

Mechanism of reduction and oxidation of some derivatives of 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole

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Dedicated to Professor S. Stankoviansky on his 70th birthday

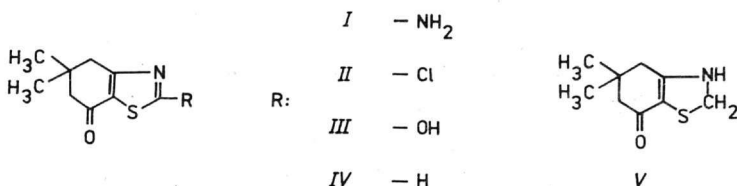
The mechanism of polarographic reduction or oxidation of 2-amino, 2-chloro, and 2-hydroxy derivatives of 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole in acid medium is cleared up. The chloro derivative is reduced in two two-electron stages through 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole to 7-oxo-5,5-dimethyl-2,3,4,5,6,7-hexahydrobenzothiazole. The amino derivative is reduced in acid medium in a single four-electron step and the product of reduction is identical with the product of four-electron reduction of chloro derivative. In alkaline medium, the amino derivative gives an anodic wave which corresponds to the dissolution of mercury entering into a chelate with the amino-enol form of the studied amine.

The 2-hydroxy derivative is polarographically inactive within the whole pH range, which is due to its oxothiazoline structure.

В работе объяснен механизм полярографического восстановления или окисления 2-амино-, 2-хлор- и 2-гидроксипроизводных 7-оксо-5,5-диметил-4,5,6,7-тетрагидробензтиазола в кислой среде. Хлорпроизводное восстанавливается на двух двухэлектронных ступенях через 7-оксо-5,5-диметил-4,5,6,7-тетрагидробензтиазол в 7-оксо-5,5-диметил-2,3,4,5,6,7-гексагидробензтиазол. Аминопроизводное в кислой среде восстанавливается на единственной четырехэлектронной ступени, образуя тот же продукт, который образуется при четырехэлектронном восстановлении хлорпроизводного. В щелочной среде наблюдается в случае аминопроизводного анодная волна, которая соответствует растворению ртути с образованием хелата с аминоксольной формой изучаемого амина.

2-Гидроксипроизводное в целом диапазоне pH полярографически не активно, что обусловлено его оксо-тиазолиновой структурой.

The problems of the tautomeric forms of the derivatives of thiazole or 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole studied on the basis of i.r. spectra are treated in [1—3]. In our preceding paper [4], we were concerned with the spectrophotometric study of the acid-base equilibria of some derivatives of 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole. In this paper, we examine the polarographic behaviour of some 2-substituted derivatives of 7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole and 7-oxo-5,5-dimethyl-2,3,4,5,6,7-hexahydrobenzothiazole



On the basis of polarographic and spectrophotometric investigations of the course of preparative electroreduction (or oxidation) on a mercury pool electrode and by using the n.m.r. spectra of the isolated products, we describe the mechanism of electroreduction in acid medium and redox properties of the products obtained by reduction of the above-mentioned compounds.

Experimental

2-Amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (I) (m.p. 207—208°C) was prepared from thiourea and bromodimedone [2]. 2-Chloro-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (II) (m.p. 43°C) was synthesized by the Sandmeyer method and 2-hydroxy-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (III) (m.p. 166°C) was prepared according to [3]. 7-Oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (IV) and 7-oxo-5,5-dimethyl-2,3,4,5,6,7-hexahydrobenzothiazole (V) were prepared and identified as described in Results and discussion. Compound IV was obtained as the product of the first-stage electroreduction of compound II or as the product of the second-stage reduction of compound II oxidized by oxygen. Compound V is the reduction product of compound I or the product of the second-stage reduction of compound II. Other chemicals used were anal. grade reagents.

