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Electrochemical Reduction of Some Cyclic Immonium Salts in Aprotic Media

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The cathodic reduction of four cyclic immonium salts has been studied in acetonitrile or *N*,*N*-dimethylformamide solutions by DC polarography and cyclic voltammetry. Product mixtures from preparative electrolyses have been carefully analyzed by gas chromatography, the corresponding enamine and saturated tertiary amine being the major products. Based on product analysis, electrochemical criteria, and stereochemical arguments a mechanism is proposed, involving hydrogen atom transfer between primarily formed radicals.

In a previous study [1] of the electrochemical reduction of some heterocyclic enammonium salts in aqueous media, the intermediacy of cyclic immonium salts was proposed in order to account for the observed products of the reaction. However, only a preliminary experiment concerning the electrochemical behaviour of such cyclic immonium salts in aprotic media was carried out. We now present a detailed study of the behaviour of the salts *1* – *4* (Table 1) in aprotic media.

Various types of immonium salts have previously been investigated by Andrieux and Savéant.[2–4] These authors have concluded that electrochemical reduction of the salts studied lead to either stable radicals or to rapid dimerization of the initially formed radicals, depending upon the structure of the initial salt.

RESULTS

Voltammetry. The results from DC polarographic measurements in acetonitrile (AN), on four immonium salts are listed in Table 1. The $E_{\frac{1}{2}}$ values are somewhat uncertain due to a pronounced streaming maximum effect which was observed in all cases, and a typical polarogram is shown i Fig. 1a. A study of the *i*-*t* curves at potentials corresponding to the maximum allowing observation of oscillatory currents characteristic of streaming maxima [5] has not been included.

The maximum was also present when stationary mercury electrodes were employed although absent with solid electrodes such as vitreous carbon or platinum. A typical cyclic voltammogram using a hanging mercury drop electrode (HMDE) is shown in Fig. 1b, illustrating the remarkable phenomenon of a cathodic peak during the anodic sweep. This effect was greatest at high concentration and low sweep rates and disappeared as the concentration was lowered or the potential sweep rate was increased. Similar observations have been noticed by French workers.[6] The phenomenon was not entirely reproducible in that it was dependent upon the state of the mercury. Twice distilled mercury was much more prone to exhibit the effect than triple distilled mercury when voltammetry was carried out using a long drop-time capillary electrode. Furthermore, it could be suppressed by the presence of the corresponding enamine in the solution.

This irregularity interfered with the study of the immonium salts by linear sweep voltammetry, since the maximum obscured the peak potentials and shapes. However, in conditions where streaming did not occur, it was observed that all four salts exhibited a single one-electron

† Deceased.

Table 1. Half-wave potentials and slope values (peak potentials *vs* log sweep rate) of immonium salts (cons. 1 mM) in acetonitrile containing 0.1 M TEAP or 0.4 M TEAFB.

Compound	No.	$E_{\frac{1}{2}}$/V *vs.* SCE	Slope/mV decade^{-1}
N-Cyclohexylidenepyrrolidinium fluoroborate	*1*	−1.67	−18.4 ± 4
N-Cyclopentylidenepyrrolidinium fluoroborate	*2*	−1.79	−23.2 ± 4
N-(2-Methylcyclohexylidene) pyrrolidinium fluoroborate	*3*	−1.73	−17.9 ± 4
N-Isopropylidene pyrrolidinium perchlorate	*4*	−1.76	−22.1 ± 4

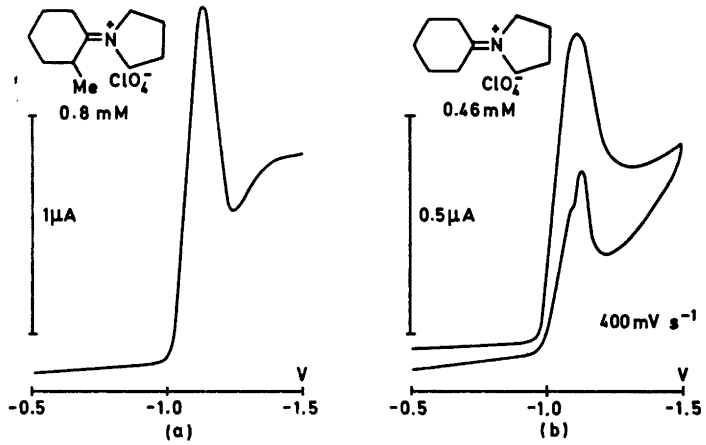

Fig. 1. (a). DC polarogram of *N*-(2-methylcyclohexylidene)pyrrolidinium perchlorate in 0.1 M $TBABF_4 - CH_3CN$. Reference electrode: Ag | AgI | 0.1 M TBAI. *(b).* Cyclic voltammogram of *N*-cyclohexylidenepyrrolidinium perchlorate in 0.4 M TEAP-CH_3CN at an HMDE. Reference electrode as (a).

