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Electrochemical Reduction of Aza-heteroaromatic Compounds. IV.[1] Stabilities of Neutral Free Radicals Electrolytically Derived from 1-Methylcyanoquinolinium Perchlorates

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Three isomers of 1-methylcyanoquinolinium perchlorates were reduced by controlled potential electrolysis for one-electron transfer, and the reduction products were identified in order to clarify their reduction mechanisms and the effect of the cyano group on the stabilities of cyanoquinolinyl radicals. The 1-methyl-4-cyanoquinolinyl radical was stable enough to survive at room temperature under anaerobic conditions. The 1-methyl-2- and 1-methyl-3-cyanoquinolinyl radicals were short-lived and were subsequently dimerized to the 1,4-dihydrotype. The 1-methyl-4-cyanoquinolinyl radical was autoxidized to 1-methyl-4-cyanoquinolinium salts in an electrolyte solution and to 1-methyl-4-cyano-2-quinolone in an ethanol solution.

The mechanisms of the reduction of aromatic compounds containing cyano groups have been studied by many investigators, even if the discussion has been limited to the field of electrochemistry. For example, in acidic media 4-cyanopyridine is reduced to 4-aminomethylpyridine through a four-electron transfer;[2,3] in alkaline media, to pyridine through a two-electron transfer accompanied by decyanation reaction,[4] and in aprotic solvents, to the 4-cyanopyridinyl radical anion through a one-electron transfer.[5] As for phthalonitrile, a reductive decyanation reaction occurs.[6,7] Moreover, in benzonitrile derivatives which have substituents such as carbonyl groups, it is possible for two reduction pathways, the reduction of the cyano and carbonyl groups, to occur.[7,8]

A cyano group with a great resonating effect as well as a great electron-attracting effect would be expected to play an important role in stabilizing a pyridinyl radical. Actually, Schwartz, Kosower, and Shain[9] have detected a relatively stable 1-ethyl-4-cyanopyridinyl radical by means of cyclic voltammetry.

It may be easily suggested that the first polarographic reduction step of quaternary ammonium salts of aza-heteroaromatic compounds (R^+) is a one-electron transfer which does not involve protonation, even in aqueous solutions.

$$R^+ \xrightarrow{e} R\cdot \xrightarrow{e} (R^- \xrightarrow{H^+}) RH$$

The overall process thus contrasts to the case of free bases (R).

$$R \xrightarrow{e} (R^{\overline{\cdot}} \xrightarrow{H^+}) RH\cdot \xrightarrow{e} (RH^- \xrightarrow{H^+}) RH_2$$

A one-electron transfer to a quaternary ammonium salt should produce a neutral free radical, which may be able to avoid the disproportionation.

In the present paper, we will discuss the characteristics of the cyano group. We chose the following quinolinium compounds for study: 1-methyl-4-cyanoquinolinium perchlorate (Ia), 1-methyl-3-cyanoquinolinum perchlorate (IIa), and 1-methyl-2-cyanoquinolinium perchlorate (IIIa). These compounds are reduced by controlled potential electrolysis for one-electron transfer, and the structures of the reduction products are identified in order to clarify the mechanisms of electrochemical reduction, the effect of the cyano group on the stabilities of radicals or dimers produced by one-electron reduction, and the coupling sites of the dimers.

Results

Polarography. 1-Methyl-3-cyanoquinolinium perchlorate (IIa) and 1-methyl-2-cyanoquinolinium perchlorate (IIIa) give complicated polarograms in a buffered solution, while 1-methyl-4-cyanoquinolinium perchlorate (Ia) gives well-defined polarograms over a wide pH range of 2—10. The dependence of the half-wave potential ($E_{1/2}$) of Ia on pH clearly indicates that the first reduction does not involve a protonation step, in contrast with the second ($\Delta E_{1/2}/\Delta \mathrm{pH} = -4$ mV for the first and -51 mV for the second).

