Stereospecificity in the Reductive Coupling of 4-Pyridinecarboxaldehyde[1,2]

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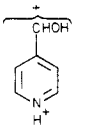
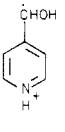
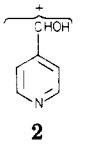
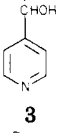
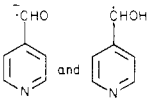
One-electron reduction of 4-pyridinecarboxyaldehyde in aqueous solutions yields a mixture of *dl*- and *meso*-pinacols. Controlled-potential electrolysis (using a DME) at a potential corresponding to the limiting current of the first one-electron wave yielded *dl*/meso ratios of 0.57, 0.35, and 1.92 at pH values of 6.1, 10.6, and 13.3, respectively. The variation of the *dl*/meso ratios can be attributed to a difference in the surface orientation of radical cations (pH 6.1), uncharged radicals (pH 10.6), and radical anions (pH 13.3) that are involved in the dimerization at these different values of pH. For all dimerizations studied, voltammetric and polarographic results indicate a radical–radical coupling mechanism.

One-electron reduction of aromatic carbonyl compounds at mercury cathodes in acidic media results in the formation of neutral radicals which can react further to yield dimeric pinacols.[4,5] In aqueous acidic solutions, these electrodimerizations show limited stereospecificity. The ratio of the amount of *dl*-pinacol to *meso*-pinacol varies between 0.7 and 1.4 for most compounds studied,[6,7] although this ratio can be affected by the presence of adsorbed substances.[8] In alkaline solutions a somewhat higher *dl*/meso ratio (2.5:3.5) was obtained for the electrodimerizations of acetophenone[6] and propiophenone, but for benzaldehyde the ratio remained close to 1.[9] These results were interpreted in terms of the influence of hydrogen bonding between the reacting species. This hydrogen bonding was considered to be more effective in alkaline solutions, where anion radicals may be involved, leading to a higher proportion of the *dl* isomers.[6,9] Preferential formation of the *meso*-pinacol in the one-electron reduction of 2-acetylpyridine[7] in alkaline solutions was interpreted in this context as being due to the *intramolecular* hydrogen bonding which, for this compound, may compete with the *interspecies* hydrogen bond formation. The influence of interspecies hydrogen bonds in solvents which form strong hydrogen bonds has been questioned,[10] and an alternative mechanism involving adsorption of the reactants was proposed. Furthermore, for dimerization involving radical anions, a reaction of $ArCHO^{-}\cdot$ with $ArCHOH$ may involve electrostatic interactions, which are different from the hydrogen bonding assumed to be involved in reactions of neutral radicals.

In the course of a detailed study[12] of the mechanism of reduction of pyridinecarboxaldehydes, the formation of mixtures of *dl*- and *meso*-pinacols in the one-electron reduction of 4-pyridinecarboxaldehyde (1) was observed. The reduction was studied by analysis of products, by polarography, and by linear-sweep voltammetry. In this paper, the mechanism of the stereospecific dimerization following electron transfer is discussed.

Table I. Species Involved in Electrodimerization of 4-Pyridinecarboxaldehyde

pH	$dE_{1/2}/dpH$,[a] mV/pH	reactants in reduction	reactants in dimerization
6.1	−64		
10.6	−72		
		2	**3**
13.3	−70		

[a] Data from ref 12.

Table II. Controlled-Potential Electrolysis of 4-Pyridinecarboxaldehyde

pH	−E, V vs. SCE	n	products	% yield[a]	dl/meso ratio
6.1	0.55	1.00	4-pyridinecarbinol	16	
			meso-pinacol	53	0.57
			dl-pinacol	30	
6.1	0.75	1.73	4-pyridinecarbinol	101	
			meso-pinacol	4	
			dl-pinacol	2	
10.6	0.93	0.89	4-pyridinecarbinol	4	
			meso-pinacol	74	0.35
			dl-pinacol	26	
10.6	1.25	1.03	4-pyridinecarbinol	20	
			meso-pinacol	46	0.83
			dl-pinacol	38	
13.3	1.25	1.18	*meso*-pinacol	36	1.92
			dl-pinacol	69	

[a] Determined by high-pressure LC.