The pH measurements were carried out on a pH-meter PHM 26 (Radiometer, Denmark) with glass electrode G 202 B and reference calomel electrode K 401. The spectrophotome-

tric measurements were performed on a recording spectrophotometer Specord UV VIS (Zeiss, Jena). A polarograph OH 102 (Radelkis, Hungary) was used for polarographic measurements. The mechanism of reduction was studied by the method of preparative electroreduction. A voltage was taken from an adjustable stabilized supply of d.c. voltage (Tesla BM-208) and put between the mercury pool cathode and carbon anode. This voltage was so chosen that the potential on the surface of cathode, measured against SCE by a technical compensator QTK, corresponded to the start of limiting current of the corresponding polarographic wave. The cathodic and anodic compartments were separated by a salt bridge consisting of a teflon membrane (0.01 mm thick) fixed to ground glass joint by means of a teflon ring. Because of the easy oxidizability of the products of reduction by air oxygen, the preparative electroreduction as well as the polarographic and spectrophotometric investigations of the course of reduction was performed in the atmosphere of pure nitrogen. The polarographic measurements were carried out directly in a vessel serving for electroreduction. The spectrophotometric measurements were carried out by a flow method while the flow cell was connected with the reduced solution by a teflon tube. The stable products of reduction were isolated by chloroform extraction and identified by means of n.m.r. spectrometry (Tesla 487 BS).

Results and discussion

The comparison of the polarographic behaviour of compounds *I*–*V* in the aqueous alcoholic Britton–Robinson buffer solutions in acid and basic medium (Fig. 1) has shown that compounds *I*, *II*, and *IV* are reducible in acid and weakly alkaline medium. Compounds *II* and *IV* are not stable in alkaline medium and

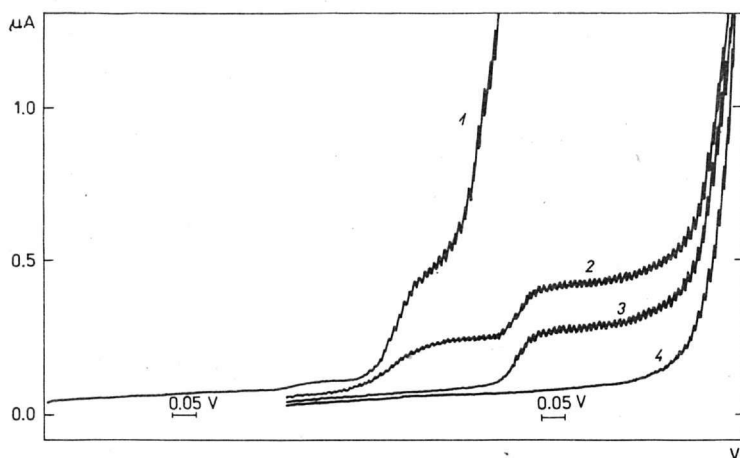


Fig. 1. Polarographic behaviour of compounds *I*–*V* in the medium of 0.25 M- H_2SO_4 and 40 volume % of ethanol.

$c_I - c_V = 4 \times 10^{-5}$ M, sensitivity 2×10^{-8} A/div 0.05 V cm^{-1} , $t_{\text{drop}} = 3$ s; start at -0.200 V against SCE.

1. *I*; 2. *II*; 3. *IV*; 4. *III* and *V*.

compound *I* is only anodically oxidizable in this medium. Compound *III* is polarographically inactive within the whole pH region. Compound *V* is not reducible in acid medium, but it is subject to oxidation by oxygen to yield a product which exhibits the same cathodic wave as compound *IV*. Compound *II* is reduced in two equally high cathodic waves and the half-wave potential of the second wave is identical with the half-wave potential of compound *IV*. Compound *I* is reduced in acid medium in single wave the height of which corresponds to the sum of both waves of compound *II*. The polarographic inactivity of compound *III* supports the conclusions of the study of i.r. spectra presented in [3] according to which this compound occurs in the oxothiazoline form.

