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Anodic Dimerization of Enamines, 2-Cyano-2-phenylvinylamines

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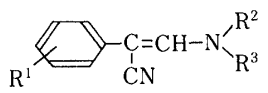
The effects of substituents (R^1, R^2, and R^3) on the electrochemical oxidation of the title enamines, R^1–C_6H_4–C(CN)=CH–NR^2R^3 (**1**) were investigated in acetonitrile at a glassy carbon electrode together with the oxidation of a related amine, Ph–CH(CN)–CH_2–NMe_2 (**5**). Cyclic voltammetry of **1** showed two or more anodic peaks depending upon the substituents. On controlled potential electrolysis at the potential of the first anodic wave, **1** with R^1=H, R^2=alkyl, and R^3=alkyl or H gave diphenylmethane derivatives in which two molecules of the starting enamine are coupled between the β-carbon atom and the phenyl ring *para* to the enamino group. Essentially the same results were obtained for **1** with R^1=*m*-Me or *m*-Cl and R^2=R^3=Me. A mechanism involving the dimerization of radical cations from **1** is proposed. Electrolysis of **1** with R^1=*p*-Cl or *p*-Me and R^2=R^3=Me, on the other hand, gave diphenylethane derivatives *via* coupling between the β-carbon atoms. No stable product was obtained from **1** with a phenyl group on the nitrogen atom. Results on electrolyses of the amine **5** and **1** with R^1=H and R^2=R^3=Me at the voltammetric peak potential of **5** argue against the possibility that an enamine is formed as an intermediate in the electrochemical dealkylation of aliphatic amines.

Keywords——β-cyanoenamine; oxidative dimerization; radical cation; electrochemical oxidation; cyclic voltammetry; controlled potential electrolysis; ESR spectrum

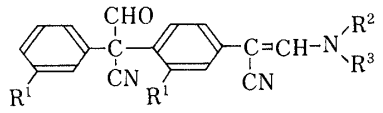
Previously we reported an anodic dimerization of 2-dimethylaminomethylene-2-phenylacetonitrile (**1a**) to produce a diphenylmethane derivative (**3a**) in acetonitrile at a glassy carbon electrode.[1] This reaction represents a new type of electrochemical oxidation of enamines in that the coupling occurred between the β-carbon and the *para* position of the phenyl ring, whereas the β-carbon had been almost the only reactive site previously reported.[2] The coupling also seems interesting from a synthetic viewpoint for forming a carbon–carbon bond.[3] We have studied the effects of the substituents, R^1, R^2, and R^3, on the electrochemistry of **1** in order to evaluate the generality of the reaction and to elucidate the mechanism of the dimerization.

Our original interest in the enamine **1a** was related to the mechanism of anodic dealkylation of aliphatic amines. Mann and co-workers[4] proposed that an enamine was a necessary intermediate for the dealkylation in acetonitrile. This was mainly based on the results that (a) they did not observe demethylation and deisopropylation from tertiary amines with the corresponding alkyl groups and (b) they obtained 2-mono-deuterio propionaldehyde in the oxidation of tri-*n*-propylamine in acetonitrile containing D_2O. However, we have argued against the enamine intermediate on the basis of our similar studies in aqueous buffer,[5] and have proposed an iminium ion as the alternative because the relative amount of dealkylation in unsymmetrical tertiary amines, including demethylation and deisopropylation, depends mostly on the number and the acidity of the α-hydrogens and further on the ease of oxidation of neutral radicals formed by initial electron transfer and the subsequent deprotonation. Ross[6] has also argued against the enamine intermediate based on the findings that (a) benzyldimethylamine and dibenzylmethylamine gave benzaldehyde as one of the



1

	R^1	R^2	R^3
a	H	Me	Me
b	H	H	Me
c	H	Et	Et
d	H	piperidino	
e	H	pyrrolidino	
f	H	morpholino	
g	H	H	Ph
h	H	H	*p*-MeO-C_6H_4
i	H	Me	Ph
j	*m*-Cl	Me	Me
k	*m*-Me	Me	Me
m	*p*-Cl	Me	Me
n	*p*-Me	Me	Me



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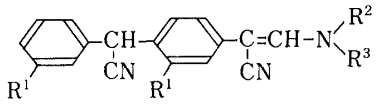

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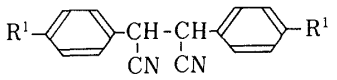

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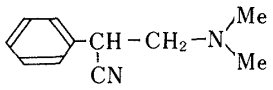

5

Chart 1

dealkylation products, but they do not form the corresponding enamines and (b) an iminium ion might give a mono-deuterio aldehyde on hydrolysis in D_2O. At present, the enamine intermediates are considered highly unlikely, as mentioned in the recent review,[7] but lack of definite evidence prevents a clear-cut conclusion.

