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(42) It should be pointed out that no direct information is available concerning the relative energies of diradicals A and B or isoxazoles **21** and **22**.
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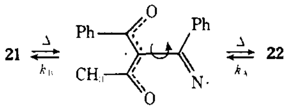

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Electrochemical Reactions of Organic Compounds in Liquid Ammonia. III. Reductive Alkylation of Quinoline

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Abstract: The electrochemical behavior of quinoline in anhydrous liquid ammonia was investigated by cyclic voltammetry and controlled potential coulometry. In the absence of added alkylating agent, quinoline is reduced in two steps to yield the radical anion and dianion both of which undergo further chemical reaction. The radical anion species dimerizes to form the dimeric dianion which is stable in the medium and can be reversibly reoxidized back to parent compound. The second-order rate constant for this dimerization reaction was found to be 1.5×10^2 l./mol sec at −40°C. In the presence of ethyl bromide or *n*-butyl bromide, reductive alkylation proceeds via an ECEC mechanism to yield approximately equal quantities of the 1,2-dihydro-1,2-dialkyl and 1,4-dihydro-1,4-dialkyl derivatives. Differences in product composition between chemical reduction with lithium and electrochemical reduction are explained.

Recently there has been an upsurge of interest in the study of reductive alkylation reactions in nonaqueous solvents because of their possible applications to organic synthesis. Previously, this technique has been used to prepare a variety of mono- and dialkyl derivatives by chemically reducing an unsaturated hydrocarbon with an alkali metal in liquid ammonia, followed by quenching of the reaction mixture with an alkyl halide.[1-4] In more recent work, these reactions have been performed in the nonaqueous solvents dimethylformamide (DMF) and acetonitrile (AN) with electrochemical reduction of the parent compound.[5-7] An advantage in this procedure over alkali metal reduction is that both reactants can be present in solution simultaneously since selective reduction of the unsaturated compound can be obtained by proper adjustment of the electrode potential. With the electrochemical procedure, the scope of the reaction has been broadened to include reduction of unsaturated carbon-oxygen, carbon-nitrogen, and nitrogen-oxygen bonds, while the use of acid chlorides or acid anhydrides as electrophiles has led to the preparation of certain acyl derivatives in addition to the alkyl derivatives available from reaction with alkyl halides.

A competing protonation reaction frequently accompanies the alkylation reaction in DMF and AN, producing a product mixture consisting of diprotonated, monoalkylated, and dialkylated derivatives, with the dialkyl derivative often occurring in very low yield. A higher yield of the alkyl derivatives as well as a better understanding of the alkylation reaction would be obtained if protonation could be eliminated. For this reason, a study of this reaction with

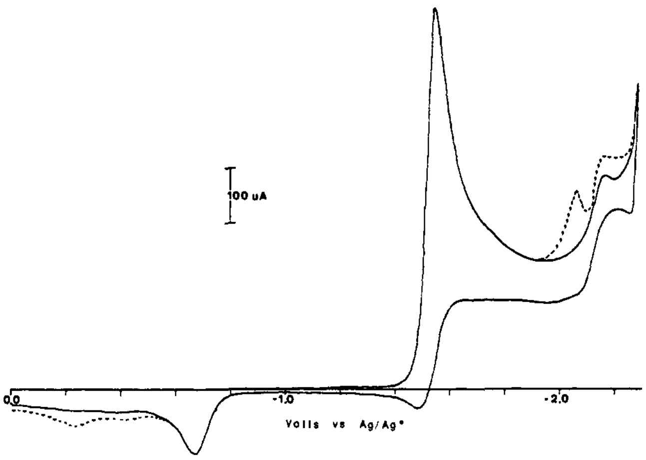


Figure 1. Cyclic voltammogram of 9.6 m*M* quinoline in anhydrous liquid ammonia–0.1 *M* KI at −40°C. Scan rate, 200 mV/sec. Dashed line shows effect of adding 1.2 m*M* isopropyl alcohol.