The 1-methylcyanoquinolinium perchlorates are sensitive to nucleophiles. The height of the polarographic waves appreciably decreases with the passage of time. IIIa is the most sensitive of the three compounds; it is readily changed to 1-methyl-2-ethoxyquinolinium perchlorate by refluxing in aqueous ethanol for about 20 min. Such nucleophilic substitution reactions by solvents are known with respect to some heteroaromatic quaternary ammonium salts. The behavior of the hydrolysis is similar to that of 1-methyl-4-cyanopyridinium perchlorate reported by Kosower and Patton.[10]

In aprotic solutions, all the cyanoquinolinium salts give well-difined polarographic waves. Table 1 shows

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[1] For Part III in this series: see S. Kato, J. Nakaya, and E. Imoto, *Rev. of Polarogr.*, **17**, Nos. 2/3 (1971).

[2] J. Volke, R. Kubicek, and F. Santavy, *Collect. Czech. Chem. Commun.*, **25**, 1510 (1960).

[3] J. Volke and J. Holubek, *ibid.*, **28**, 1597 (1963).

[4] J. Volke and A. M. Kardos, *ibid.*, **33**, 2560 (1968).

[5] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).

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[7] P. Zuman and O. Manoušek, *ibid.*, **34**, 1580 (1969).

[8] P. Cársky and P. Zuman, *ibid.*, **34**, 498 (1969).

[9] W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Amer. Chem. Soc.*, **83**, 3164 (1961).

[10] E. M. Kosower and J. W. Patton, *Tetrahedron*, **22**, 2081 (1966).

TABLE 1. HALF WAVE POTENTIAL AND WAVE HEIGHT OF REDUCTION- AND OXIDATION-WAVES

Material	Solution	Before electrolysis $E_{1/2}$(V *vs.* SCE) (i_l(μA))		After electrolysis of controlled lst wave $E_{1/2}$(V *vs.* SCE) (i_l(μA))	
		R_1[a]	R_2	O[a]	R
Ia	pH 7	−0.56 (1.75)	−0.93 (1.70)	—	—
Ia	DMF	−0.57 (1.70)	−1.53 (1.25)	−0.56 (1.53)	−1.52 (1.53)
Ia	CH_3CN	−0.33 (2.65)	−1.31 (2.08)	−0.31 (2.23)	−1.30 (2.10)
IIa	pH 5	*ca.* −0.5 (2.03)	no	—	—[b]
IIa	DMF	−0.45 (1.70)	−1.70 (0.38)	—	—[c]
IIa	CH_3CN	−0.31 (2.73)	−1.66 (0.75)	+0.31 (2.73)	
IIIa	pH 5	*ca.* −0.4 (2.03)	no	—	—[b]
IIIa	DMF	−0.26 (1.25)	—[c]	−0.24 (0.70)	
IIIa	CH_3CN	−0.21 (2.90)	—[c]	−0.14 (2.15)	

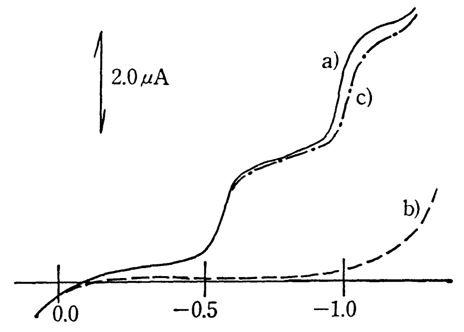
a) R; reduction wave, O; oxidation wave.
b) The precipitates were formed after electrolysis.
c) indistinct wave.

TABLE 2. THE ELECTRON NUMBERS (*n*) REQUIRED FOR THE REDUCTION

Material	Concn. (mM)	Solution	Controlled wave	Controlled potential (-*E*, V *vs*, SCE)	*n*
Ia	0.5	pH 7	1 st	0.70	1.02
Ia	5.0	pH 7	1 st	0.70	1.06
Ia	0.5	pH 7	2 nd	1.05	2.21
Ia	5.0	pH 7	2 nd	1.05	1.99
Ia	0.5	CH_3CN	1 st	0.50	1.05
Ia	0.5	DMF	2 nd	2.10	2.22
IIa	0.5	pH 5	1 st	0.80	1.00
IIa	7.5	pH 5	1 st	0.80	0.99
IIa	7.5	DMF	1 st	0.80	0.91
IIa	0.5	CH_3CN	1 st	0.60	0.93
IIIa	0.5	pH 2	1 st	0.70	1.13
IIIa	5.0	pH 5	1 st	0.70	1.10
IIIa	0.5	CH_3CN	1 st	0.40	1.03

the $E_{1/2}$ values of the quinolinium salts. It is clear that the cyano group has an effect on the positive shift of the reduction potential compared with quinolinium salts[1)] by *ca.* 0.47 V.