In general, enamines assumed to be produced in the oxidation of simple aliphatic amines are unstable and rather difficult to prepare in a pure form suitable for use as starting materials in electrochemical investigations. However, since the enamine **1a** was found to be stable to hydrolysis, the major reaction of **1a** when formed in the anodic oxidation of the corresponding amine (**5**) could be further oxidation to give the dimer **3a**.[1] A survey of the products in an electrolyzed solution of **5** may then provide important information about the possibility of intermediacy of **1a**. Anodic oxidation of **5** was also examined in the present study.

Results

Cyclic Voltammetry

The enamine **1a** showed two anodic peaks at 0.79 and 0.96 V *vs.* S.C.E. in acetonitrile containing 0.1 M sodium perchlorate. Under the experimental conditions used (at 25 °C; voltage sweep rate, 50 mV/s), no cathodic counterpart for the first peak was observed, though some reversible character was noticed in the second peak. In the presence of 1% pyridine, the first anodic peak increased by a factor of about 1.4 and two new peaks appeared in the place of the original second peak. Typical voltammograms are illustrated in Fig. 1. Similar voltammetric results were obtained for **1b**—**f**, **j**, and **k**, as summarized in Table I. In the case of **1k**, which has a *m*-Me substituent on the *β*-phenyl ring of **1a**, the ratio of peak height for the second anodic peak to that for the first peak was somewhat lower than with **1a** and **j**, and this tendency was more pronounced at higher voltage sweep rates.

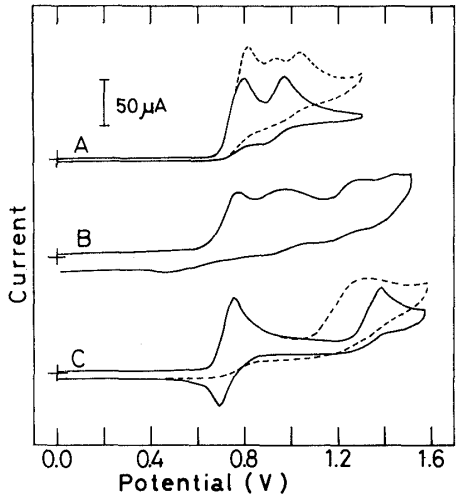

Fig. 1. Cyclic Voltammograms of **1a** (A), **1h** (B), and **1n** (C)

In acetonitrile containing 0.1 M $NaClO_4$ (solid line, without added base; dashed line, with 1% pyridine). The concentration of the substrates was *ca.* 5 mM. Glassy carbon anode (area = 0.071 cm^2); voltage sweep rate, 50 mV s^{-1}; at 25 °C.

TABLE I. Electrochemical Results on the Enamines **1**

Compound	Cyclic voltammetry[a]				Controlled potential electrolysis[b]		
	E_{p1}[c]	i_p/C[d]	E_{p2}[c]	E_{p3}[c]	E_{app}[e]	*n*-Value[f]	Products (yield/%)[g]
1a	0.79	16.6	0.96		0.75	0.86	**3a** (76)
1a[h]	0.80	21.8	0.95	1.04	0.75	1.17	**3a** (46)
1b	0.81	16.2	0.96		0.72	0.87	**3b** (52)
1c	0.75	16.0	0.93		0.67	0.97	**3c** (71)
1d	0.76	16.0	0.93		0.73	0.63	**3d** (40)
1e	0.76	16.0	0.93		0.73	0.73	**3e** (63)
1f	0.86	16.0	0.99		0.79	0.76	**3f** (63)
1g	0.88	17.6	1.3		0.87	1.05	Tar
1h	0.77	13.4	0.98	1.28	0.76	1.30	Tar
1i	0.93	21.0	1.08		0.87	0.98	Tar
1j	0.86	15.4	1.04		0.80	1.20	**3j** (52)
1k	0.72	15.0	0.89		0.73	0.80	**3k**[i]
1m	0.86	16.6	1.6		0.83	1.17	**4m** (39)
1n	0.76	14.8	1.42		0.63[h]	1.00[h]	**4n** (26)[h]

