenyl-1,3-indandione takes place stereospecifically and that its product is *cis*-3-hydroxy-2-phenyl-1-indanone (*I*). A similarly stereospecific course of the electroreduction of the carbonyl group in the 1,3-indandione skeleton was observed also in derivatives of 2-benzylidene-1,3-indandione¹⁴ and in 2-acetyl-1,3-indandione¹⁵, while derivatives of *cis*-3-hydroxy-2-benzyl-1-indanone and *cis*-3-hydroxy-2-acetyl-1-indanone were obtained as products.

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Translated by Ž. Procházka.