electrochemical reduction of the unsaturated species was conducted in liquid ammonia, a solvent which clearly possesses greater stability toward reduced species with respect to protonation than any of the more frequently used nonaqueous solvents.[8-10]

The compound chosen for this study is the aromatic nitrogen heterocycle quinoline. The electrochemical behavior of quinoline in AN[11] and DMF[12] has been reported so that these results could be compared with those obtained in liquid ammonia. Also available for comparison are results of the reductive alkylation of quinoline in liquid ammonia brought about by alkali metal reduction of the parent compound.[13]

Experimental Section

The general experimental techniques including handling and purification of the solvent, as well as a detailed description of the electrochemical cell used in this study has been given previously.[8]

Quinoline (reagent grade, Matheson Coleman and Bell) was vacuum distilled immediately before use. Ethyl bromide and *n*-butyl bromide (reagent grade, J. T. Baker Co.) were used as received. Gas chromatographic analysis indicated a 99+% purity of all reagents used. The supporting electrolyte, potassium iodide (reagent grade, Baker and Adamson) was ground into a fine powder, dried at 110°C for 48 hr, and stored over phosphorus pentoxide.

All electrochemical experiments were performed with a PAR Model 170 electrochemistry system (Princeton Applied Research Corporation, Princeton, N.J.) using positive feedback to compensate for solution resistance. Cyclic voltammograms at scan rates greater than 500 mV/sec were obtained with a Tektronix Type 564 storage oscilloscope. NMR analyses were performed on a Perkin-Elmer Model 12 instrument, in carbon tetrachloride using tetramethylsilane as an internal reference.

Results and Discussion

Electrochemical Behavior in the Absence of Alkylating Agent. A cyclic voltammogram of quinoline in liquid ammonia shows one reduction wave at −1.56 V (vs. Ag|Ag$^+$) and a smaller second reduction wave at −2.15 V (Figure 1). At low concentrations of parent compound and at fast sweep rates, the first reduction wave shows an i_{pa}/i_{pc} ratio of 1.0 (where i_{pc} and i_{pa} are the cathodic and anodic peak currents, respectively) while, at slower sweep rates and/or higher concentrations of quinoline, the peak current ratio decreases (Table I) and an oxidation wave appears at −0.64 V. Addition of isopropyl alcohol, a weak proton donor, has no apparent effect on the height of the first reduction wave or on the oxidation wave at −0.64 V. A detailed analysis of the second reduction wave could not be undertaken because of its proximity to the cathodic limit of the solvent. However, qualitatively we observed that addition of isopropyl alcohol increased the height of the second reduction wave and also resulted in the appearance of an oxidation wave at −0.24 V.

Table I. Cyclic Voltammetric Results and Rate Constants for Dimerization of Quinoline in Liquid Ammonia[a]

Scan rate (v), V/sec	$i_{pc}/v^{1/2}C$	i_{pa}/i_{pc}	ω^b	k_2, l./mol sec
		C = 2.99 m*M*		
0.20	60	0.55	2.97	0.9×10^2
0.50	59	0.64	1.57	1.2×10^2
1.00	54	0.76	0.71	1.1×10^2
2.00	55	0.82	0.47	1.4×10^2
5.00	53	0.86	0.32	2.4×10^2
10.00	50	0.91	0.18	2.7×10^2
		C = 5.97 m*M*		
0.50	53	0.59	2.55	1.0×10^2
1.00	52	0.64	1.62	1.2×10^2
2.00	52	0.73	0.88	1.3×10^2
5.00	50	0.81	0.49	1.9×10^2
10.00	51	0.88	0.26	2.0×10^2
		C = 8.95 m*M*		
1.00	53	0.58	2.43	1.2×10^2
2.00	53	0.71	1.02	1.0×10^2
5.00	52	0.78	0.60	1.5×10^2
10.00	50	0.87	0.28	1.4×10^2
			Av:	1.5×10^2