a) In acetonitrile containing 0.1 M $NaClO_4$ at 25 °C; glassy carbon anode (area = 0.071 cm^2); voltage sweep rate, 50 mV s^{-1}.
b) In acetonitrile containing 0.1 M $NaClO_4$ at 0 °C.
c) Peak potentials of the first, second, and third anodic waves, respectively: V *vs.* S.C.E.
d) Peak current of the first anodic wave: μA/mM.
e) Electrolysis potential: V *vs.* S.C.E.
f) See the text.
g) Isolated yield after recrystallization.
h) In the presence of 1% pyridine.
i) See the text.

Introduction of a phenyl ring on the enamine nitrogen atom (**1g**–**i**) caused a considerable change in the voltammetric behavior. While the potential and the peak current of the first electron transfer were not so far from those without the phenyl ring, the second anodic peak was no longer well-defined and in some cases many small waves were observed (Fig. 1), indicating that the initial electron transfer is followed by complex chemical and electrochemical processes.

Para substituents on the β-phenyl ring, in contrast to those on the *meta* position, brought about a significant change in the electrochemistry. The first anodic peak of **1m** and **n** showed

reversible character and the peak corresponding to the second anodic peak of the other enamines was not observed, but a new irreversible peak appeared in a higher potential region (> 1.4 V) (Fig. 1). Addition of 1% pyridine or 2,6-lutidine quenched the cathodic peak in the first wave completely while the anodic peak was little affected.

Controlled Potential Electrolysis

Table I includes typical results of controlled potential electrolysis of the enamines **1** at the potential of the first anodic wave. In the cyclic voltammogram of the electrolyzed solution of **1a**, the original first anodic peak had almost disappeared and the second anodic peak remained, indicating that the latter peak is due to one of the oxidation products at the first wave. High performance liquid chromatography (HPLC) of the electrolyzed solution showed two product peaks: one of them (with shorter retention time) was predominant. When aqueous sodium carbonate was added to the solution, the major peak disappeared and the minor peak, whose retention time coincided with that of isolated **3a**, was enhanced. As described previously,[1] since the primary electrolysis product of **1a** must be the aldehyde **2a**, which has been found to give **3a** upon alkaline treatment, the initial major peak in HPLC and consequently, the second anodic peak in the voltammetry of **1a** (Fig. 1) can be ascribed to **2a**. In acetonitrile the isolated product **3a** showed an irreversible anodic peak at 0.12 V less positive potential than that of the second anodic peak of **1a**. Similar results were obtained in the electrolysis of **1b**—**f** and **j**, and the corresponding diphenylmethane derivatives **3** were isolated as the final products. In the case of **1k**, the formation of a considerable amount of tarry products prevented the isolation of **3k** in pure form, but its presence was confirmed by nuclear magnetic resonance (NMR) spectroscopy.

In these electrolyses, the current decreased exponentially with time in the initial stage, but finally reached a constant value which was considerably higher than the background. This phenomenon seems to result from further oxidation of the products, **2** and/or **3**, owing to the closeness of the electrolysis potential and that of the second anodic wave. Therefore, the electrolysis was usually discontinued just after the current leveled off to avoid loss of the products. The *n*-value in Table I refers to the electricity (F/mol) consumed up to this stage. The theoretical *n*-value for the formation of **2**, and hence **3**, is expected to be unity. In fact, **1a** and **3a** were each detected in 50% yield by HPLC when the electrolysis was stopped at the point of 0.5 F/mol, followed by alkaline treatment of the electrolyzed solution.

Added pyridine did not cause significant change in the overall electrode process in spite of its effect on the voltammetry (see Fig. 1). Electrolysis of **1a** in the presence of 1% pyridine also gave **3a** as the main product (Table I). The decrease in the yield accompanied by the increase in the coulometric *n*-value may be attributable in part to further oxidation of **3a** formed under basic electrolysis conditions, since conversion of the primary product **2a** to **3a** is catalyzed by base[8] and **3a** is oxidized at a less positive potential than **2a**.