General Electrolysis. The coulometric data (Table 2) suggest that Ia absorbs one electron per molecule by controlled potential electrolysis corresponding to the first wave, and two electrons per molecule, by the electrolysis corresponding to the second wave. As for IIa and IIIa, one-electron reduction also occurs by the electrolysis at the potential corresponding to the first wave.



E(V) *vs.* SCE

Fig. 1. Polarographic behavior of 1-methyl-4-cyanoquinolinium perchlorate (I_a), before and after one-electron electrolysis (pH 7).
a) before b) just after c) 15 min. after

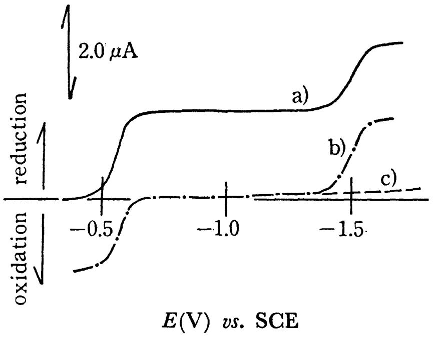
TABLE 3. THE RECOVERY[a] OF REDUCTION PRODUCTS

Material	Reduction Product	pH	Time (min)	Yield (%)
Ia	1 e	7	3	90
Ia	2 e	7	15	trace
IIa	1 e	2	20	87
IIIa	1 e	2	20	29

a) The yields were measured polarographically after stirring at room temperature under aerobic condition.

One-electron reduction products formed by electrolysis precipitate in buffered solutions. A reduction wave is not observed when electrolysis is completed. However, it becomes observable at the original position after stirring at room temperature under aerobic conditions (Fig. 1). The recovery yield becomes larger in the order of IIIa<IIa<Ia (Table 3). On the contrary, the recovery yield of the two-electron reduction product of Ia is very slight; therefore, it may be concluded that the two-electron reduction product is not so sensitive to air as the one-electron reduction product.

When the quinolinium salts are subjected to one-electron electrochemical reduction in aprotic solvents under the same conditions as in the polarographic measurement, oxidation waves appear in all the cases (Table 1). In the case of Ia, an oxidation and a reduction wave are observed at the potentials identical with those of the first and the second waves of Ia respectively. Moreover, the heights of the oxidation and the reduction waves are almost identical with those of the first and the second waves of Ia (Fig. 2). On the other



E(V) *vs.* SCE

Fig. 2. Polarographic behavior of 1-methyl-4-cyanoquinolinium perchlorate (I_a), before and after electrolysis (in DMF).
a) before electrolysis
b) just after one-electron reduction
c) just after two-electron reduction

hand, both the solutions after the one-electron reduction of IIa and IIIa have oxidation waves at potentials less negative than those of the original reduction waves. The discordance in potential in those cases suggests the formation of the dimers. The two-electron reduction product of Ia shows no oxidation wave; this serves to confirm the lower oxidizability of two-electron reduction products.

Structure of the One-electron Reduction Product of 1-Methyl-4-cyanoquinolinium Perchlorate (Ia). Kosower and his co-worker11) reported that 1-alkyl-4-cyanopyridinyl radicals are relatively stable, but that subsequent dimerizations cause decyanation reduction, thus forming alkylviologen radicals. As has been shown above, Ia shows an oxidation wave at the same potential as does the original reduction wave. Moreover, Ia is almost quantitatively recovered by the autoxidation, and the electron required for the reduction of one molecule of Ia is no more than unity. Moreover, the solution after the one-electron reduction of Ia shows a considerably different UV spectrum from the corresponding two-electron reduction product (Fig. 3). Hence, the one-electron reduction product of Ia seems to be a stable neutral radical which involves no decyanation reaction.

