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REACTIVITY OF PYRROLE PIGMENTS. PART 6[1].

ELECTROCHEMICAL REDUCTION OF SOME 5(1H)-PYRROMETHENONES AND 5-ARYLMETHYLENE-3,4-DIMETHYL-3-PYRROLIN-2-ONES

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Abstract - The electrochemical reduction of some 5(1H)-pyrromethenones and 5-arylmethylene-3-pyrrolin-2-ones in dimethylformamide (DMF) has been studied by polarography and by identification of their electrochemical reduction products. The reduction processes observed depend on the presence on the type of supporting electrolyte, $LiClO_4$ or tetraethyl ammonium perchlorate (TEAP) and, when TEAP is used, they also depend on the presence of water. Polarographic curves show two monoelectronic diffusion waves in anhydrous DMF both with $LiClO_4$ and with TEAP. The reaction products from (Z)-3,4-dimethyl-5-[(4-methylphenyl)methylene]-3-pyrrolin-2-one and from (Z)-2-[(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl) - methylene]-1H-pyrrole for the electrolysis at controlled potentials and under different experimental conditions have been isolated and identified. In all cases a stereoselective reductive dimerization occurs but, at second wave potentials, the reduction compounds corresponding to the hydrogenation of the exocyclic double bond are also formed. The electrolysis yields can be optimized in order to make the process synthetically useful.

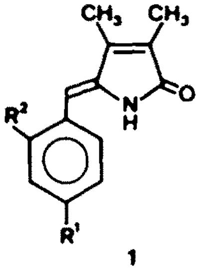
The electrochemical behaviour of bile pigments and their partial models (e.g. pyrromethenones or pyrromethenes) has not been as widely studied as the electrochemistry of the cyclic pyrrole pigments. Much of the published work in linear tetrapyrrolic systems is concerned with the rubin structure or with the interconversion between the rubin and the verdin structures[2]. The anodic oxidation of pyrromethenones and pyrromethenes has been studied by Falk[3]. The cathodic reduction of pyrromethenones was studied in a Ph.D. Thesis[4], but the results have been only partially published in a review[5a]: these results showed that among the electrochemical reduction products of isoneoxanthobilirubic acid methyl ester [5(1H)-2,2'-pyrromethenone], the compound reduced at the exocyclic double bond was detected.

In this work, we report our results from the polarographic study in dimethylformamide (DMF) of 3,4-dimethyl-5-arylmethylene-3-pyrrolin-2-ones (1) and of some pyrromethenones (2-6) lacking vinyl groups. We also describe the products obtained by electrochemical reduction of (Z)-3,4-dimethyl-5-[(4-phenyl)methylene]-3-pyrrolin-2-one (1a) and of (Z)-2-[(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl)methylene]-1H-pyrrole (2).

RESULTS AND DISCUSSION

Polarography- The d.c. polarographic curves of $5\cdot10^{-4}$ M solutions in anhydrous DMF of the compounds 1a-1g, 2-6 show, when $LiClO_4$ is used as supporting electrolyte, the presence of two waves whose half-wave potentials ($E_{\frac{1}{2}}$) and diffusion intensities (i_d) are indicated in table 1 . A.c. phase sensitive polarography confirms the existence of two peaks corresponding to these two waves. The last are diffusion controlled, as proven by their good agreement with the Ilkovic equation. Accurate coulometric measurements (see below) on the first wave show it to be

	R^1	R^2
a	CH_3	H
b	H	H
c	H	CH_3
d	CH_3O	H
e	OH	H
f	$(CH_3)_2N$	H
g	CO_2CH_3	H
h	Br	H



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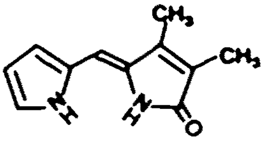

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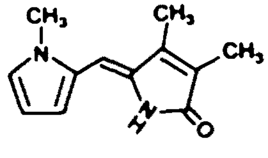

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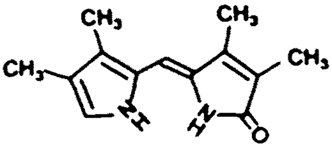

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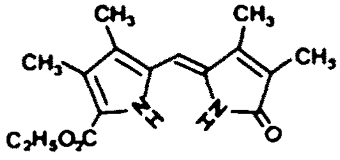

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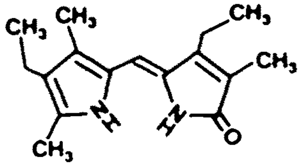

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Table 1 - Polarographic half-wave potentials ($E_{1/2}$) and diffusion intensities (i_d) of 3,4-dimethyl-5-ylidene-3-pyrrolin-2-ones (1-6) $5\cdot10^{-4}$ mol·dm^{-3} in anhydrous DMF (0.1 mol·dm^{-3} $LiClO_4$; drop time2 s; 0.95 mg Hg·s^{-1}).