Results and Discussion

A knowledge of the nature of species predominating in the bulk of the solution together with observance of changes in the wave heights and characteristic potentials obtained by dc and differential-pulse polarography (DPP) with pH enabled[11] elucidation of the structure of the species involved in both the one-electron reduction of 4-pyridinecarboxaldehyde (1) as well as the dimerization following electron transfer at each value of pH studied[12] (Table I). At pH 6.1 the diprotonated form of 4-pyridinecarboxaldehyde is reduced at the DME in two waves with half-wave potentials of −0.49 and −0.63 V. Electrolysis at a potential corresponding to the limiting

(1) Based upon a thesis submitted by J.F.R. in Aug 1979 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) Presented at the 178th National Meeting of the Americal Chemical Society, Washington, DC, Sept 1979.
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current of the more positive wave yields pinacols, as identified by TLC, high-pressure LC, and spectrophotometry. The *dl*/meso ratio was found to be 0.57 (Table II). Electrolysis at a potential corresponding to the limiting current of the more negative wave yielded the carbinol as a product of the two-electron reduction.

No indication of the formation of anodic peaks was observed by cyclic voltammetry (CV) at any of the pH values studied, at sweep rates (v) between 0.05 and 30 V/s. The current function ($i_p/v^{1/2}$) obtained by LSV at pH 6.1 for the most positive one-electron peak was found to be independent of sweep rate. The peak potential was shifted to more negative potentials with increasing sweep rate, but it is, in particular, the observed shift of the peak potential to more positive values with increasing concentration of the aldehyde which proved[4,13,14] a useful diagnostic tool which enables one to distinguish between alternative mechanisms of the dimerization process. This is possible because the value[13,14] of $dE_p/\log C$ is 19.7 mV/log C for a radical–radical coupling, 29.6 mV/log C for a radical–parent molecule coupling, and 14.6 mV/log C for an ion–parent molecule reaction. The experimentally found shift of the peak potentials of 21 mV/log C for 4-pyridinecarboxaldehyde at pH 6.1 strongly indicates that a radical–radical dimerization is involved in which the coupling is the rate-determining step.

At pH 10.6 the monoprotonated form of 4-pyridinecarboxaldehyde is reduced in two waves[12] at −0.77 and −0.96 V. The more positive wave corresponds to a one-electron reduction, whereas the height of the more negative wave is only 20% of that of the first wave. Electrolysis at a potential corresponding to the limiting current of the more positive wave yielded a mixture of the pinacols (Table II), as determined by high-pressure LC, TLC, and UV spectrophotometry. Formation of the *meso*-pinacol was favored at this pH, with the *dl*/meso ratio being 0.35.

The current function ($i_p/v^{1/2}$) obtained by LSV at pH 10.6 was independent of the sweep rate. With increasing concentration of the aldehyde at this pH, both half-wave potentials and peak potentials were shifted to more positive values by 24 mV/log C. This is consistent with a radical–radical coupling mechanism.[4,13,14] Dependence of the half-wave potential of the first one-electron wave on pH (Table I) proves that there is a proton-transfer preceding the first electron uptake. Thus the species generated at the potential of the limiting current of the most positive wave of 1 is an uncharged radical, and it is this species which participates in the coupling reaction. The structure of the 1,2-diol, confirmed as the product of this coupling, suggests that monoprotonation of the aldehyde occurs on the carbonyl group rather than on the pyridine ring. Therefore, the transfer of the single proton to the aldehyde 1 occurs prior to the uptake of the first electron under kinetic rather than thermodynamic control.