[a] The solution contained 0.1 *M* KI at −40°C. [b] Log $\omega = \log k_2 C\tau + 0.034(a\tau - 4)$, where $a = (nF/RT)v$, $\tau = (E_\lambda - E°)/v$, and E_λ is the switching potential.[14]

Controlled potential coulometric analysis at the potential of the first reduction wave gave an average n_{app} value of 1.0 (where n_{app} is the number of coulombs consumed per mole of quinoline) and produced a dark-green solution. A cyclic voltammogram of the reduced solution showed only the irreversible oxidation wave at −0.64 V, the height of which was approximately one-half the height of the original reduction wave (Figure 2B). Coulometric oxidation of the reduced species at a potential of 0.0 V gave an n_{app} value of 0.93 and, during the course of the electrolysis, the color of the solution changed from green to yellow-brown and became colorless at the completion of the experiment. A cyclic voltammogram of the reoxidized product was the same as that of parent compound (Figure 2C).

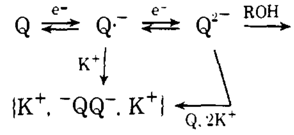
The electrochemical behavior of quinoline in liquid ammonia agrees with the behavior expected for formation of a dimeric dianion via coupling of radical anion species.[14] The increase in the peak current ratio (i_{pa}/i_{pc}) with increasing scan rate for the first reduction wave indicates that the radical anion species is involved in a fast following chemical reaction, but protonation can be eliminated as a possible reaction route since addition of a proton donor had no effect on the reduction wave. Furthermore, the magnitude of the change in cathodic peak current function ($i_{pc}/v^{1/2}C$) with scan rate (v), which was approximately 20%, suggests a reaction mechanism which is greater than first order in radical anion since the maximum current increase for a first-order reaction is about 11%.[15]

In a study of the ESR spectra of heterocyclic aromatic compounds, Szwarc et al.[16] found that treatment of quinoline with 1 equiv of sodium metal in hexamethylphosphortriamide (HMPA) resulted in a quantitative yield of monomeric radical anion species, while the same procedure carried out in tetrahydrofuran (THF) resulted in a 99+% yield of dimeric dianion. The driving force for dimerization was assumed to be ion pair formation between the radical anion and the alkali metal cation according to the equilibrium:

$$2M^+ + 2Q\cdot^- \rightleftharpoons \{M^+, {}^-QQ^-, M^+\}$$

In solvents of high dielectric constant, the ions are freely dissociated and the equilibrium lies far to the left while, in solvents of low dielectric constant, ion pairing predominates and the equilibrium lies far in the direction of the dimer dianion. Liquid ammonia has a dielectric constant of 22, approximately midway between that of HMPA (ϵ 46) and that of THF (ϵ 7.6) so that one might expect approximately appreciable quantities of both dimeric and monomeric species. However, a cyclic voltammogram of the solution after coulometric reduction (Figure 2B) shows that the wave associated with oxidation of the dimeric dianion at −0.64 V is considerably larger than the wave associated with reoxidation of the free radical anion indicating that, in liquid ammonia in the presence of potassium ion, the above equilibrium lies far to the right, similar to the behavior observed in THF. The second-order rate constant for coupling of the radical anion species, calculated from cyclic voltammetric data (Table I) using the method developed by Nicholson et al.[14] was found to have an average value of 1.5×10^2 l./mol sec at −40°C.

The dimerization reaction lowers the concentration of radical anion at the electrode surface so that when the scan is continued to the potential where the radical anion is further reduced to the monomeric dianion (Q^{2-}, −2.14 V vs. Ag|Ag$^+$), only a small wave appears. The absence of anodic current on scan reversal for this wave indicates that the dianion is also involved in a following chemical reaction. Protonation is a probable reaction, with the anodic wave at −0.24 V then representing oxidation of the anionic species (QH^-). The enhancement of both the reduction wave at −2.15 V and the oxidation wave at −0.24 V with addition of the proton donor, isopropyl alcohol, is evidence for this reaction. Another possibility is the transfer of an electron from Q^{2-} to a neutral molecule of quinoline to form two molecules of the radical anion species, which would then rapidly dimerize. In fact, since previous studies on the electrochemical behavior of organic compounds in liquid ammonia have shown that electrochemically generated dianion species are stable with respect to protonation by solvent on the cyclic voltammetric time scale, this latter reaction scheme may be more likely. The overall reduction mechanism can be written as:



The reported electrochemical behavior of quinoline in DMF using tetraethylammonium iodide as supporting electrolyte is similar to that observed in liquid ammonia, a single one-electron reversible reduction wave at a fast scan rate which becomes irreversible as the scan rate is diminished.[12] However, the presence of the dimeric dianion was not detected. This result is not entirely unexpected since previous work in this solvent has shown that electrochemically generated dianion species are unstable with respect to protonation. In this case, formation of the dimeric dianion is probably followed by rapid protonation to yield a nonelectroactive product.

In AN using tetraethylammonium perchlorate as supporting electrolyte quinoline reportedly gives a single two-electron reduction wave.[11] Since in this study it has been shown that dimerization does not facilitate further addition of electrons, the two-electron process is most likely caused by protonation of the radical anion yielding the free radical species, QH·, which is reducible at the imposed potential. Additional evidence for this mechanism is given in the anodic portion of the cyclic voltammogram which exhibits a wave approximately 1.3 V positive of the original reduction wave, believed to correspond to the oxidation of the anion species, QH^-. Noticeably absent is an anodic wave corresponding to oxidation of the dimeric dianion. Of the three nonaqueous solvent systems used to study the electrochemical reduction of quinoline, the order of stability toward anionic species in the different solvents is AN < DMF < ammonia.