	FIRST WAVE		SECOND WAVE	
	$E_{1/2}$(V)	i_d(μA)	$E_{1/2}$(V)	i_d(μA)
1a	-1.72	0.89	-1.94	1.09
1b	-1.67	0.87	-1.88	1.03
1c	-1.70	0.88	-1.83	0.74
1d	-1.76	0.77	-1.99	0.90
1e	-1.63	0.44	-1.85	0.56
1f	-1.78	0.80	-1.96	0.88
1g	-1.46	0.52	-1.52	0.70
1h	-1.62	1.55[a]	----	----
2	-1.80	0.40	-1.94	0.35
3	-1.78	0.70	-2.02	0.40
4	-1.84	0.34	-1.98	0.34
5	-1.62	0.42	-1.80	0.80
6	-1.95	0.42	-2.08	0.50

[a] Two electron wave (see text)

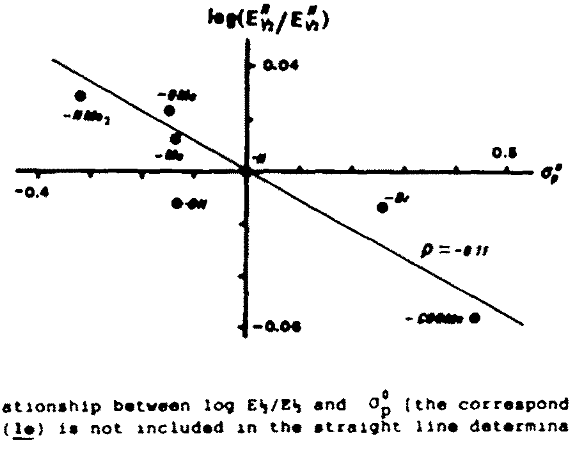


Fig. 1 - Relationship between log $E_{1/2}/E_{1/2}$ and σ_p^0 (the corresponding point to p-OH (1e) is not included in the straight line determination)

monoelectronic (n=1); the similar diffusion intensities between the first and second waves for each compound permit to extrapolate this result to the second wave. However, the coulometric analysis of the second wave leads to larger n values (n=1.0 - 1.3), because two different processes take place during the electrolysis at the second polarographic wave potentials (see below). The para bromo derivative 1h presents a two electron wave (determined from coulometric measurements): the analyis of its electrochemical reduction products indicates that, besides the formation of reductive dimers as from 1a and 2 (see below), the reduction to 1b is also important.

Table 1 shows how alkylation on the carbon atoms of the pyrromethenone pyrrole ring makes the compound more difficult to reduce, as expected.The pyrromethenone 5 has half-wave potentials closer to those of the arylanalogs 1 than the pyrromethenones 2, 3, 4, and 6 do; this agrees with the known effect of the alkoxycarbonyl group on the reactivity of the pyrromethenone skeleton[1].

The i_d observed at the first wave for 1a, 1b, 1c, 1d, 1f, and 3 is lower than that for 1e, 1g, 2, 4, and 6, which can be related to the larger capability of the latter compounds to hydrogen bond and consequently, to their distinct interaction with the solvent (DMF).

Semilogarithmic plots (E vs. log i/i_d-i) indicate that the shapes of the waves do not correspond to what can be expected for a simple monoelectronic process[7]. By analogy with the electrochemistry of other unsaturated systems, the process is probably irreversible, i.e. electron transfer followed by very rapid reactions. This behaviour is shown and discussed later on the light of the isolated electrochemical reduction products.

Linear free-energy relationships are not very meaningful in the discussion of the substituent effects on $E_{\frac{1}{2}}$ values, because the last are not only function of the charge transfer step but also of the irreversible chemical reaction which follows it. However, in our case we think that the analysis of such a relationship, together with the study of the structure of the electrolysis reduction products is useful to get an additional information about the reaction pathway. Fig. 1 shows the plot of log $E_{\frac{1}{2}}/E_{\frac{1}{2}}$ against the unbiased substituent constant[8] σ_p°. The OH substituted compound remains out of the line defined by the other groups, regardless of the para substituent constant chosen. This behaviour of 1e cannot be attributed to the influence of the phenolic hydroxyl group on the acidity of the medium, because the polarography of 1a under the conditions of table 1 but with addition of an equimolecular amount of phenol gives half-wave potentials which differ only on the second decimal place from the values of table 1. We attribute the behaviour of 1e to a reaction pathway different from that of the rest of the series (1a - 1d, 1f - 1h), and which will be explained below taking account of the results just discussed and of the electrolysis experiments.