Controlled-potential electrolysis at pH 10.6 at a potential corresponding to the limiting current of the more negative wave yielded 20% of 4-pyridinecarbinol, the two-electron product. This corresponds exactly to the relative height of the second dc polarographic wave. In addition to the carbinol, isomers of pinacol were also formed at this potential (Table II).

The height of the second wave at −0.97 V shows a nonlinear dependence on concentration of the aldehyde 1. This nonlinearity is not caused by adsorption, as was proved by ac polarography and by measurement of the instantaneous current as a function of time on the single mercury drop (i vs. t curves). The observed nonlinear dependence is thus attributed to a reaction which is second order in aldehyde, the rate of which governs the height of the second wave. Either the dimerization reaction has such a rate that is competitive with the second electron transfer or the initial product of the second electron transfer, Py-CHOH$^-$, is involved in a disproportionation with the protonated aldehyde 2 (Table I) to yield the radical 3. The *dl*/meso ratio of 0.83 for electrolysis at more negative potentials indicates a loss of stereospecificity. In light of the above discussion, this could result either from a change in the orientation of the reactants at the electrode surface with the change in potential or from generation of the reactant 3 by disproportionation, followed by homogeneous dimerization in the solution in the vicinity of the electrode.

Polarographic reduction of 4-pyridinecarboxaldehyde at pH 13.3 occurred in a single one-electron wave with a half-wave potential of −1.00 V. Dimers were obtained as products in a *dl*/meso ratio of 1.92 This ratio is similar to those observed for acetophenone and propiophenone under conditions where radical anions formed in the first electron uptake may participate in the dimerization reaction.[6,9] Both the half-wave and peak potentials are shifted by 20 mV/log C to more positive values with increasing concentration of the aldehyde, indicating, as in previously discussed cases, a radical–radical coupling mechanism.[4,13,14]

The electroactive species in this alkaline medium is the free aldehyde 1. The observed shift of its half-wave potential with pH is due to the loss of the hydroxide ion from the geminal diol anion, predominating in the bulk of the solution, prior to the electron transfer. The primary product of the one-electron reduction of free aldehyde 1 is the radical anion. This species participates in the coupling reaction, either with another radical anion or with a neutral radical.

It seems difficult to invoke interspecies hydrogen bonding[6,7,9] to explain the observed differences in the isomer ratios for coupling of cation radicals, neutral radicals, and anion radicals of 4-pyridinecarboxaldehyde. The *dl*/meso ratios for 2-acetylpyridine,[7] which have been found to be 0.55 at pH 6.5 and 0.31 at pH 8.3, are similar to the ratios found for 4-pyridinecarboxaldehyde in a similar pH range (Table II). Since radical cations or radicals of 4-pyridinecarboxaldehyde cannot form *intramolecular* hydrogen bonds, such interactions, evoked[7] to explain the data for 2-acetylpyridine, cannot control the stereochemical course of these reactions. It may be recalled that application of the concept of hydrogen bonding was also unable to explain the experimental findings for benzaldehyde.[8,9]

It is significant that stereospecificity is observed for the dimerization of single-electron reduction products of 4-pyridinecarboxaldehyde but not for benzaldehyde. It is known[15,16] that pyridine derivatives interact more strongly with the mercury surface than benzene derivatives. It can be thus assumed that when dimerization occurs with a stereochemical preference, the electric field at the surface of the electrode may govern the structure of the transition state. The orientation of the reacting species at the mercury surface, where it is electrogenerated, is strongly influenced by the localized charges on such species. This interpretation can explain the observed variations of stereospecificity with the charge of the reactant (Table II). The statement[17] that "pinacol formation does not seem to