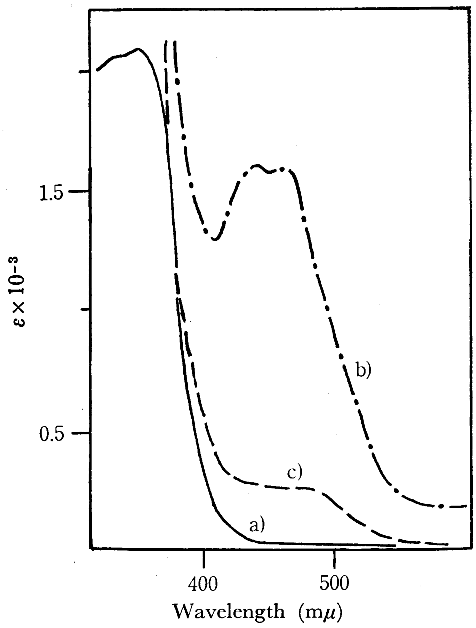


Fig. 3. Electronic spectra of 1-methyl-4-cyanoquinolinium perchlorate (I_a), before and after electrolysis (in DMF).
a) before electrolysis
b) just after one-electron reduction
c) just after two-electron reduction

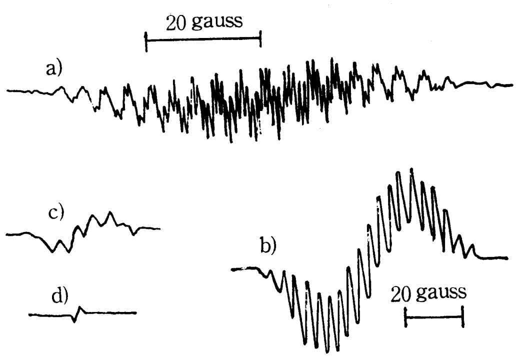


Fig. 4. ESR spectra of the one-electron reduction product of 1-methyl-cyanoquinolinium perchlorates in acetonitrile solution.
a) I_a, modulated width 1.5 gauss
b) I_a, modulated width 4.5 gauss
c) III_a, intermediate
d) II_a, intermediate

During and after the electrolysis of an acetonitrile solution of Ia at the potential corresponding to the one-electron reduction (−0.9 V *vs.* $\mathrm{Ag/AgClO_4}$), an ESR signal with a hyper-fine structure of $19\times5=95$ lines is observale (Fig. 4). The deep yellow crystalline precipitates obtained by the one-electron reduction of Ia also show an ESR signal in the solid state or in a solution. The solution, after reduction with zinc powder, also shows the ESR spectrum. When the 5w/v-% acetonitrile solution of Ia is reduced by zinc dust, no signal is observed in its NMR spectrum (Fig. 5). The removal of zinc dust from the solution causes a quantitative recovery of the signals of Ia. Therefore, it is obvious that the one-electron electrochemical reduction product of Ia is a stable radical, one which is identical with the reduction product with zinc dust, and that the radical is stable even at high concentrations or in the solid state.

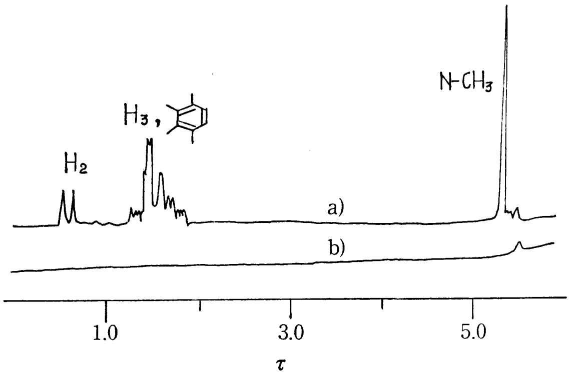


Fig. 5. NMR spectra of 1-methyl-4-cyanoquinolinium perchlorate (I_a), before and after Zn reduction (in CH_3CN).
a) before b) after

Autoxidation of 1-Methyl-4-cyanoquinolinyl Radical (Ib). When the solution after the electrolysis of Ia is exposed to air, Ib is autoxidized to Ia almost quantitatively. When Ib is refluxed in ethanol, 1-methyl-4-cyano-2-quinolone (IV) is isolated from the solution by means of recrystallization or sublimation. Accordingly, Ib seems to react with oxygen at the 2-position in the quinoline ring under aerobic conditions, forming a peroxide with a 1,2-dihydro structure which may decompose to IV. This spectrophotometric behavior further supports the idea that Ib intermediately produces the peroxide with the 1,2-dihydro structure. The ethanol solution of Ib shows the same UV maximum (360 mμ) as that of 1-methyl-4-cyano-1,2-dihydroquinoline (Ic), and Ib shows a strong band at

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11) E. M. Kosower and J. L. Cotter, *J. Amer. Chem. Soc.*, **86**, 5524 (1964).