The $E_{1/2}$ in anhydrous DMF are more cathodic when TEAP is used as supporting electrolyte as compared to $LiClO_4$, but the diffusion intensities are nearly the same in both cases [e.g. for 1a with 0.1 M TEAP and conditions of table 1, the values are 1.88 V(0.59 μA) and 2.22 V(0.95 μA)]. However, in the case of TEAP the observed electrochemical processes strongly depend on the presence of even traces of water. The figures 2a and 2b show the waves relative to 1a obtained at different water concentrations. With $LiClO_4$ no different polarograms were obtained after water addition; only at high water concentrations (>4 M) a small variation on the first wave $E_{1/2}$ and on i_d was observed (see fig. 2a). With TEAP a decrease of the first wave reduction potentials (> 1 M H_2O) and a progressive decrease of the second wave $E_{1/2}$ ($>5\cdot 10^{-2}$ M H_2O) was observed. With the last electrolyte, it is even more significant that the water addition produces a new wave between the original two; this new wave substitutes progressively the second one (see fig. 2a). With $LiClO_4$ the reaction products isolated from the electrochemical reduction are principally the lithium carboxamidure salts (see below); in good solvating aprotic solvents these salts are relatively stable towards hydrolysis, as we had previously observed on the reaction products from the nucleophilic attack of cyanide ion to 5-ylidene-3-pyrrolin-2-one systems[9]

Electrochemical Reduction Products - The results discussed in this section were obtained from the observation, at first and second waves, of the influence of supporting electrolyte ($LiClO_4$ or TEAP), water concentration (zero or 0.55 M), and substrate concentration ($1\cdot 10^{-2}$ M or $5\cdot 10^{-2}$ M) following a factorial experiment design. Furthermore, experiments on the influence of acidity and of larger water concentration were carried out in order to attain higher yields of compounds 7 and 8. Under some of these experimental conditions, additional accurate coulometric measurements were obtained to correlate the yields of 7 with those of 8 and 9. Table 2 show the yields from some typical experiments.

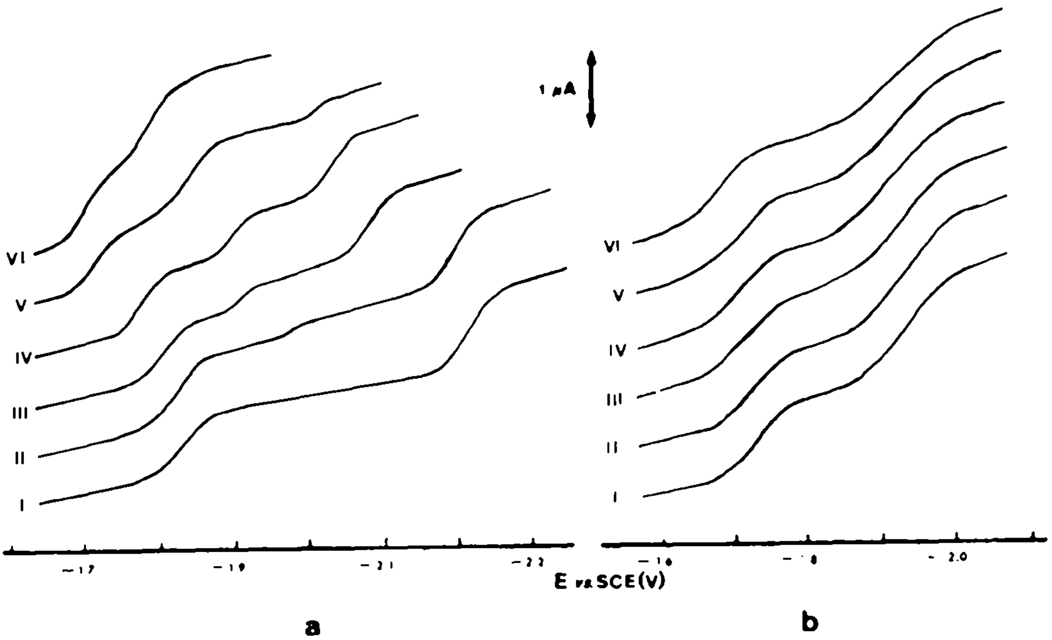
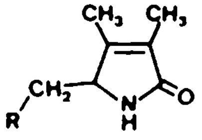


Fig. 2 - Effect of water addition on the polarograms of 1a in DMF (same experimental conditions as in the table 1). a: with TEAP 0.5 mol·dm^{-3}. b: with LiClO$_4$ 0.5 mol·dm^{-3}. Water concentration: I) anhydrous medium, II) 5·10^{-2}, III) 5.0·10^{-1} IV) 9.8·10^{-1}, V) 3.73, VI) 8.55 mol·dm^{-3}.