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occur on the surface" has limited validity and does not seem to apply to reductions of either 4-pyridinecarboxaldehyde or 2-acetylpyridine.[7] No evidence for a strong adsorption of the radical intermediates was obtained by LSV or ac polarography for 4-pyridinecarboxaldehyde, but surface orientation of a short-lived intermediate may escape detection by such methods, which offer positive proof of formation of strongly adsorbed layers involving complete surface coverage. Moreover, for 3-acetyl- and 3-propylpyridine,[18] interaction of the radical with mercury was proved in 1 M H_2SO_4. That surface orientation of the radicals or radical ions, formed in the electron-transfer step, may be influenced by the increasingly negative potentials at which the reduction occurs as pH is increased cannot be ruled out. This factor, nevertheless, does not seem to have as predominant a role as in the asymmetric reduction of 2- and 4-acetylpyridines.[17] The difference in the *dl*/meso ratios observed at pH 10.6, when electrolysis was carried out at −0.93 and −1.25 V, is complicated by formation of the product of the two-electron reduction and can be caused either by the dependence of reactant orientation on potential or by disproportionation involving the parent compound.

Thus the difference in the ratios of the yields of stereoisomers observed (Table II) is attributed to the difference in the surface orientation of radicals bearing different charges at different values of pH. The stereospecificity of the reaction is pH dependent because the nature of the reactants depends on pH.

Experimental Section

Materials, Solutions, and Apparatus. 4-Pyridinecarboxaldehyde (98%) and 4-pyridinecarbinol were obtained from Aldrich Chemical Co. The aldehyde was freshly distilled in an inert atmosphere at a pressure of 3–5 mmHg before use. *meso*-4,4-Dipyridyl-1,2-ethanediol was supplied by ICN Pharmaceuticals and had a melting point of 214 °C (lit.[19] mp 214 °C) and an octahedral crystal form as observed previously[7] for other *meso*-hydrobenzoins. The latter compounds, used as a standard for analysis, contained about 2% of the *dl* epimers of the pinacol, which can be separated by high-pressure LC, identified spectrophotometrically, and estimated by the rate of periodate oxidation.[20,21]

Solutions of sodium hydroxide were prepared by dilution of a 50% solution of sodium hydroxide (Fisher Certified Reagent) with carbon dioxide free water and standardized by titration against dried primary standard grade potassium acid phthalate. For the polarographic experiments, 0.04 M phosphate buffers (pH 6.1 and 10.6), adjusted to an ionic strength of 0.20 by addition of sodium chloride, and 0.2 M sodium hydroxide were used as supporting electrolytes. For voltammetry and preparative electrolysis, the concentration of the phosphate buffers was 0.10 M.

A Princeton Applied Research Model 174 polarographic analyzer with a mechanical drop control and an MFE Model 815M Plotamatic X-Y recorder were used for dc polarography. A Cambridge Model 82P polarographic analyzer with a Hewlett-Packard Model 7001AM X-Y recorder was used for ac polarography and microscale controlled-potential electrolysis (CPE). For linear-sweep voltammetry (LSV) and cyclic voltammetry (CV) at scan rates greater than 0.1 V s^{-1} and for measurement of instantaneous current–time curves, the Cambridge Model 82P output was recorded on a Tektronix Type 564B storage oscilloscope. This oscilloscope was equipped with Type 2A63 and Type 3A9 differential amplifiers for the CV and LSV experiments and with a Type 3A9 differential amplifier and Type 3B3 time base for current–time measurements. The resistance of electrochemical cells was measured by using a Leeds and Northup Model 4760 ac Wheatstone bridge and a Cenco No. 70029 audiofrequency oscillator. The Tektronix oscilloscope was used as the null detector. pH was measured by using a Sargent-Welch digital pH meter, Model NX, and a Sargent S30072-15 combination glass electrode.

Dc and ac polarography were carried out in a Kalousek cell employing a saturated calomel reference electrode. Cell resistance was typically 300–450 Ω. The capillary characteristics of the dropping mercury electrode (DME) used for polarography were m = 1.98 mg s^{-1} and t_1 = 4.2 s (1 M KCl) at h = 70 cm, where m is the mercury flow rate and t_1 is the drop time. Unless otherwise stated, the polarograms were run at 80 cm. All potentials were reported as volts vs. SCE.