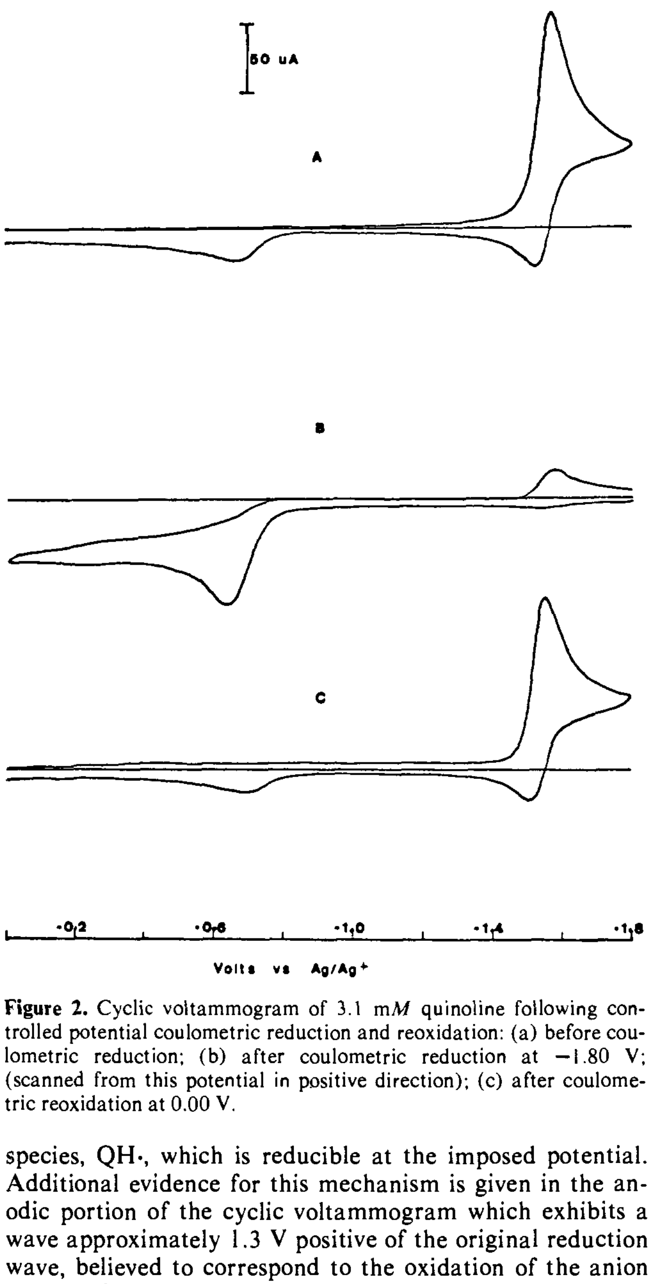


Figure 2. Cyclic voltammogram of 3.1 mM quinoline following controlled potential coulometric reduction and reoxidation: (a) before coulometric reduction; (b) after coulometric reduction at −1.80 V; (scanned from this potential in positive direction); (c) after coulometric reoxidation at 0.00 V.

Electrochemical Behavior in the Presence of Alkylating Agent. The alkylating agents used in this study, ethyl bromide and *n*-butyl bromide, reduce at a sufficiently negative potential (E_p = −2.0 V vs. Ag|Ag$^+$) so as not to interfere with the first reduction wave of quinoline and do not react with ammonia under our experimental conditions.[17] However, when either of these two compounds was added to a solution of quinoline in liquid ammonia, the peak current for the first reduction process increased in height (Table II). In addition, the anodic waves corresponding to reoxidation of the radical anion and dimeric dianion disappeared and a new wave appeared at about −0.14 V (Figure 3). Controlled potential coulometry performed at the first reduction wave of quinoline gave an n_{app} value of 2.0 when 2 or more equiv of alkyl bromide was present. The solution was yellow during the electrolysis but at completion became clear and a white film was deposited on the walls of the cell.

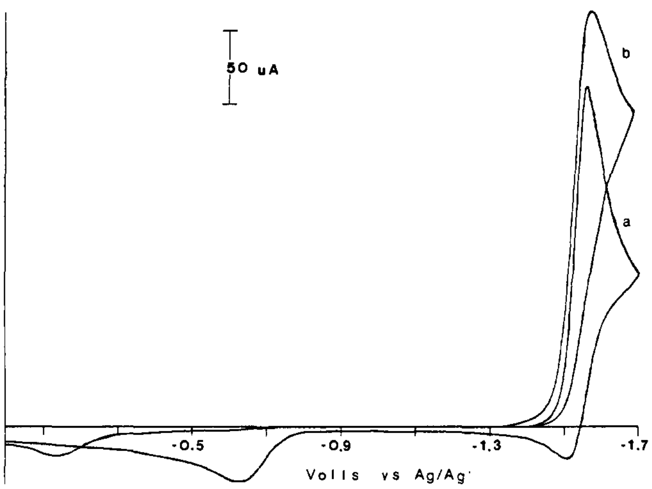


Figure 3. Cyclic voltammogram of quinoline in the presence of *n*-butyl bromide: (a) 8.95 m*M* quinoline; (b) 8.95 m*M* quinoline plus 10.9 m*M* *n*-butyl bromide. Scan rate 200 mV/sec, −40°C.

Table II. Increase in Peak Current of the First Reduction Wave of Quinoline with Addition of Alkylating Agent[a]

A. 3.1 m*M* quinoline

Ethyl bromide/ quinoline[b]	i_{pc}, μA[c]	i_{pc},[d] μA
0	117	87
0.45	127	95
0.82	135	110
1.38	140	110
2.04	145	120

B. 9.1 m*M* quinoline

n-Butyl bromide/ quinoline[b]	i_{pc},[c] μA
0	230
0.17	252
0.34	265
0.47	260
0.71	268
1.21	280

[a] The solution contained 0.1 *M* KI at −40°C. [b] Mole ratio. [c] v = 200 mV sec^{-1}. [d] v = 100 mV sec^{-1}.

A cyclic voltammogram of the electrolyzed solution indicated only the presence of unreacted alkyl bromide. When less than 2 equiv of alkyl bromide was present, the experiment gave a coulometric n_{app} value of less than 2.0 with the solution turning yellow during the initial stages of the electrolysis, then changing to green as the electrolysis neared completion.