In order to clear up the behaviour of compounds *I*, *II*, *IV*, and *V*, we subjected compounds *I* and *II* to preparative electroreduction on a mercury pool cathode at a controlled potential. The spectrophotometric record of the course of reduction of compound *II* at the potential corresponding to the beginning limiting current of the first cathodic wave is shown in Fig. 2. The corresponding polarographic record of the course of this reduction (Fig. 3) shows that the first wave drops and vanishes

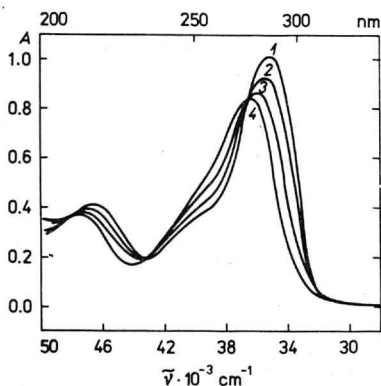


Fig. 2. Spectrophotometric record of the course of preparative electroreduction of compound *II* in acid medium at the potential corresponding to the region of limiting current of the first wave.

$$C_{II} = 1 \times 10^{-4} \text{ M}, d = 1 \text{ cm}, E_{\text{red}} = -0.550 \text{ V/SCE}$$

1. Before reduction; 2., 3. during reduction; 4. after reduction.

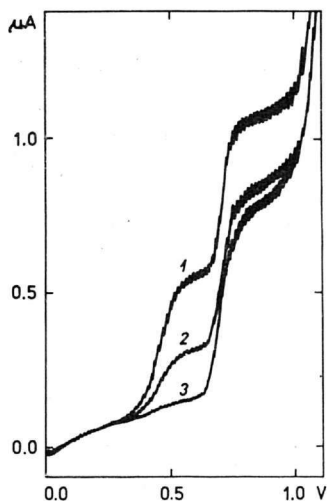


Fig. 3. Polarographic record of the course of preparative electroreduction of compound *II* in acid medium at the potential corresponding to the region of limiting current of the first wave. $c_{II} = 1 \times 10^{-4} \text{ M}$, sensitivity $2 \times 10^{-8} \text{ A/div}$ 0.100 V cm^{-1} , start at 0.0 V against SCE, $E_{\text{red}} = -0.550 \text{ V/SCE}$.

1. Before reduction; 2. during reduction; 3. after reduction.

while the second wave not only preserves the value of half-wave potential but also, contrary to expectation, slightly increases. The product of this reduction is stable in acid and neutral medium even in the presence of air. It was isolated by chloroform extraction from the acid solution and its n.m.r. spectrum was measured.

By using tetramethylsilane as internal standard, the following signals are to be observed in the ^1H -n.m.r. spectrum measured in CDCl_3 with 80 MHz working frequency. There are the singlet signal at $\delta = 1.17$ corresponding to six protons of two methyl groups, the singlet two-proton signals at $\delta = 2.53$ and $\delta = 3.00$, and the singlet one-proton signal at $\delta = 9.00$. The position of all signals corresponds to suggested compound *IV*. The position of the one-proton signal at $\delta = 9.00$ evidences a considerable electron dilution on the carbon between the heteroatoms which is due to conjugation with the carbonyl group. A similar position is to be observed in case of nitrobenzene.

The spectrophotometric record of the course of cathodic reduction of compound *IV* obtained as the product of the first-stage reduction of compound *II* is presented in Fig. 4. The product of this reduction is stable in acid medium only in an inert atmosphere. In the presence of air oxygen, it undergoes oxidation. The spectrophotometric record of the course of this oxidation is equal to the reverse course of reduction presented in Fig. 4. The polarographic record of the oxidized product of the second-stage reduction of compound *II* corresponds to the second stage of