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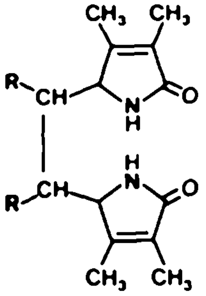

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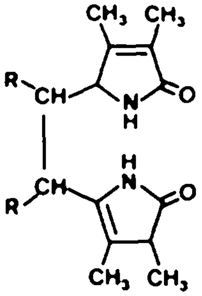

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	7, 8, and 9
a	R = 4-CH$_3$-C$_6$H$_4$
b	R = 2-pyrrolyl

Table 2 - Yields resulting from some characteristic experiments on the cathodic reduction of 1a or 2 (see experimental part).

	ELECTROLYSIS POTENTIAL AT	SUPPORTING ELECTROLYTE	WATER CONCENTRATION (mol·dm^{-3})	SUBSTRATE CONCENTRATION (mol·dm^{-3})	YIELD (%) 7	8 + 9	8	9
1a	second wave	LiClO$_4$	-----	5·10^{-2}	5	95	52	43
1a	second wave	TEAP	-----	1·10^{-2}	14	86	0	86
1a	first wave	LiClO$_4$	8.5	5·10^{-2}	0	100	84	16
1a	second wave	LiClO$_4$	-----[a]	1·10^{-2}	92	8	8	0
2	second wave	LiClO$_4$	8.5	5·10^{-2}	4	96	80	16

[a] Phenol is used instead of water (phenol concentration is 0.5 mol·dm^{-3}).

The electrochemical reduction of 1a and 2 at substrate concentrations between 1·10^{-2} and 5·10^{-2} M (20 - 40 ml of DMF solutions within a 50 ml electrolysis cell) affords only the respective reductive dimers 8 and 9 at potentials corresponding to the plateau of the first wave, and the same dimers 8 and 9 plus the compound 7 (corresponding to the reduction of the exocyclic double bond) when the potential is maintained at the plateau of the second wave. The relative amounts of these three compounds depend principally on whether LiClO$_4$ or TEAP are used as electrolyte, it is also determined by the presence of water. The yields of 7 however are low (< 15 %) except when the proton activity in the medium is markedly increased, e.g. by phenol addition to

0.5 M concentration (see table 2).

The formation of dimerization products (8 and 9) indicates that the exocyclic double bond of pyrromethenones and their arylanalogs can react as an olefin substituted with electron-withdrawing groups; this type of olefin is know to yield the corresponding electrohydrodimerization compound[10].

Accurate coulometric measurements at the plateau of the first wave using TEAP as the supporting electrolyte show an important residual current. The analysis of the final products indicates permanent formation of the starting material from the electrochemical reduction product. This is attributed to the well documented process of catalytic current[11] illustrated as follows[11b]:

$$\text{Substrate} + e^- \longrightarrow \text{Substrate}^-$$

$$\text{Subst.}^- + Et_4N^+ \longrightarrow \text{Subst.} + Et_3N + 1/2\ C_2H_6 + 1/2\ C_2H_4$$

In our case, the above sequence equilibrates at 51 % of initial product ($1 \cdot 10^{-2}$ M 1a, 0.1 M TEAP in anhydrous DMF).With $LiClO_4$ the dimerization at the first wave is quantitative, in agreement with the coulometric measurements performed. The coulometric measurements at the second wave are also in accord with the yields of dimers 8 and 9, and reduced compound 7.

The dimers 8a and 8b are highly insoluble in all solvents assayed (e.g. H_2O, CH_3OH, $CHCl_3$, DMF) and could only be solubilized in strong acids. 8a is isolated as a single diastereoisomer and 8b as a 7:3 mixture of two diastereoisomers. Using $LiClO_4$ as supporting electrolyte, 8 is obtained principally as a mixture of its lithium carboxamidure salts; the amount of these salts is significantly reduced by the addition of water. A careful observation of the electrolytic process shows the highly insoluble dimer to be formed during the first stages and under all experimental conditions; however, depending on these experimental conditions the amount of the precipitate 8

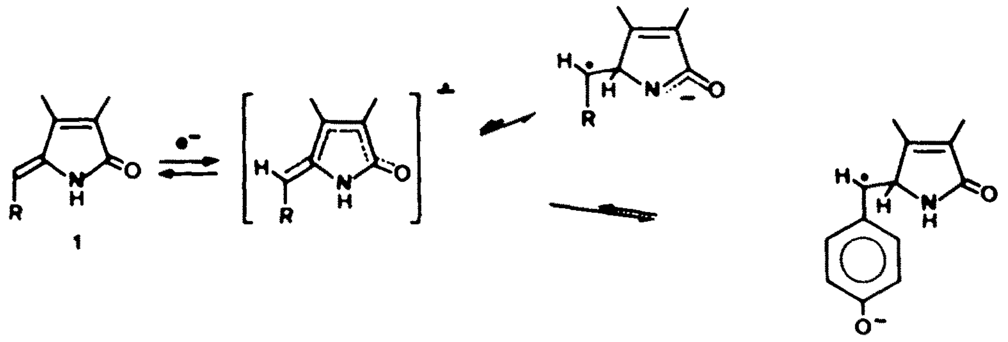

Fig. 3 - Proposed prototropic pathway, following the capture of one electron by the substrate, to explain the different behaviour of 1e.