Microscale controlled-potential electrolyses (CPE) were carried out at a DME with m = 3.9 mg s^{-1} and t_1 = 2.2 s (1 M KCl) at h = 50 cm. The microcell design was originated by Manoušek[22] and contained a calomel reference electrode separated from the sample compartment by a glass frit and an agar salt bridge. This cell allowed electrolysis to be carried out at the DME for long periods of time and in solution volumes of 0.2–2.0 mL.

LSV and CV were carried out in a three-electrode cell supplied by Metrohm, Model No. EA 875-20. A DME with m = 0.35 mg s^{-1} and t_1 = 20.1 s (1 M KCl) at h = 30 cm was the working electrode. The potential scan was initiated at a fixed time after the beginning of drop growth, usually 18 s. The reference electrode was a Metrohm Model EA 427 Ag/AgCl electrode. A Metrohm Model EA 285 platinum electrode was used as the counterelectrode. Cell resistance was approximately 400 Ω.

A solution of thallium(I) in 0.2 M phosphate buffer (pH 7) was used to calibrate the LSV–CV system. The peak potential of the thallium(I) standard was measured, and the average value of $E_p(v) - E_p(0.05\ V\ s^{-1})$ was plotted vs. scan rate (v). This graph was used to provide an ohmic correction to the peak potentials measured in this study. At low scan rates the correction was negligible, but corrections in excess of 50 mV were required at scan rates greater than 10 V s^{-1}. For this reason changes of peak potential with scan rate have been reported in this paper only in a qualitative manner.

High-pressure liquid chromatography (LC) was carried out by using an instrument composed of components manufactured by Waters Associates. These components were a Model U6K injector, a Model 6000A solvent-delivery system, and a Model 440 absorbance detector with an incident wavelength of 254 nm. The detector output was monitored with a Houston Instruments Omniscribe strip-chart recorder. The chromatographic column was Waters Associates μ-Bondapak C-18, Model 27324, and was 30 cm in length. Thin-layer chromatography (TLC) was performed on Eastman chromatogram sheets (No. 13181) coated with silica gel absorbent which contained a fluorescent indicator. Ultraviolet and visible absorption spectra were obtained by using a Unicam SP800A spectrophotometer.

Electrochemical Procedures. Stock solutions of 4-pyridinecarboxaldehyde were prepared in water and were stable for at least 3 weeks when stored at 5 °C. All polarographic and voltammetric experiments were carried out at 25 °C and at a concentration of aldehyde of 0.20 mM unless otherwise stated.

Controlled-potential electrolysis at the DME was carried out in solutions 0.7–1.0 mM in aldehyde. Solution volumes of 500 μL were typically used. The course of the electrolysis was followed by recording polarographic curves at regular intervals. The number of electrons transferred was estimated[11] from the slope of a plot of the logarithm of limiting current vs. time. For minimization of the systematic error due to depletion of electroactive material in the vicinity of the electrode previously encountered with this method, the sample solution was stirred with a stream of nitrogen before the recording of each polarographic curve. In a typical experiment 12 h were required for 95% completion of the electrolysis. At the end of this time period, the pH of the sample solution was adjusted to fall between 6 and 11 (if necessary) and was diluted with water to a total volume of 2.0 mL. The standard for the analysis was usually a solution containing the

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Table III. Chromatographic and UV Spectrophotometric Characteristics Used for Analysis of Electrolysis Products[a]

	R_f (TLC)	HPLC retention time, min	λ_{max} (UV), nm
4-pyridine-carboxaldehyde	0.62	7.1	256, 283[b]
meso-pinacol	0.02	7.6	251
dl-pinacol	0.06	8.6	
4-pyridinecarbinol	0.28	5.3	253

[a] See the Experimental Section for the conditions used. [b] Corresponding absorption bands; molar absorptivities are a function of pH (cf. ref 12).

expected electrolysis product subjected to an identical treatment as the sample, but without electrolysis. Typical recoveries were 80–90%. In alkaline solutions the extent of chemical decomposition of the aldehyde during the period of the electrolysis was determined by using a control solution.