In the above electrolysis, except for the runs with **1a** in the presence of pyridine and with **1k**, the solution usually turned from colorless to pale yellow with the progress of the electrolysis. In the case of **1g**—**i**, however, a deep red or brown-red color developed from the initial stage of the electrolysis and no stable product other than tarry materials was obtained. These results together with the voltammetric results on **1g**—**i** suggest that the phenyl group on the nitrogen atom takes part in the chemical and/or electrochemical reactions following the initial electron transfer to complicate the overall process. Further studies on these enamines were not carried out.

On electrolysis of **1m** and **n**, which showed a first anodic peak with reversible character (Fig. 1), a bright purple color developed at the anode at the start of electrolysis. When the current flow was stopped, the color remained for 30—40 s and 5—6 min with **1m** and **n**, respectively, but faded instantly on addition of a drop of pyridine or 2,6-lutidine. An electron

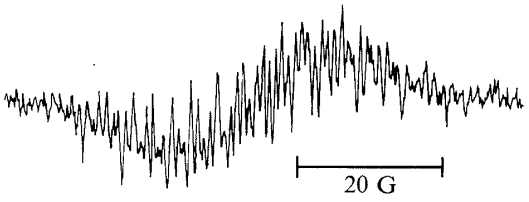

Fig. 2. ESR Spectrum of an Electrolyzed Solution of **1n**

In acetonitrile containing 0.1 M $NaClO_4$; electrolysis potential, 0.63 V; at 0 °C.

spin resonance (ESR) spectrum obtained for the colored solution from **1n** by the flow method is shown in Fig. 2, but its character seemed equivocal, and further analysis was not attempted. A similar but even less-resolved spectrum was observed with **1m**. A cyclic voltammogram of the electrolyzed solution had lost the second anodic peak (see Fig. 1) along with the first anodic peak, indicating that the second anodic peak is due to the oxidation of an intermediate, probably the corresponding radical cation (see below), formed at the first wave. From the electrolyzed solution of **1m**, the 1,2-diphenylethane derivative **4m** was isolated as a final product; this must have originated from β-β dimerization of the starting enamine. The yield of the dimer tended to increase on electrolysis under basic conditions. Thus, **4n** was not obtained in the electrolysis of **1n** in acetonitrile without added base, but was isolated in the presence of 1% pyridine.

Electrochemistry of the Amine 5

The amine, which is expected to have **1a** as an intermediate in the oxidation process according to the suggestion of Mann and co-workers,[4] showed a single irreversible anodic peak at 1.17 V in acetonitrile. Controlled potential electrolysis at the peak potential, where the solution was colorless throughout the run, gave an *n*-value of 1.7—1.8, and about 50% of the substrate was recovered in protonated form. Since the formation of dimethylamine (80—90% based on the consumed substrate) was detected in the resulting solution, another possible product must be the aldehyde, Ph–CH(CN)–CHO (**6**), but in fact it could not be detected. The oxidation potential of **6** under the same conditions was found to be 1.20 V. Electrolysis of **1a** at 1.17 V caused deep coloration of the solution to wine-red with an *n*-value of 1.3—1.5, and a considerable amount of tarry material was obtained, though formation of dimethylamine (about 50%) was also detected.

Discussion

The initial oxidation step for the enamine **1n** must be a one-electron transfer from the substrate to form the radical cation **7n**. This is supported by the fact that in cyclic voltammetry the anodic and the cathodic peaks are separated by 60 mV (theoretically 58 mV for a one-electron process)[9] and by the observation of an ESR signal in the controlled potential electrolysis. It is reasonable to consider that the other enamines used in the present study are also oxidized to the corresponding radical cations at the first anodic wave, because the first anodic peaks are closely related to that of **1n** with respect to shape and peak current. The fate of the radical cations thus formed, and hence the final products of controlled potential electrolysis, seems to depend largely on the substituents on the enamine nitrogen atom and those on the β-phenyl ring, as is well reflected in the voltammetric curves of **1** subsequent to the first anodic peaks.