reduction peak which was irreversible even at the highest sweep rates employed (300 V s^{-1}) in both AN and *N*,*N*-dimethylformamide (DMF) containing tetraalkylammonium salts as supporting electrolyte. All of the salts exhibited an anodic shift of peak potential with increasing substrate concentration and a cathodic shift with increasing sweep rate. Using a long drop-time capillary electrode and a low concentration of depolariser in order to minimize the effect of uncompensated resistance, the peak potentials were measured for a range of sweep rates. After correcting for residual uncompensated resistance by comparison with the behaviour of the one-electron reversible wave of benzophenone under the same conditions, the peak potentials gave linear plots (correlation coefficients > 0.99) against the logarithm of the sweep rate (v) and the slopes of the lines are given in Table 1.

The compound *4* has previously been studied by this method [3] using more accurate equipment and is included here as a test of the less sophisticated equipment used in this study. The value of the slope obtained agrees well with that previously reported.

In agreement with these authors,[3] we have found that the addition of a proton donor such as phenol has no effect on the value of the peak potential. However, for salts *1*−*3* a marked increase in the peak current was observed, the amount of the increase being dependent upon

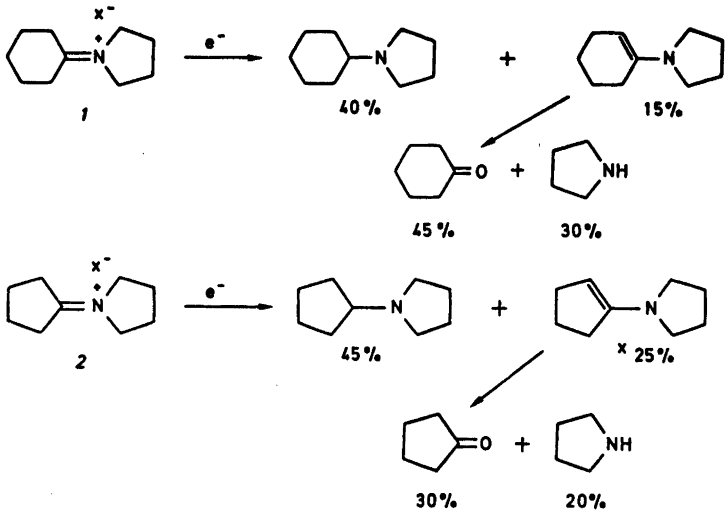

Fig. 2. Preparative electrolyses of cyclic immonium salts. X = BF^-_4 or Cl^-_4; electrodes: Hg, Pt, or graphite; solvents: DMF or CH_3CN; electrolytes: TBABF or FBAP, LiBF, LiCl.

the proton donor concentration. The effect on the peak of salt *4* was much smaller. Addition of phenol also tended to increase the occurrence of the maxima described above. Consequently, it was hoped that complete removal of acidic impurities by the addition of activated alumina [7] to the solution might decrease the occurrence of streaming maxima. Unfortunately, this caused the peak to disappear completely, presumably due to strong adsorption of the substrate on to the alumina.

It proved difficult to study the voltammetry of the salts in the presence of lithium cations due to the proximity of the reduction waves to the discharge potentials of the lithium salts. However, it appeared that the behaviour was very similar to that described above.

Table 2. Results from preparative reductions of salt *3* (fluoroborate perchlorate, 0.1 M) in 0.1 M TBAFB (A) or TBAP (B). Products: 1 = pyrrolidine, 2 = 2-methylcyclohexanone, 3 = *N*-(2-methyl-1-hexenyl)-pyrrolidine, 4 = *N*-(2-methylcyclohexyl)pyrrolidine. Mercury pool at −1.6 V *vs.* Ag | AgI | 0.1 M TBAI unless otherwise stated.