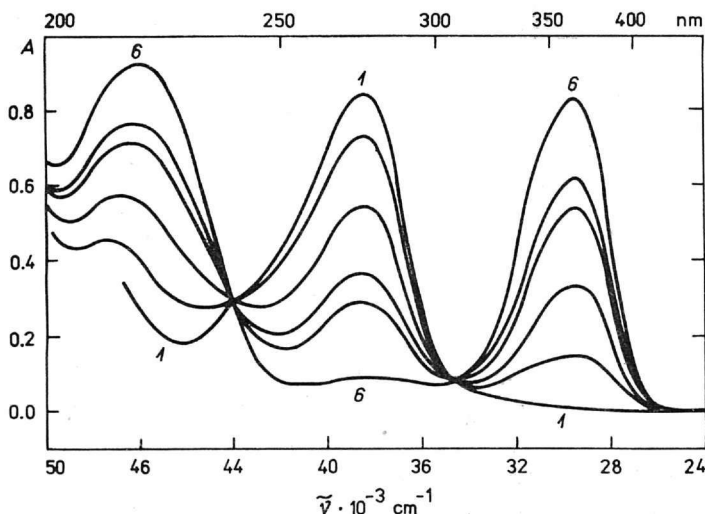
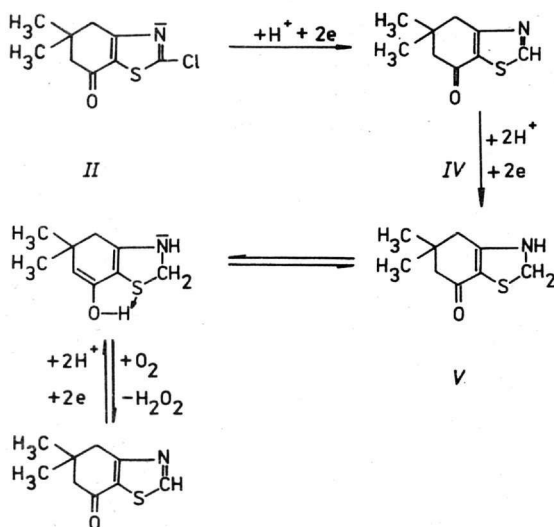


Fig. 4. Spectrophotometric record of the course of preparative electroreduction of compound *II* in acid medium at the potential corresponding to the region of limiting current of the second wave.

$$c_{II} = 1 \times 10^{-4} \text{ M}, d = 1 \text{ cm}, E_{\text{red}} = -0.900 \text{ V/SCE.}$$

1. Before reduction; 2.—5. during reduction; 6. after reduction.

reduction of compound *II*, i.e. to the product of the first-stage reduction of this compound. The n.m.r. spectrum of the oxidized product of the second-stage reduction of compound *II* is identical with the n.m.r. spectrum of the stable product of the first-stage reduction of this compound. The u.v. spectrum of the product of the second-stage reduction of compound *II* (Fig. 4) shows that the absorption maximum of the reduced form is shifted to lower wavenumbers in comparison with the corresponding oxidized form. The position of absorption maximum of the reduced form ($\tilde{\nu} = 27\,400\text{ cm}^{-1}$) corresponds to the position of absorption maximum of the enol form of nonreduced amine *I* [4] or to the position of the Hg chelate of compound *I* (Fig. 7). Therefore, the product of the second-stage reduction of compound *II* may be regarded as the enol form of compound *V*. The mechanism of electroreduction of compound *II* in acid medium and the oxidation of the product of this reduction may be described by Scheme 1



Scheme 1

The spectrophotometric record of the course of preparative electroreduction of compound *I* in acid medium is presented in Fig. 5. The reduction of the protonated form [4] of compound *I*, the absorption maximum of which is at $\tilde{\nu} = 33\,700\text{ cm}^{-1}$, gives a product the absorption maximum of which ($\tilde{\nu} = 27\,400\text{ cm}^{-1}$) has equal position as the absorption maximum of form *V*. In order to eliminate a random agreement of the positions of absorption bands, we confronted the behaviour of this reduction product towards oxygen with the behaviour of compound *V* obtained by the second-stage reduction of compound *II*. The course of air oxidation of the reduced form of compound *I* in acid medium is shown in Fig. 6.