In an effort to duplicate the observed behavior of quinoline in ammonia under conditions of chemical reduction, 2 equiv of solvated electrons was generated in a solution not containing quinoline by stepping the potential to beyond the cathodic limit of the solvent (approximately 2.3 V) and then monitoring the integrated current (coulombs) until the proper concentration of electrons was achieved. One equivalent of quinoline was then added, and the solution changed from dark blue to green. The solution was allowed to stir for 10 min at −40°C, and then the alkylating agent was added. It was found that 2 equiv of alkylating agent was necessary to completely discharge the green color of the solution.

Analysis for the reduction products was made difficult by their rapid decomposition into a red oil upon exposure to air. However, an NMR spectrum could be obtained before appreciable decomposition had occurred by allowing the ammonia to evaporate, adding deuterated acetone or carbon tetrachloride to the cell and analyzing immediately. The NMR spectrum of the reduction product of quinoline in the presence of ethyl bromide was compared with spectra obtained for other quinoline derivatives,[18-20] and it showed that the product consisted of approximately equal quantities of 1,2-diethyl-1,2-dihydroquinoline and 1,4-diethyl-1,4-dihydroquinoline.[21]

Table III

δ, ppm (multiplicity, relative area)	1,2-Diethyl-1,2-dihydroquinoline	1,4-Diethyl-1,4-dihydroquinoline
0–2.0 (m, 16)	$-CH_2CH_3$ (C2); $-CH_3$(N) (m, 8)	$-CH_2CH_3$ (C4); $-CH_3$(N) (m, 8)
3.3–3.8 (m, 4)	NCH_2- (q, 2)	NCH_2- (q, 2)
4.0–4.4 (m, 2)	C(2) (m, 1)	C(4) (m, 1)
4.48 (dd, 1)		C(3) (dd, 1)
5.64 (dd, 1)	C(3) (dd, 1)	
5.89 (d, 1)		C(2) (d, 1)
6.0–7.2 (m, 9)	C(4) + carbocyclic (m, 5)	Carbocyclic (m, 4)

The large increase in the peak current for the first reduction wave of quinoline with addition of the alkyl halides suggests a fast following chemical reaction accompanied by additional electron transfer. Furthermore, the absence of an oxidation wave for either the radical anion or dimeric dianion indicates that this reaction proceeds at a faster rate than dimerization. The correct stoichiometry is given by coulometric n values which show that the complete reaction occurs only when at least 2 mol of alkyl halide per mole of parent compound is present. The most likely mechanism involves an ECEC-type reaction which can be represented as:

$$Q \overset{e^-}{\rightleftarrows} Q\cdot^-$$

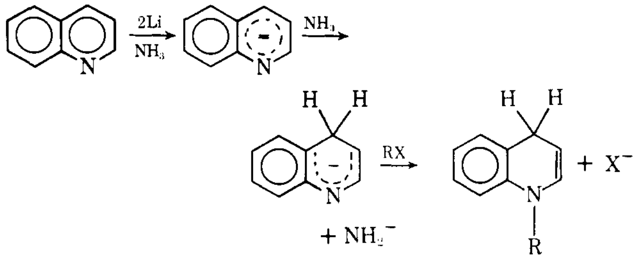
$$Q\cdot^- + RBr \longrightarrow QR\cdot + Br^-$$

$$QR\cdot + e^- \rightleftarrows QR^-$$

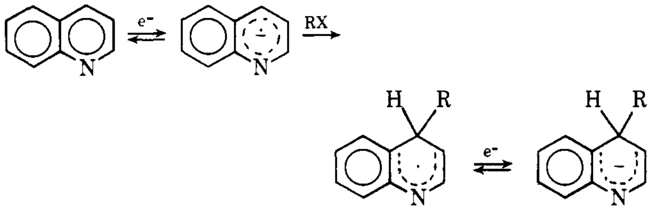
$$QR^- + RBr \longrightarrow QR_2 + Br^-$$