Solvent	Electrolyte	Initial current mA	*n*/F mol^{-1}	Yields (% GLC) 1	2	3	4	*cis*: *trans*
AN	A	300	0.97	15	23	28	43	5.2
DMF	A	240	1.02	2	—	3	46	5.6
AN[a]	A	160	1.07	23	30	6	37	5.3
AN[b]	A	230	1.01	12	16	39	42	2.0
AN[b]	$LiBF_4$	10	0.98	2	52	4	17	1.1
AN	B[c]	260[f]	1.00	29	35	9	54	4.2
DMF	B[c]	250[f]	0.98	7	—	0	34	3.7
AN	B[d]	300	2.06	3	33	17	62	2.4
DMF	B[d]	260	1.21	5	—	3	39	5.2
DMF	B[e]	250	1.24	0	—	4	38	3.7
AN	B	250[h]	1.08	18	50	6	31	5.9
AN	B	40[n]	0.90	7	45	0	52	2.7

[a] Carbon; [b] Platinum; [c] +0.1 M $LiClO_4$; [d] +0.1 M phenol; [e] +0.2 M phenol; [f] −1.2 V; [g] −1.1 V; [h] 0.01 M *3*; [i] DMF and ketone 2 could not be fully separated.

Table 3. Results from preparative reductions of salt *4* (0.1 M) on mercury in 0.1 M TBAP. Reference electrode: Ag | AgI | 0.1 M TBAI.

Solvent	Working potential V	n/F mol^{-1}	% *N*-Isopropylpyrrolidine
AN	−1.2	0.99	21
AN	−2.0	0.99	21
AN	−1.6[a]	1.99	39
DMF	−1.6	0.99	21

[a] +0.2 M phenol.

Preparative electrolysis. The general results of salts *1* and *2* are summarized in Fig. 2, and the results of electrolysis of salt *3* are listed in Table 2.

Electrolysis of salt *4* gave, after addition of water to the catholyte and subsequent extraction with ether, a white solid similar to that described earlier. However, the melting point of the solid was somewhat lower (190 °C), and examination of the ^{1}H NMR spectrum showed the presence of both the monomer and dimer amines. The results of GLC-analysis of the catholyte for *N*-isopropylpyrrolidine are shown in Table 3. Unfortunately, in our hands, the dimer could not be obtained in a pure form, and we were consequently unable to analyse for it.

DISCUSSION

The voltammetric behaviour observed for salts *1*–*3* was very similar to that of some of the types of immonium salts previously studied indicating that, although the final products of reaction were monomers rather than dimers, the kinetic characteristics of the follow-up reaction were the same. The results of the preparative electrolyses seem to confirm the absence of dimerization reactions for the type of immonium salt studied here. Furthermore, the direct observation by GLC of the reaction products confirms the formation of enamines in the present reactions.

In order to rationalize the experimental findings it is necessary to consider several possible pathways for the reduction of immonium salts. These are listed in Table 4 together with the theoretical slopes [8,9] of the E_p-log v diagrams and the preferred stereoisomer of the resultant amine when the substrate immonium salt is substituted in the 2-position of the cyclohexyl ring (compound *3*). The stereochemical reasoning which allows one to predict this is somewhat different from that previously proposed.[1]

It is first of all necessary to consider the molecular shape of the species involved in the reaction as shown in Fig. 3. The substrate salt

Table 4. Survey of reaction possibilities for reduction of immonium salts AH^+.