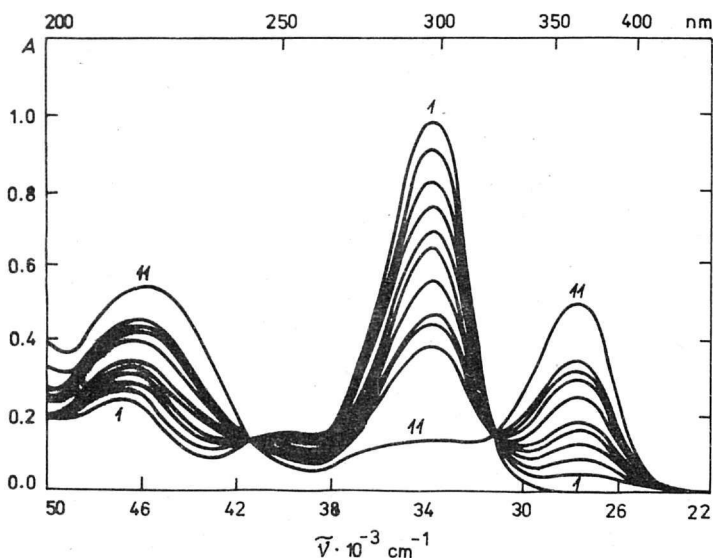


Fig. 5. Spectrophotometric record of the course of preparative electroreduction of compound *I* in acid medium.

$$c_I = 7 \times 10^{-5} \text{ M}, d = 1 \text{ cm}, E_{\text{red}} = -0.940 \text{ V/SCE.}$$

1. Before reduction; 2.—10. during reduction; 11. after reduction.

The comparison of Fig. 6 with Fig. 4 indicates the presence of equal forms in both cases. The position, shape, and height of the polarographic wave (Fig. 1) of the oxidized reduction product of compound *I* are equal to those obtained with the oxidized product of the second-stage reduction of compound *II*. The oxidized reduction product of compound *I* as well as the oxidized product of the second-stage reduction of compound *II* was quantitatively extracted from acid medium into chloroform. Still, we detected the presence of the ammonium salt in the aqueous layer. We alkalinized the concentrated aqueous solution, freed ammonia by boiling and proved its presence. The n.m.r. spectrum of the evaporation residue of the oxidized reduction product of compound *I* is also equal to the n.m.r. spectrum of the oxidized product of the second-stage reduction of compound *II*. Therefore, we may state that the reduction of compound *I* gives equal product as it is formed in the second-stage reduction of compound *II*, i.e. the enol form of compound *V*.

The sharp isosbestic point in Fig. 5 indicates that a simple equilibrium between one oxidized and one reduced form occurs during the reduction of compound *I*. The fact that the four-electron reduction of compound *I* proceeds in a single polarographic step (Fig. 1) demonstrates that the degradation of the amino group must take place on the mercury dropping electrode already during the reduction.

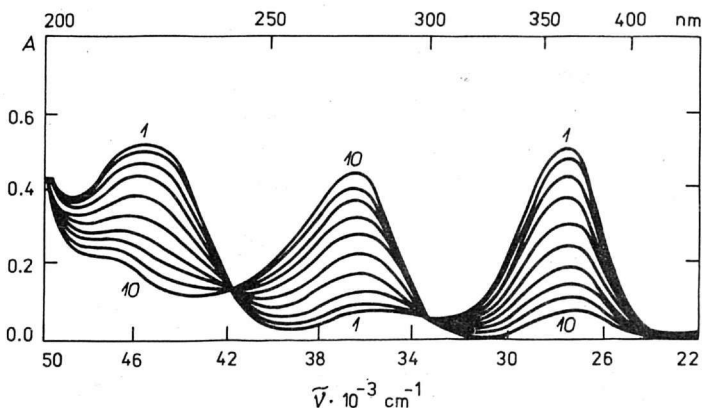


Fig. 6. Spectrophotometric record of the course of oxidation by air of the reduced form of compound *I* in acid medium.

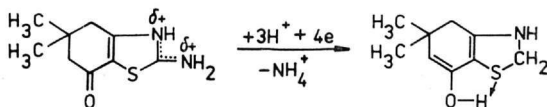
$c = 7 \times 10^{-5}$ M, $d = 1$ cm.

1. Before oxidation; 2.—9. during oxidation; 10. after oxidation.

The curves were recorded in the intervals of 25 min.

The reduction mechanism of compound *I* in acid medium is, therefore, to be described by Scheme 2. The spectrophotometric and polarographic characteristics of compounds *I*—*V* are summarized in Table 1.