The oxidation wave at −0.14 V, which is in the same potential region as oxidation of QH^-, probably represents oxidation of the transient species QR^-. Assuming a reversible electron transfer process, addition of an alkyl group to the quinoline radical anion must be the rate-determining step in the reaction since the free radical species QR· reduces at a less negative potential than the parent compound. Addition of the second alkyl group is apparently very rapid as indicated by coulometric analysis at a RBr/Q ratio of less than 2:1. For example at a mole ratio of 1:1, slow addition of the second alkyl group would result in a quantitative yield of the species QR^- with an overall n_{app} value of 2.0. Instead, however, an n_{app} value of less than 2.0 is obtained and the appearance of the green dimeric dianion toward completion of the electrolysis indicated depletion of alkyl halide from the solution.

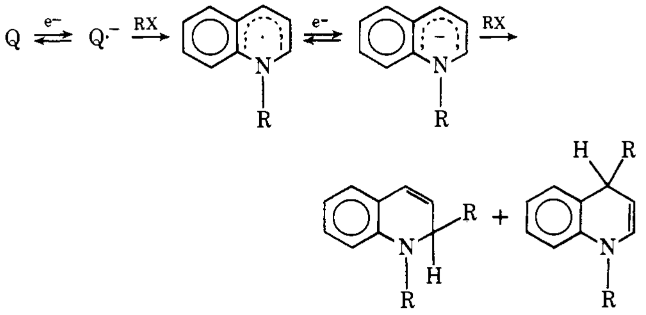
In a recent study of the reductive alkylation of quinoline by lithium metal in liquid ammonia, the product mixture was found to contain a high yield of the 1,4-dihydro-1-alkyl derivative.[13] The proposed reaction mechanism involves generation of the dianion, abstraction of a proton from solvent to saturate the C-4 position, and then further reaction of the anion species with the alkyl halide.



Since in the electrochemical reduction the reaction proceeds via the radical anion rather than the dianion, protonation by solvent does not occur, allowing formation of the dialkyl derivatives. According to Hückel calculations and experimental evidence, the greatest charge density in the quinoline radical anion is at the C-4 carbon atom with the next greatest charge density occurring on the nitrogen atom.[16] The most likely point of attack by the electrophile would then be at the C-4 carbon which, when followed by addition of another electron, would yield an intermediate similar to that hypothesized for the alkali metal reduction mechanism.



Therefore, a high yield of the 1,4-dihydro-1,4-dialkyl derivative would also be expected for this reaction route. However, NMR analysis shows approximately equal concentrations of both the 1,2-dialkyl and 1,4-dialkyl isomers suggesting an alternate reaction pathway. One very probable mechanism would be attachment of the first alkyl group to the nitrogen atom which, although it possesses a lower electron density than the C-4 carbon, is also probably less sterically hindered. Further reduction would then lead to an anionic species displaying approximately equal reactivity at both the C-2 and C-4 positions.



Finally, the necessity of adding 2 equiv of alkyl halide to quench a solution of quinoline in which 2 equiv of solvated electrons has been generated electrochemically suggests that the dialkyl derivatives can be prepared via chemical reduction. The electrochemical generation of solvated electrons in the presence of potassium ion is essentially the same as direct addition of potassium metal to the solution. The choice of alkali metal has been shown to have an effect on the product composition, with dialkylated derivatives produced by reduction with sodium metal while lithium metal reduction yields almost exclusively the monoalkylated derivative.[1-2] In the recent study of the alkylation of quinoline in liquid ammonia, all reductions were carried out with lithium metal.

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(21) The following are the results of the NMR analysis of the reaction product mixture obtained when ethyl bromide was used as the alkylating agent. This spectra resembles very closely the spectra expected for approximately equal quantities of the 1,2-dihydro- and 1,4-dihydroquinoline derivatives with the exception of the large adsorption in the region between δ 0 and 2 ppm, which indicates addition of two ethyl groups rather than two protons. The information and interpretation are as shown in Table III.