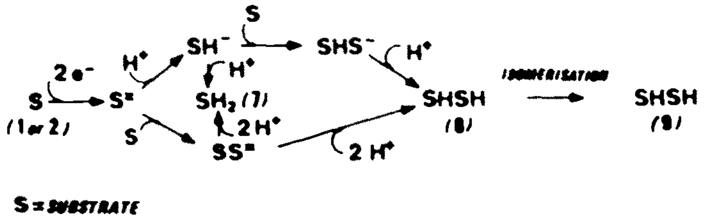

Fig. 4 - Reaction pathways for the processes at second wave potentials for 1a and 2.

diminishes with time (in some cases it even dissappears). The same experimental conditions are responsible for the variation of the ratio between the two dimers in favour of 9, as well as for the higher basicity of the medium owed to the carboxamidure anions formed as the final reaction products. Addition of water in high concentration both at first and second wave conditions increases the yields of 8, but not the yields of total dimer (8 + 9); water addition decreases the basicity of the medium. Our conclusion is that 9 is formed from 8 by base-catalyzed tautomerism.

At the first wave, the substrate concentration has no influence upon the dimer formation. At the second wave, the substrate concentration seems to slightly decrease the ratio of reduced compound (7) to total dimer (8 + 9).

At the plateau of the first wave, the formation of the dimer 9 is the only detectable electrochemical reaction; however, the polarographic results do not agree with a simple reaction scheme. The reaction mechanism from the radical anion (resulting when the substrate acquires one electron) to the dimer requires a prototropic pathway : the results suggest that in aprotic media the proton comes from the substrate lactam hydrogen except when the substrate contains a more acidic hydrogen (as in the case of 1e). Fig.3 shows the mechanism proposed for the early steps of the process at the first wave potential. A stabilizing effect of the lithium cation on the carboxamidure salt would explain the different results with lithium as compared to the ammonium cation; the stabilizing effect of lithium cation on carbanions and its use for synthetical applications is described in the literature[15]. More work is in progress to elucidate between the possible dimerization mechanisms at the first wave.

The fig. 4 shows the possible mechanisms for the processes at second wave potentials. The presence of water favours the reaction pathways through protonated species. That would explain the new wave that appears after water addition using TEAP as the supporting electrolyte. A strong increase of the proton activity is responsible for production of 7 as the more important process. The dimerization occurs through the nucleophilic attack of either $S^{=}$ or SH^- (see Fig. 4) to the bridge carbon atom of the substrate, for this is the most reactive position in such a reaction[10].

We must emphasize here that these dimerization processes both at first and at second wave are highly stereoselective: the unique diastereoisomer of 8a obtained and the two diastereoisomers of 8b show by ^{1}H-NMR and ^{13}C-NMR an internal symmetry element and an ap conformation between the two hydrogens of the bridge carbon atoms: Dreiding and space-filling molecular models of the four possible diastereoisomers having an internal symmetry element show how the two meso forms are clearly the ones with lower steric hindrance. We attribute the configuration of the obtained diastereoisomers of 8 to these meso forms.

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EXPERIMENTAL

Melting points were determined on a Kofler-Reichert microhot stage apparatus. UV/VIS spectra were recorded on a Perkin-Elmer Lambda 5 instrument. IR spectra were recorded on a Perkin-Elmer 681 spectrometer. Mass spectra (MS) on a Hewlett-Packard 5700-A instrument. ^{1}H-NMR spectra were determined on a Perkin-Elmer R-12A (60 MHz) or on a Varian XL 200 (200 MHz) instrument. ^{13}C-NMR spectra were determined with the Varian XL 200 spectrometer. High pressure liquid chromatography (HPLC) was carried out on Radial Pak silica columns with a Waters double pump (2 ml·min^{-1})using a variable wavelength detector 5 FA 339: semipreparative HPLC (PHPLC) was achieved by repetitive injection using the same system and conditions as for analytical HPLC.

Mercury was chemically purified before being doubly distilled . Dimethylformamide (DMF) was anhydrous and p.a. quality. Water was tridistilled. Anhydrous $LiClO_4$ was obtained[13] from p.a. $LiClO_4 \cdot 3H_2O$. Anhydrous tetraethyl ammonium perchlorate (TEAP) was obtained[14] from polarographic quality TEAP. The preparation and properties of the following compounds are described in the literature: 1a[15], 1b[16], 1c[17], 1d[17], 1e[18], 1f[18], 1g[19], 1h[10], 2[20], 3[6], 4[21], 5[22], 6[6].