Reaction Type	Reaction Scheme	Slope mV/decade	Isomer preferred
(1) Electron transfer at electrode	$AH^+ + e^- \rightleftharpoons AH^{\cdot}$	–	–
(2) Radical-radical dimerization	$AH^{\cdot} + AH \rightarrow HAAH$	−19.7	–
(3) Radical-substrate dimerization	$AH^{\cdot} + AH^+ \rightleftharpoons HAAH^{+\cdot}$ $HAAH^{+\cdot} + e^- \rightarrow HAAH$	−29.6	–
(4) Ion-substrate dimerization	$AH^{\cdot} + e^- \rightleftharpoons AH^-$ $AH^- + AH^+ \rightleftharpoons HAAH$	−14.8	–
(5) Radical-radical H-atom transter	$AH^{\cdot} + AH^{\cdot} \rightarrow AH_2 + A$	−19.7	*cis*
(6) Radical-radical electron transfer	$AH^{\cdot} + AH^{\cdot} \rightleftharpoons AH^+ + AH^-$ $AH^- + AH^+ \rightarrow AH_2 + A$	−19.7	*trans*
(7) Radical-substrate H$^+$-ion transfer	$AH^{\cdot} + AH^+ \rightleftharpoons AH_2^{+\cdot} + A$ $AH_2^{+\cdot} + e^- \rightarrow AH_2$	−29.6	*trans*
(8) Radical-substrate H$^+$-ion transfer	$AH^{\cdot} + AH^+ \rightleftharpoons AH_2^{+\cdot} + A$ $AH_2^{+\cdot} + AH^{\cdot} \rightarrow AH_2 + AH^+$	−29.6 [a] −19.7 [b]	*trans*
(9) Radical-substrate H-atom transfer	$AH^{\cdot} + AH^+ \rightarrow AH_2 + A^{+\cdot}$ $A^{+\cdot} + e^- \rightarrow A$	−29.6	*cis*
(10) Ion-substrate proton transfer	$AH^{\cdot} + e^- \rightleftharpoons AH^-$ $AH^- + AH^+ \rightarrow AH_2 + A$	−14.8	*trans*

[a] Protonation rate determining. [b] Protonation fast and electron transfer rate determining.

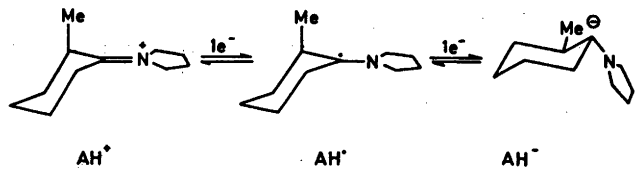

Fig. 3. Shapes of molecules involved in the reduction of the *N*-(3-methylcyclohexylidene)pyrrolidinium cation.

AH^+ is believed [10] to exist with the 2-methyl substituent in the axial position in order to avoid steric interaction with the pyrrolidine ring which must be in the same plane as the C=N bond. It is useful to consider the energies of the filled orbitals in the C=N bond. Since both the σ-bonding and the π-bonding orbitals are completely filled in the immonium salt, any further electrons go into the π^*-antibonding orbital. Now, if only one electron is added then retention of π-character still results in a net gain in orbital energy over the situation where π-character is completely lost. Therefore, the radical would prefer to remain planar, provided the π-energy gain was greater than the destabilization energy of the 1,3-diaxial strain due to the axial position of the 2-substituent. If not, then the situation would be the same as for the case where two electrons are added to the substrate salt, and the π-character is lost. In this case the molecule would change its shape in order to minimize the steric strain and, consequently, the planarity about the carbon-nitrogen bond would be lost (Fig. 3). Therefore, from these considerations it seems reasonable to assume that the intermediate radical is flat and the 2-substituent remains in the axial position.

One must now consider the various types of reactions which determine the stereochemistry of the products (Table 4): (a) hydrogen atom transfer (5,9), (b) proton transfer followed by addition of one electron either at the electrode or in solution (7,8), (c) prior electron transfer either at the electrode or in solution followed by proton transfer (6,10).

The case of (a) is outlined in Fig. 4. Inspection of a molecular model of the radical will illustrate the steric hindrance that exists on one side of the molecule towards approach by the hydrogen atom donor. In consequence, the *cis* form of the product amine ought to be the preferred form.

In case (b) addition of a proton to the intermediate radical $AH\cdot$ by the substrate AH^+ is subject to the same stereochemical constraints as above. However, the protonation would be expected to take place on the nitrogen of the radical in analogy with the protonation of the enamines.[11] Rapid reduction of this protonated radical would follow leading to a molecular shape similar to that of the anion AH^- (Fig. 3). Finally, rearrangement of the proton to give the product amine favours the *trans* isomer, since the molecular geometry has already been determined by the second electron transfer.

For case (c) protonation of the anion AH^- also leads to the predominance of the *trans* isomer following similar reasoning as for (b). The step which determines the resultant stereochemistry is the addition of a proton to the bent AH^- species. The possibility of a hydride ion transfer from AH^- to AH^+ is not thought to be significant.