Analysis for Products. The sample solution, after dilution, was subjected to analysis by UV spectrophotometry (Table III). Subsequently, the standard and sample solutions were filtered through polycarbonate membrane filters (Nucleopore Corp., 0.2 μm, stock no. 100406) and analyzed by high-pressure LC. The eluant for high-pressure LC was composed of 80% (by volume) of 0.02 M sodium phosphate buffer (pH 6.9) and 20% methanol–water mixture (60/40 v/v). A flow rate of 2.0 mL min^{-1} was used, and the column pressure was in the range of 2000–2500 lb $in.^{-2}$ Sample solutions were delivered to the injection valve by using a Precision Sampling Corp. 100-μL syringe (catalogue no. 100025). The column was equilibrated with eluant for at least 1 h prior to use. Under the conditions of the analysis, the response of the detector was linear for 4-pyridinecarbinol and *meso*-4,4-dipyridyl-1,2-ethanediol for amounts of solute between 0.1 and 4.0 μg. Product concentrations in the sample solutions were calculated by comparing peak heights for the sample solutions with those of the appropriate standards. Retention times for both dimers (Table III), the aldehyde, and the carbinol agreed with those found in the analysis of the electrolysis products within ±0.1 min.

Prior to investigation by TLC, the sample solution was extracted with chloroform. Water was removed from the organic extract with sodium sulfate. The solvent was removed by using a stream of nitrogen, and the residue was chromatographed in a closed container which had been preequilibrated with solvent. The chromatograms were eluted for a distance of 5 cm by using ethyl acetate as the solvent. Quenching of fluorescence of the TLC plate by the sample components in ultraviolet light was used for detection. R_f values (Table III) agreed with those for the corresponding electrolysis products within ±0.01.

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Registry No. 1, 872-85-5; 4-pyridinecarbinol, 586-95-8; *meso*-pinacol, 4972-49-0; *dl*-pinacol, 5486-06-6.

Ab Initio Self-Consistent-Field Study of Favorskii Rearrangement Intermediates

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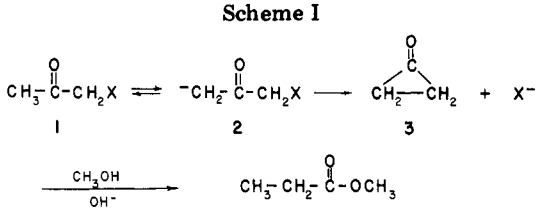
Single-configuration SCF calculations using Pople's 4-31G basis were carried out on cyclopropanone and on oxyallyl. C_{2v} symmetry was assumed for both, but, otherwise, the geometries were optimized completely. Oxyallyl is computed to close disrotatorily to cyclopropanone with no energy barrier and is thus excluded as a possible intermediate in the Favorskii rearrangement.

One of the most intensely studied mechanisms in organic chemistry has been that of the Favorskii rearrangement.[1] Mechanisms have been proposed involving virtually every reactive intermediate known to organic chemists. A number of these were eliminated, first by McPhee[2] and then by Loftfield,[3,4] whose work indicated that a symmetrical intermediate, most likely a cyclopropanone, was present. This gained further support when Turro[5] found that tetramethycyclopropanone rearranged in basic methanol solution to give methyl 2,2,3-trimethylbutanoate. There is now general agreement that the mechanism is as shown in Scheme I.

Scheme I



More recent studies, in particular the extensive work of Bordwell,[6] have concentrated on the second step of the mechanism, i.e., conversion of the carbanion 2 to cyclo-

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