In alkaline medium, compound *I* is not more polarographically reducible and in contrast to acid or neutral medium, it becomes anodically oxidizable. In order to interpret the observed anodic wave, i.e. decide whether the process involved a surrender of electrons in relation with the formation of a higher degree of oxidation of the amino group or an anodic dissolution of mercury into a product with compound *I*, we performed the following experiment: We connected the mercury pool electrode situated under the alkaline aqueous alcoholic solution of compound *I* through a salt bridge and microammeter with carbon electrode. The anodic current passed through the cell. We investigated the effect of this current on the composition of solution by the simultaneous use of polarographic and spectrophotometric method. We observed that the anodic wave vanished during the flow of current whereas the cathodic wave with the value of half-wave potential $E_{1/2} = -0.600$ V/SCE increased. The absorption curves simultaneously recorded (Fig. 7) showed a decrease in the band $\bar{\nu}_{\max} = 30\,640$ cm^{-1} and an increase in the band



Scheme 2

Table 1

Spectrophotometric and polarographic characteristics of compounds I—V
in the medium of 1 M-H₂SO₄

Compound	$\tilde{\nu}_{\max}$ cm ⁻¹	ϵ_{\max} l mol ⁻¹ cm ⁻¹	$E_{1/2}$ V/SCE	Note
I	33 700	14 300	-0.910	Reduction gives V
II	35 000	10 000	-0.390	Reduction gives IV
			-0.660	Reduction gives V
III	33 400	11 400	—	
IV	36 300	8 400	-0.660	Reduction gives V
V	27 400	8 400	—	It is oxidized by air and gives IV

$\tilde{\nu}_{\max} = 27\,400\text{ cm}^{-1}$ the absorption maximum of which had the same position as that of the enol form of compound I [4]. After anodic oxidation, we put the negative potential corresponding to the start of limiting current of the new cathodic wave on the large-surface mercury electrode. This wave decreased, the original anodic wave

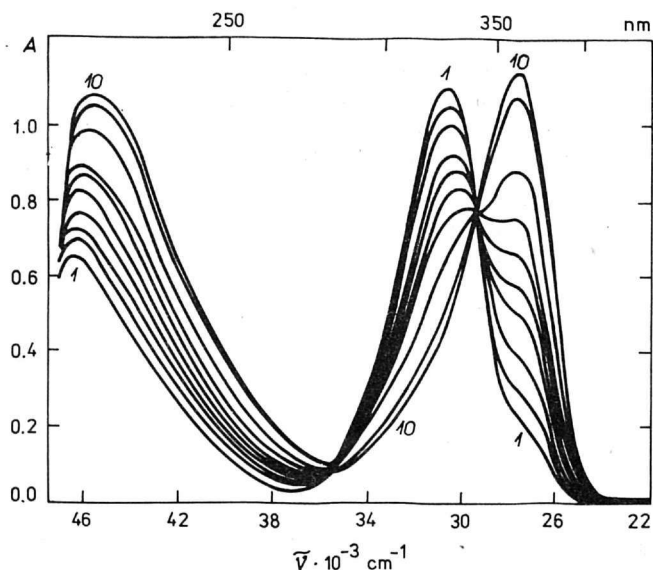
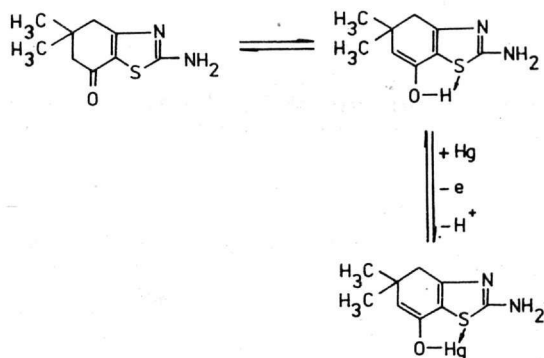


Fig. 7. Anodic dissolution of mercury into the product with compound I in alkaline medium.

$c_I = 3.5 \times 10^{-5}\text{ M}$, $c_{\text{NaOH}} = 10^{-2}\text{ M}$, $d = 2\text{ cm}$.

1. Before anodic oxidation; 2.—9. during anodic oxidation; 10. after anodic oxidation.



Scheme 3

increased and the simultaneous spectrophotometric measurement gave equal but reverse record as shown in Fig. 7. On the basis of these observations, we can state that the anodic wave of compound *I* in alkaline medium is to be interpreted by Scheme 3.

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