The results of preparative reduction of *3* at mercury, platinum, or graphite in DMF or AN containing tetraalkylammonium salts as supporting electrolyte (Table 2) consistently demonstrate that the *cis* isomer is the predominant form of the product amine. Taking into account the experimental slope values found (Table 1) the remaining possibilities of Table 4 (5 or 9) can be distinguished. Our conclusion is that

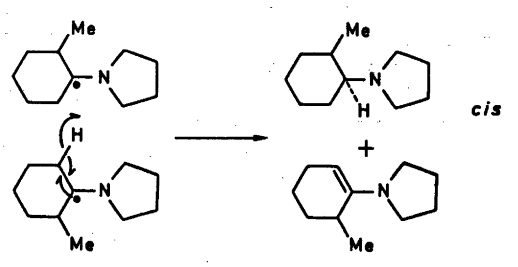

Fig. 4. H-atom disproportionation mechanism.

the mechanism of reduction of salt *3* in aprotic conditions consists of a *one-electron transfer followed by a rate-determining radical-radical disproportionation reaction involving hydrogen atom transfer.*

It is of interest to compare the observed isomer ratios of the product amine with the ratio obtained in the case of the formic acid reduction [12] of the corresponding enamine (*cis*:*trans* = 5.5). This value is very similar to the ratios obtained in the reductions at mercury and carbon electrodes. This is what one would expect from the stereochemical considerations outlined above providing the electron transfer is followed by a *homogenous* reaction and lends support to the assumption made above concerning the planarity of the intermediate radical.

The isomer ratio observed in the reduction at platinum (Table 3) is appreciably different. This may possibly be attributed to a surface effect since the other factors in the reaction are the same as in the reduction at graphite. It is possible that the intermediate radical is adsorbed on the metal electrode such that the sterically free side of the molecule is blocked thus preventing the normal reaction from taking place and bringing into play one of the other possible mechanisms (*e.g.* 10, Table 4). This seems to be not unreasonable in view of the surface activity at Hg displayed by the substrate salt and the enamine with respect to the streaming maxima observed in polarography and voltammetry. The absence of an adsorption effect on the isomer ratios in the case of mercury even at low concentration may have been due to the agitation of the mercury surface which, of course, is not possible with platinum.

The presence of phenol or lithium cations in solution also appears to have some effect on the mechanism. The observation of no change of peak potential on addition of phenol to the solution implies that the reaction kinetics remain the same. This rules out participation by pathways 7, 8a and 10 (Table 4) where phenol takes the place of AH^+ as proton donor. Both of the remaining pathways 6 and 8b would be consistent, not only with the peak potential remaining constant, but also with the observation of an increase of peak current on addition of phenol to the solution. However, it is difficult to see how the presence of Li^+ cations in solution would favour route 8b, whereas the obvious possibility of ion-pair formation (AH^-/Li^+) should favour route 6 by shifting the equilibrium to the right.

The results of electrolyses of salt *4* (Table 3) illustrate the duality of the dimerization and atom transfer disproportionation reactions which have previously been remarked upon.[8,9] It is also of interest that addition of phenol to the solution almost doubles the amount of monomer formed. If a mechanism similar to 8b was operating, then it might be expected that more monomer than this might be found due to the fast protonation of the radical. However, since an analysis for the dimer was not carried out, one can only assume that the dimerization reaction was not interfered with in some other way.

It is to be noted that the mechanistic conclusions, although in harmony with those of Andrieux and Savéant, are somewhat different from the previous mechanistic proposals for reduction of this type of immonium salt.[1] The proposal that the reduction proceeds *via* pathway 7 in aprotic media where the substrate salt acted as a proton donor now appears to be erroneous. However, the result of electrolysis at a potential (−1.1 V) such that the initial current flowing (40 mA) is considerably less than normal is interesting in this respect. It appears that the substrate salt is acting as a proton donor but, in view of what was said above it is more likely that it is protonating the anion produced *via* route 6 than protonating the radical as in routes 7 and 8. This is because the rate of electron transfer has been reduced by the low potential employed thus allowing the concentration of substrate to remain higher than normal in the region of the electrode for the major part of the reaction and, consequently, pulling the equilibrium of 6 towards the right.

Finally, it must be stated that, although the stereochemical and mechanistic considerations proposed here are capable of explaining all the results observed in this study, it is somewhat more difficult to rationalize all the results of the previous study [1] in a simple manner. However, the conditions prevailing in those experiments would be much more complicated due to the parallel cleavage, hydrolysis and acid-base type reactions whose effects are more difficult to define.