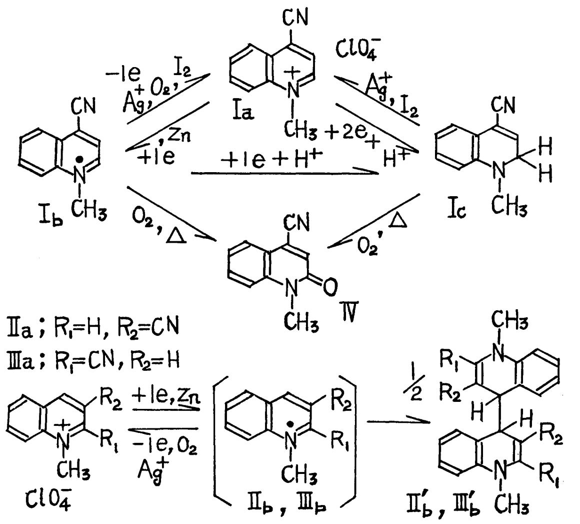
Table 4. UV- and IR-spectra of reduction products

Material	Reduction product	λ_{max}(mμ)	ν_{max}^{KBr}(cm^{-1})
Ia	1 e	447, 465 (DMF) 360 (EtOH)	2200, 2300 (C≡N) 1665 (C=C)
Ia	2 e	360 (EtOH) 361 (CH_3CN)	2230, 2300 (C≡N) 1645 (C=C)
IIa	1 e	330 (EtOH)	2200 (C≡N) 1645 (C=C)
IIIa	1 e	326 (EtOH) 344 (DMF)	2230 (C≡N) 1636 (C=C)

1665 cm^{-1} due to an absorption of cyclic amide and two bands due to the cyano group in its IR spectrum (Table 4).

Structure of the Two-electron Reduction Product of Ia. The two-electron reduction product of Ia has a UV maximum at about 360 mμ whether the solvent is protic or not; this indicates the formation of Ic. The fact that IV is obtained by the autoxidation of Ic also supports the 1,2-dihydro structure.

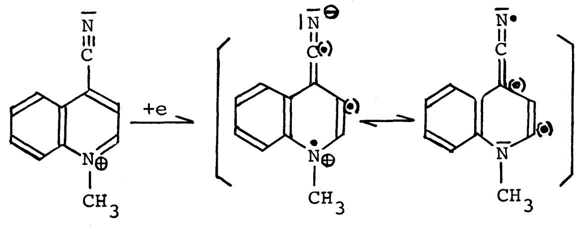
One-electron Reduction Products of 1-Methyl-3-cyanoquinolinium Perchlorate (IIa) and 1-Methyl-2-cyanoquinolinium Prechlorate (IIIa). The one-electron reduction products of IIa and IIIa show UV maxima at 330 and 326 mμ respectively, and IR maxima at 1648 and 1636 cm^{-1} due to ethylenic stretching vibration. These data support the idea that both products are the dimers of a 1,4-dihydro type structure. That they are dimers is proved by the results of elemental analysis and the molecular-weight determination. When the one-electron reduction of IIa or IIIa is performed in an ESR cavity, the ESR signal is detectable only by the *in situ* method (Fig. 4). Each signal intensity is extraordinarily small in comparison with that of Ia under identical conditions. Moreover, the intensity of the intermediary radical derived from IIa is smaller than that of IIIa. These results suggest that the rate of dimerization of the radical (IIb) is greater than that of the radical (IIIb). The fact that the one-electron electrochemical reduction product of IIa and the reduction product with zinc dust are the same dimer (IIb'), one which is oxidizable to IIa with silver perchlorate, is confirmed by UV and NMR spectroscopy.



The reduction mechanisms of Ia—IIIa and the oxidation reaction of their reduction procucts are summarized in the following scheme.