Polarographic Measurements - Polarograms have been carried out with an Amel 471 multipolarograph and a Tacussel knock (GCMS-MP 03). All measurements were made at 25 + 0.1° in a thermostabilized three-electrode cell of 25 ml. Dry nitrogen, saturated with solvent vapours, was used to deareate the solutions before all experiments, and then it was bubbled through the cell during the measurement. The reference electrode was saturated calomel electrode (SCE) separated from the solution by a salt bridge (Luggin capillary) with the used supporting electrolyte. The auxiliary electrode was a platinum sheet immersed in a solution of the supporting electrolyte, and separated from the solution to be investigated by a sintered glass. The working electrode was a Metrohm EA

671 capillary (mercury flow = 0.95 $mg \cdot s^{-1}$ at 50 cm). The results of the table 1 were obtained at 2 s drop time, mercury flow 0.95 $mg \cdot s^{-1}$, $5 \cdot 10^{-4}$ M solutions in anhydrous DMF 0.1 M $LiClO_4$.

Electrolysis and Coulometric Measurements - Electrolysis at constant potential was carried out by means of a Potentiostat Amel 555 A. The progress of the reaction was followed by plotting the intensity vs. the reaction time. Experiments have been performed in a 50 ml thermostabilized cell (25±1°), the anode and the cathode compartments being separated by a double sintered glass. The working electrode was a mercury pool magnetically stirred. The reference and auxiliary electrodes are the sames as in polarographic experiments. Nitrogen saturated with solvent vapours was bubbled through the solution 20 minutes before and during the electrolysis. The amounts of solution were of the order of 20 - 40 ml of $1 \cdot 10^{-2}$ - $5 \cdot 10^{-2}$ M substrate (100 - 200 mg substrate) using a 0.1 M solution of supporting electrolyte. The applied electrolysis potentials were determined from a polarogram of the solution.

The coulometric measurements were carried out in an analogous but smaller cell (15 ml) with 10 ml of $1 \cdot 10^{-2}$ M substrate solution. In this case an integrator Amel 721 was used to measure the charge.

At the end of the reaction, the DMF solution was filtered to separate 8a or 8b. The filtrate was rotoevaporated (oil pump vacuum). Water was added to the solid residue, and the resulting solution was extracted repeatedly with $CHCl_3$. The organic phase was washed with water, dried with Na_2SO_4 and evaporated. The residue was separated in fractions by column chromatography (20 cm x 1 cm) in silica gel (60 F, 200 - 400 mesh, Merck). Elution from low to high polarity [benzene, $CHCl_3$, ether and $CHCl_3/CH_3OH$ (30:1)] allowed the separation of the electrochemical reduction products. The benzene and chloroform fractions contained small amounts of non-polar impurities. The starting material 1a and the reduced compound 7a were eluted in the ether fraction. The $CHCl_3/CH_3OH$ fraction contained the diastereoisomers of 9a or 2, 7b and the diastereoisomers of 9b.

3,4-Dimethyl-5-[(4-methylphenyl)methyl]-3-pyrrolin-2-one (7a). Obtained as indicated above, from the ether fraction of the column chromatography. Without acid addition the electrolysis at the second wave affords yields lower than 17 %. Addition of phenol (0.1 M) increases the yield to 92 % (see table 2).
m.p. 136 - 141°.
^1H-NMR ($CDCl_3$, δ, 200MHz): 7.05 (center of aromatic AA'BB' system), 5.76 (broad s, NH), 4.04 (m, J_{AX}=10.6 Hz, J_{MX}=4.0 Hz, C^5-H), 3.16 (dd, J_{AM}=13.2 Hz, J_{MX}=4.0 Hz, $ArCH_A$-CH_M), 2.35 (dd, J_{AM}=13.2 Hz, J_{AX}=10.6 Hz, Ar-CH_M-H_A), 2.32 (s, $ArCH_3$), 1.96 (m, CH_3-4), 1.79 (m, CH_3-3).
IR (KBr): 3210, 1680, 770 cm^{-1}.
UV/VIS (iso-octane): λ = 211 (16900), 219 (15400) nm (ε).
MS(m/e, 70 eV): 215 (M^+, 10 %), 110 (37), 105 (100), 91 (10), 82 (12), 79 (17), 67 (17).
Anal. calc. for $C_{14}H_{17}NO$: C 78.10, H 7.96, N 6.50. Found: C 77.92, H 8.15, N 6.40 %.