EXPERIMENTAL

Apparatus. Polarographic experiments were carried out with a Metrohm P 305 three-electrode Polarograph in conjunction with a Metrohm E 506 Polarocord. Linear and triangular sweep voltammetry were performed with either a home-built operational amplifier or a Chemical Electronics TR 70/2A potentiostat which was driven by a Chemical Electronics Waveform Generator Type R.B.1. Voltamograms were recorded on either a Hewlett-Packard 7045A or Bryans Model 21005 X-Y recorder for slow sweep rates ($\leq$ 400 mV s^{-1}) and on a Tektronic 5103N storage oscilloscope for higher sweep rates. Preparative electrolyses were carried out by means of Juul Electronic 100V/3A or 300V/1A potentiostat while the consumption of electricity was measured by an electromechanical integrator.

Analytical GLC (double column) was performed on a H-P 5711A Gas Chromatograph coupled with either an H-P 3370B or an H-P 3380A Integrator for data reduction. The columns were 2 m, 6 mm OD glass columns packed with 10 % Carbowax 20 M, 1 % KOH on Chromosorb W (87 – 100 mesh). Preparative GLC was performed on a Perkin-Elmer F21 Gas Chromatograph with a 3 × 1 m, 9 mm OD SS column packed with 10 % Carbowax 20 M, 3 % KOH on Chromosorb W (60 – 87 mesh).

Polarography and voltammetry were carried out in the same cell (Metrohm). The counter electode was a platinum wire and the reference electrode was either SCE, Ag | 0.1 M Ag^+ or Ag | AgI | 0.1 M TBAI. The working electrode for polarography consisted of a capillary which had a flow-rate of 4.8 mg Hg/s and a forced drop-time of 0.8 s. The working electrodes for stationary electrode voltammetry were polished platinum wire or vitreous carbon rod set in glass, or mercury electrodes which were either a hanging mercury drop electrode or a long drop-time (50 – 100 s) capillary electrode.

Preparative electrolyses were carried out in a convential H-type cell.[13] Mercury working electrodes consisted of a pool of mercury of about 15 cm^2 area. Platinum working electrodes consisted of a platinum gauze of similar area to that of the mercury while carbon working electrodes were graphite rods of indeterminate surface area. Counter electrodes were either platinum gauze or graphite rod. The reference electrode was Ag | AgI | 0.1 M TBAI in all cases.

Materials. Acetonitrile (technical grade) was purified and dried by the method of Forcier and Olver.[14] DMF (Fluka, *Purum*) was dried over Molecular Sieves Type 4A and passed through a column of activated alumina immediately prior to use. Tetraalkylammonium salts were recrystallized from abs. ethanol and dried *in vacuo* at 60 °C prior to use. Lithium salts were Fluka Anhydrous and used without further purification. Immonium salts *1* – *4* were prepared according to the literature in similar yields [15] and after recrystallisation from ethanol, gave satisfactory analyses. These salts slowly decomposed in air and were therefore kept under vacuum until use. Enamines and amines, which were formed in the electrochemical reaction were also prepared chemically according to the literature [12,16] in good yields. These compounds were used for calibration of the analytical GLC and were purified beforehand by preparative GLC.

Procedures. For preparative electrolyses the composition of the solution and the conditions were varied as in Table 3. When no more current was observed to be flowing, the cell was disconnected and a known amount of the GLC internal standard (1-butanol or cyclohexanol), was added to the catholyte solution. Samples (0.5 μl) of the catholyte solution were then injected into the gas chromatograph which had previously been calibrated by the internal standard method for quantitative analysis. Different temperature programs had to be employed depending on the initial immonium salt and the solvent used. Repeatability of injections was affected by presumed decomposition of supporting electrolyte salts on-column and consequently each catholyte mixture was injected at least five times to ensure correctness. The product enamines were also unstable, adding further to the uncertainty.

The *cis* and *trans* isomers of the product amine from salt *3* were assigned by the comparison of ^{1}H NMR spectra and GLC retention times with those of previously assigned samples.[12]

In linear sweep voltammetry, allowance was made for the effect of uncompensated resistance by use of a long drop-time capillary electrode in the manner described by Savéant and coworkers.[3,17]

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