Discussion

Stability of the Radical. As has been mentioned above, only Ia was able to stay as the radical in the solution. This is because the cyano group at the 4-position sufficiently resonates with the quinoline ring, and the unpaired electron can delocalize on each atom in the pyridine ring. On the other hand, IIb has a

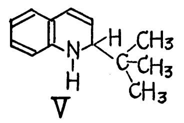


Ia Ib

cyano group at the position *meta* to ring nitrogen; as a result, the unpaired electron is difficult to delocalize. In the case of IIIb, the neighboring *N*-methyl group may sterically prevent it from keeping the co-planarity between the cyano group and the quinoline ring. Therefore, neither IIb nor IIIb is sufficiently stable, and so each radical dimerizes. The fact that the conjugated nitrile ($>\!C{=}C\!<_{CN}$) of IIIb' has a higher frequency than that of IIb' in the IR spectrum (Table 4) suggests steric hindrance by the *N*-methyl group. However, the mighty radical-stabilizing effect of the cyano group is supported by the fact that even IIb or IIIb can be detected intermediately by ESR spectroscopy, though it is rather short-lived.

Elimination of the Cyano Group. Ib does not lead to a decyanation reaction in an aprotic or buffered solution. The stability of Ib is explanined in terms of the great conjugated system which causes the delocalization of the unpaired electron in comparison with the 1-ethyl-4-cyanopyridinyl radical.[11] The 1-methyl-2-cyanoquinolinyl radical, IIIb, does not lead to decyanation because it dimerizes at the 4-position, where the cyano group is not attached.

Oxidation of the One-electron Reduction Product. The fact that the recovery yield of the one-electron reduction product or the reactivity for oxygen decreases in the order of Ib>IIb'>IIIb' is reasonable in view of the structures of the reduction products. Ib is somewhat resistant to dimerization, but since its unpaired electron is in the antibonding molecular orbital, it is very reactive to oxidizing agents. Though IIb' and IIIb' are dimers and the covalent bonds are formed by the reduction, the 4-4' single bond of the dimers is not very resistant to oxidants because of the hindered resonance of the dihydroquinoline ring and the steric effect. The cyano group may sterically affect the stability of the bonding, and so IIb' seems to be more reactive than IIIb'. The oxidative cleavage of such a single C–C bond has been reported for several dihydroquinoline derivatives, such as V,[12] VI,[13] and VII.[14]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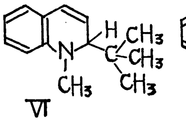
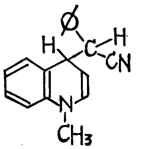

VI


VII

As has been described previously, Ib is autoxidized to the 1-methyl-4-cyanoquinolinium ion in electrolyte solution, while it is autoxidized to 1-methyl-4-cyano-2-quinolone in ethanol. Accordingly, the peroxide initially formed by air-oxidation is considered to have two ways of decomposition: the ionic way (in a buffered solution) and the radical one (in a solution which contains no electrolyte).

Experimental

The polarographic measurements (Yanagimoto Polarograph, Model P8-AP) and controlled potential electrolysis (Nichiakeiki Potentiostat Type NP-1A) for the coulometry were performed with a concentration of 5×10^{-4}M. In the case of the isolation of reduction products, the electrolysis were performed on solutions ranging in concentration from 5×10^{-3}M to 2×10^{-2}M. The IR spectra of the precipitates obtained from electrolyzed solutions were measured as KBr tablets or chloroform solutions. The molecular-weight was determined in benzene with an Hitachi Molecular-Weight Measuring Apparatus, Model 115.

The Nuclear Magnetic Resonance spectra were recorded with a Hitachi Perkin-Elmer R-20 High Resolution NMR Spectrometer at 60 MHz, using tetramethylsilane as the reference. The spectra of Ia were measured at a concentration of about 5w/v-% in acetonitrile, hydrogen oxide, deuterium oxide, and d_6-dimethyl sulfoxide (d_6-DMSO). After the first spectroscopic measurements, a sufficient amount of zinc powder or sodium dithionite was added to the solution, and the solution was warmed for a few minutes. Then the NMR spectra of the resulting deep red solution were again recorded.

The Electronic Spin Resonance spectra were recorded with a Hitachi ESR Spectrometer, Model MES-4001. Twenty m*l* of a 1-mM acetonitrile solution of a sample containing 0.1 M of TBAP was electrolyzed both *in situ* and in macroscale, using a platium cathode and a platium anode. The nitrogen used to degas the solution was previously passed over a hot copper gauze. The reference electrode used in in this experiment was an Ag/AgClO$_4$ electrode.