3,4-Dimethyl-5-[(2-pyrrolyl)methyl]-3-pyrrolin-2-one (7b). Obtained as indicated above from the $CHCl_3/CH_3OH$ fraction of the column chromatography followed by PHPLC (see below for 9b).
m.p. 111-113°.
^1H-NMR ($CDCl_3$, δ, 200 MHz): 8.70 (broad s, NH), 6.74 (broad s, NH), 6.68, 6.13, and 5.98 (m, pyrrolic CH), 4.08 (m, J_{AX}=8.8 Hz, J_{MX}=3.2 Hz, H-C^5), 3.16 (dd, J_{AM}=14.7 Hz, J_{MX}=3.2 Hz, Ar-CH_A-H_M), 2.55 (dd, J_{AM}=14.7 Hz, J_{AX}=8.8 Hz, Ar-CH_M-H_A), 1.97 (m, CH_3-4), 1.77 (m, CH_3-3).
IR(KBr): 3300, 1690, 715 cm_{-1}.
UV/VIS (CH_3OH): λ = 220 (7100) nm (ε).
MS (m/e, 70 eV): 190 (M^+, 2 %), 145 (2), 110 (7), 82 (15), 80 (100).
Anal. calc. for $C_{11}H_{14}N_2O$: C 69.45, H 7.42, N 14.72. Found: C 69.29, H 7.57, N 14.58 %.

1,2-Bis(4-Methylphenyl)-1,2-Bis(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl)ethane (8a). Obtained as indicated above from 1b, by filtration of the electrolysis solution. The presence of the lithium carboxamidures was eliminated by contact with 1 N HCl. The washed and dried obtained powder (8a) is insoluble in water and in all polar and non-polar assayed solvents. Solubilization of 8a can only be achieved in strong acids.
8a does not melt below 350°.
^1H-NMR [$CDCl_3$/TFA(80/20), δ, 200 MHz]: 6.87 (center of aromatic AA'BB' system, J_{AB}=8 Hz), 4.94 (broad s, NC-H), 3.84 (broad s, Ar-CH), 2.17 (broad s, Ar-CH_3 and CH_3-3'), 1.58 (broad s, CH_3-4'). By observation of the signal at 3.84 of a solution 0.5 M of 8a in $CDCl_3$/TFA(90:10) the ^{13}C satelite peaks were detected, showing a ^{13}C-^{13}C coupling constant of 130 Hz and a coupling conatant for ArCH-CHAr of 12-14 Hz, which means an ap conformation of these two hydrogens. For this measurement, 80° pulse of 6 s, acquisition time of 3 s, 1000 accumulations, and double precision with floating point were used.
^{13}C-NMR [$CDCl_3$/TFA(80/20), δ, 50.3 Hz): 178.6 (CO), 160.5, 157.8, 131.0, 129.1, 127.59, and 127.57 (quaternary C atoms), 64.5 (HCN), 48.5 (Ar-CH), 20.7 (Ar-CH_3), 12.4 (CH_3-3'), 7.3 (CH_3-4').
IR (KBr): 3205, 1685, 770 cm^{-1}.
MS (m/e, 70 eV): 428 (M^+, 25 %), 413 (1), 427 (1), 399 (1), 385 (1), 371 (1), 356 (7), 336 (2), 323 (5), 318 (15), 302 (15), 289 (5), 274 (10), 220 (100), 214 (23), 213 (26), 208 (12), 205 (20), 193 (8), 178 (10), 177 (9), 149 (5), 110 (46), 105 (40).
Anal. calc. for $C_{28}H_{32}N_2O_2$: C 78.47, H 7.53, N 6.54. Found: C 78.06, H 7.55, N 6.52 %

1,2-Bis(2-Pyrrolyl)-1,2-Bis(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl)-ethane (8b). Obtained from 2 as indicated above by filtration of the electrolysis solution. The washed (DMF and benzene) and dried powder (8b) is insoluble in water and in all polar and non-polar organic solvents tried. Solubilization of 8b can only be achieved using concentrate strong acids.
8b does not melt below 350°.
The analysis of 8b by NMR indicates the presence of two diastereoisomers in the ratio 7:3 ; the data written first in each of the following pairs of chemical shifts (both for ^1H-NMR and ^{13}C-NMR spectra) corresponds to the isomer in higher concentration.
^1H-NMR [$CDCl_3$/TPA(90/10), δ, 200 MHz]: 6.68, 6.14, and 5.99 (m, pyrrole CH of the two diastereoisomers), 4.06 and 4.52 (broad s, NC-H), 3.67 and 3.84 (broad s, Ar-CH), 1.95 and 2.00