1-Methyl-4-cyanoquinolinium Perchlorate (Ia). In a 300-m*l* three-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser, we placed 14.9 g of 4-cyanoquinoline (0.097 mol) and 80 m*l* of benzene, and then 12.3 g of dimethyl sulfate (0.098 mol) were added, drop by drop. The mixture was refluxed for about 12 hr on an oil bath. The precipitates thus formed were filtered, washed with benzene, and dried. The precipitates were added to an aqueous solution of 13.5 g (0.097 mol) of potassium perchlorate. The mixture was warmed on a water bath and then cooled. The resulting white precipitates (22.0 g, 0.082 mol, 85%) were recrystallized twice from 200 m*l* of 50 percent ethanol to give 19.7 g of Ia, mp 200—201°C.

Found: C, 48.96; H, 3.28; N, 9.86%. Calcd for $C_{11}H_9N_2O_4Cl$: C, 49.17; H, 3.38; N, 10.43%.

As will be described below, the conversion to the quinolinium perchlorate was possible by the used of hydrogen perchlorate instead of potassium perchlorate.

1-Methyl-3-cyanoquinolinium Perchlorate (IIa). 3-Cyanoquinoline (2.0 g, 0.013 mol) was dissolved in 50 m*l* of benzene, and then 1.8 g (0.014 mol) of dimethyl sulfate were added, drop by drop. The mixture was refluxed for 20 hr. The precipitates thus formed were filtered, washed with benzene, and dried to give 2.9 g (0.010 mol, 79%) of 1-methyl-3-cyanoquinolinium methylsulfate (IIa′).

To a solution of 2.8 g (0.010 mol) of IIa′ in 50 m*l* of water, we added 1.55 g (0.011 mol) of 70 percent hydrogen perchlorate. White precipitates were filtered out, washed with water and dried. The recrystallization of 2.2 g (0.008 mol, 82%) of the precipitates from 45 mol of 70% ethanol furnished 2.05 g of white needles of IIa, mp 200—202°C.

Found: C, 49.28; H, 3.31; N, 10.47%. Calcd for $C_{11}H_9N_2O_4Cl$: C, 49.17; H, 3.38; N, 10.43%.

1-Methyl-2-cyanoquinolinium Perchlorate (IIIa). 2-Cyanoquinoline (5.0 g, 0.0324 mol) was dissolved in 50 m*l* of benzene, and to the solution there were then added, drop by drop, 10.0 g (0.0794 mol) of dimethyl sulfate. The mixture was worked up as above. The aqueous solution (100 m*l*) of 7.0 g of 1-methyl-2-cyanoquinolinium methylsulfate was decolorized with Norit and then filtered. To the filtrate was added 4.5 g (0.027 mol) of 60 percent hydrogen perchlorate. The resulting white crystallines were filtered by suction, washed with water, and dried to give 4.25 g (0.016 mol, 63%) of IIIa, mp 204—205.5°C.

Found: C, 49.53; H, 3.36; N, 10.17%. Calcd for $C_{11}H_9N_2O_4Cl$: C, 49.17; H, 3.38; N, 10.43%.

1-Methyl-2-ethoxyquinolinium Perchlorate. A solution of 1.4 g (0.0052 mol) of IIIa in 32 m*l* of 90% ethanol was refluxed for a few hours and then cooled to give 0.66 g (0.0023 mol, 44%) of 1-methyl-2-ethoxyquinolinium perchlorate as white needles, mp 182—183°C.

Found: C, 49.74; H, 4.58; N, 4.82%. Calcd for $C_{12}H_{14}NO_5Cl$: C, 49.92; H, 4.90; N, 4.85%.

NMR spectrum (d_6-DMSO, τ): 0.86 (d,1, J=9.75Hz, H_4), 1.58—2.14 (m, 5, H_3 and aromatic H), 5.18 (q,2, J=5.94Hz, $-OC\underline{H}_2CH_3$), 5.81 (s,3, N-CH_3), 8.43 (t,3, J=5.94Hz, $-OCH_2C\underline{H}_3$).

One-electron Reduction of 1-Methyl-4-cyanoquinolium Perchlorate (Ia). In a 500-m*l* electrolytic cell were placed 2.00 g (0.0075 mol) of Ia, 3.80 g of sodium sulfate, 320 m*l* of Britton-Robinson buffered solution (pH 7), and 80 m*l* of distilled water. The solution was then deaerated by a stream of nitrogen while being continuously stirring with a magnetic stirrer. After complete deaeration, electrolysis was carried out at the cathodic potential of −0.70V *vs.* SCE with successive stirring under nitrogen. The electrolysis was stopped when almost no appreciable current passed through. The deep yellow precipitates thus produced were filtered by suction, washed with water, and dried. The precipitates were easily soluble in ether, ethanol, ethyl acetate, and benzene, but insoluble in water and ligroin. Immediately after the precitates were dissolved in solvents, the solutions assumed a dark yellow color; there after they turned light yellow.

Autoxidation of One-electron Reduction Product of Ia. The deep yellow precipitates obtained by the one-electron electrochemical reduction of 2.00 g of Ia were dissolved in ethanol, and the filtrate was evaporated to dryness. The light brown residue was recrystallized from 22 m*l* of ethanol to give 0.290 g

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[12] H. Staudinger, H. W. Klever, and P. Kober, *Ann. Chem.*, **374**, 1 (1910).

[13] W. Bradley and S. Jeffrey, *J. Chem. Soc.*, **1954**, 2770.

[14] J. Leonard and R. L. Foster, *J. Amer. Chem. Soc.*, **74**, 3671 (1952).

(0.0016 mol, 21%) of 1-methyl-4-cyano-2-quinolone. The melting point, the results of elemental analysis, and the UV, IR, and NMR spectra were in agreement with those of the authentic sample.

When the residue of the ethanol solution was sublimed under reduced pressure, 1-methyl-4-cyano-2-quinolone was also obtainable in a 34% yield.

Autoxidation of Two-electron Reduction Products of Ia. A buffered solution (pH 7) of 2.00 g of Ia was electrolyzed at the potential of −1.50V *vs.* SCE in the same way as in the one-electron reduction. The solution of resulting solid in ethanol was filtered, and the filtrate was evaporated to dryness. The residue was sublimed under reduced pressure to give 0.166 g (0.001 mol, 12%) of 1-methyl-4-cyano-2-quinolone.

Oxidation of the Two-electron Reduction Product of Ia with Iodine. Ia (2.00 g) was electrolyzed at −1.50V, and the resulting precipitates were dissolved in 30 m*l* of pyridine. A solution (40 m*l*) of 1.89 g (0.0075 mol) of iodine in methanol was added to this solution. The solvent was evaporated off, and the red-brown, oily material was extracted with water. The water was evaporated, and the residue was recrystallized twice from ethanol to give 0.057 g (3%) of 4-cyanoquinoline methiodide. The melting point, the results of elemental analysis, and the IR and UV spectrum were identical with those of the authentic sample.

One-electron Reduction of 1-Methyl-3-cyanoquinolinium Perchlorate (IIa). The solution of 0.806 g (0.003 mol) of IIa in 200 m*l* of a buffered solution (pH 5) was electrolyzed at −0.80V. The resulting precipitates were dissolved in 40 m*l* of methanol. The solution was poured into 500 m*l* of water after it had been filtered. The mixture was allowed to stand overnight, filtered, and dried to give 0.301 g (0.0009 mol, 59%) of a yellow dimer.

Found: C, 78.18; H, 5.42; N, 16.55%; mol wt, 342. Calcd for $C_{22}H_{18}N_4$: C, 78.07; H, 5.37, N, 16.56%; mol wt, 338.

The solution of 0.201 g (0.00075 mol) of IIa and 1.48 g of potassium perchlorate in 100 m*l* of DMF was electrolyzed at −0.80V. The resulting yellow solution was poured into water and allowed to stand overnight in a refrigerator to give 0.081 g (0.00024 mol, 64%) of the yellow dimer.

One-electron Reduction Product of 1-Methyl-2-cyanoquinolinium Perchlorate (IIIa). The solution of 0.537 g (0.002 mol of IIIa in 200 m*l* of a buffered solution (pH 5) was electrolyzed at −0.70V. The resulting gray reduction product was extracted with ether, and the extract was dried with sodium carbonate. The ether was evaporated to dryness at room temperature under reduced pressure to give an unidentified red-brown resin.