(broad s, CH_3-4'), 1.61 and 1.62 (broad s, CH_3-3').
^{13}C-NMR [$CDCl_3$/TFA(90:10), δ, 50.3 MHz]: 178.3 and 177.6 (CO), 159.3 and 156.2, 127.2 and 128.6, 123.9 and 123.9, 118.5 and 118.5, 109.5 and 109.5, and 107.1 and 107.1 (quaternary C atoms), 65.0 and 65.7 (CHN), 44.40 and 44.57 (Ar-CH), 12.16 and 12.56 (CH_3-3'), 7.58 and 7.94 (CH_3-4').
IR (KBr): 3360, 1675, 730 cm^{-1}.
MS (m/e, 70 eV): 378 (M⁺, 3 %), 311 (5), 268 (21), 220 (15), 189 (47), 158 (100).
Anal. calc. for $C_{24}H_{26}N_4O_2$: C 71.62, H 6.51, N 13.92. Found: C 71.05, H 6.70, N 14.02 %.

1,2-Bis-(4-Methylphenyl)-1-(3,4-dimethyl-5-oxo-2-pyrrolyl-2-yl)-2-(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl)ethane (9a). Obtained from 1a, as it is indicated above, in the $CHCl_3/CH_3OH$ fraction of the column chromatography. 9a is thus obtained as a mixture of several diastereoisomers, which were identified by spectrometric analysis of the two fractions obtained from PHPLC [$CHCl_3/CH_3CN/CH_3OH$ (78:21:1)]. The first fraction contains a pure diastereoisomer and the second fraction - the major one - is a mixture of diastereoisomers (mainly two) whose NMR, IR, UV/VIS, and M spectra were also interpreted. The data for the pure diastereoisomer of 9a are the following.
Product does not melt below 350°.
^1H-NMR ($CDCl_3$, δ, 200 MHz): 9.15 (broad s, NH), 7.02 (broad s, center of one aromatic AA'BB' system), 6.97 (center of one aromatic AA'BB' system, J_{AB}=8 Hz), 5.18 (broad s, NH), 4.07 (broad s, NCH), 4.04 (d, J=12.4 Hz, ArCH), 3.98 (d, J=12.4 Hz, ArCH), 3.18 (q, J=7.2 Hz, COCH), 2.20 (s, $ArCH_3$), 2.18 (s, $ArCH_3$), 2.10 (broad s, CH_3-3' Δ^3-pyrrolinone ring), 1.67 (broad s, CH_3-4' Δ^3-pyrrolinone ring), 1.16 (d, J=7.2 Hz, CH_3-4' Δ^2-pyrrolinone ring), 1.07 (broad s, CH_3-3'' Δ^2-pyrrolinone ring).
IR (KBr): 3300, 1700, 1680 cm^{-1}.
MS (m/e, 70 eV): 428 (M⁺, 8 %), 265 (2), 264 (4), 236 (13), 220 (100), 164 (17), 149 (29).
Anal. calc. for $C_{28}H_{32}N_2O_2$: C 78.47, H 7.53, N 6.54. Found: C 78.35, H 7.25, N 6.40 %.

1,2-Bis-(2-pyrrolyl)-1-(3,4-dimethyl-5-oxo-2-pyrrolin-2-yl)-2-(3,4-dimethyl-5-oxo-3-pyrrolin-2-yl)ethane (9b). Obtained from 1a as indicated above, in the $CHCl_3/CH_3OH$ fraction of the column chromatography. The obtained 9b is a complex mixture of diastereoisomers, identified by spectrometric analysis of the four fractions separated by preparative HPLC [$CHCl_3/CH_3CN/CH_3OH$ (76/20/4)]. The first fraction contains 7b and the other three fractions were diastereomeric mixtures of 9b. The last fraction contains principally one diastereoisomer. Its data are:
^1H-NMR ($CDCl_3$, δ, 200 MHz): 8.25-9.09 (m, 4 H, NH), 6.70-6.47 (m, 2 H, pyrrole CH), 6.18-5.78 (m, 4H, pyrrole CH), 4.05-3.60 (m, 3 H, NCH and ArCH-CH-Ar), 1.99 (broad s, 3 H, CH_3-3' Δ^3-pyrrolinone ring), 1.77 (broad s, 3 H, CH_3-4' Δ^3-pyrrolinone ring), 1.50 (s, 3 H, CH_3-3'', Δ^2-pyrrolinone ring), 1.17 (d, J=7.6 Hz, 3 H, CH_3-4'' Δ^2-pyrrolinone ring).
IR (KBr): 3300, 1695, 1670 cm^{-1}.
MS (m/e, 70 eV): 378 (M⁺, 1 %), fragmentation according to the proposed structure (analogous to the fragmentation of 9a).
Anal. calc. for $C_{24}H_{26}N_4O_2$: C 71.62, H 6.51, N 13.92. Found: C 71.15, H 6.81, N 13.85 %.

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