The pathway shown in Chart 2, which includes coupling of the radical cations **7**, is proposed for the formation of the diphenylmethane derivative **3** from **1a**—**f**, **j**, and **k**. Radical cations have also been suggested as a species undergoing dimerization in the electrochemical oxidation of enamino ketones or esters[2a] and *N*,*N*-dimethylaminoalkenes,[2b] where the main

products were β-β coupled dimers. In the radical cations derived from the latter enamines, it has been shown that the center of positive charge is the nitrogen atom and the position with the highest unpaired electron density is the β-carbon atom.[2b] Thus, coupling of the radical cations **7** at the β-carbon atom and/or at one of the carbon atoms conjugated with the β-carbon seems reasonable.

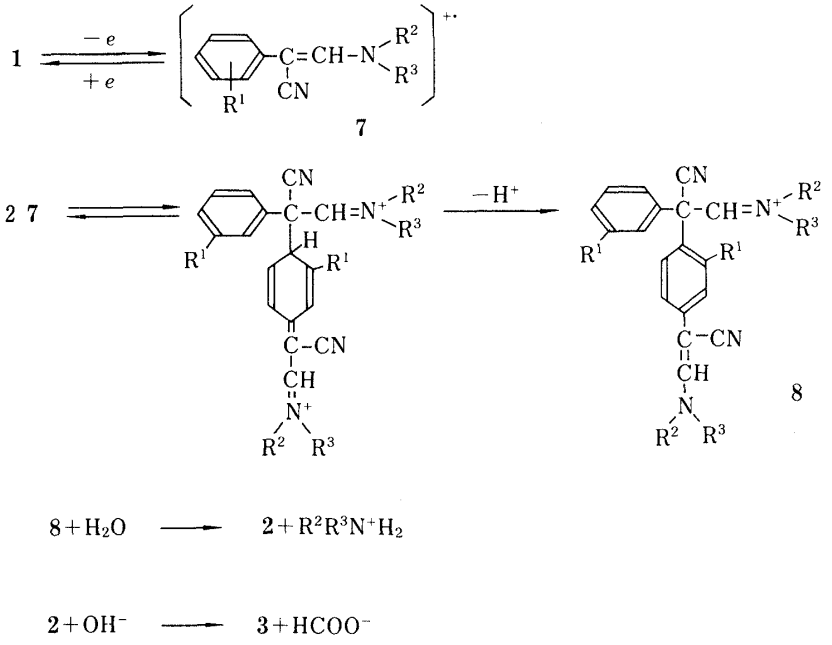

Chart 2

Although the reason for the exclusive, or at least predominant, formation of **3** is not clear from the present results alone, the following explanation is attractive. If a sandwich-type approach of the β-phenyl ring is energetically favored in the coupling of **7** as suggested in the case of phenoxy radicals,[10] a configuration in which the enamino groups are located *trans* to each other would be preferred owing to the electrostatic repulsion between the two positive charges on the nitrogen atoms. In such configuration, formation of *para-β*, *para-ortho*, and *ortho-ortho* coupled dimers would be feasible. The latter two dimers, if they were formed, would rapidly aromatize to give biphenyl derivatives, which would be oxidized further at the electrolysis potentials used.

The increased stability of radical cations **7m** and **n** (see Figs. 1 and 2) may in part arise from the requirement for the type of approach described above. The *para*-substituents on the β-phenyl ring would not sterically hinder the dimerization to a large extent,[11] and similar *para-β* coupling of the radical cations can be expected. However, since the resulting dimer would not easily aromatize (*cf.* Chart 2) and, therefore, would be thermodynamically unstable, it may be in equilibrium with the monomer to give the cathodic peak in the voltammetry and the ESR signal.[11] Although the diphenylethane derivative **4** isolated in the electrolysis of **1m** and **n** must be formed *via* a radical coupling at the β-carbon atom, the exact sequence for the formation and the role of added pyridine in the process are unclear.[12]

Another possible pathway for the dimerization, as an alternative to that in Chart 2, might be nucleophilic attack of the starting enamine **1** on the radical cation **7** followed by further one-electron transfer and loss of a proton to give the intermediate (**8**); this mechanism is similar to that suggested for various anodic substitution reactions (an ECE mechanism).[13] In the present case, however, this mechanism seems incompatible with the results on electrolysis of **1a** in the presence of added pyridine. Since pyridine would be a stronger nucleophile than **1a**

as judged from the basicity[14] and the size of the molecule, it seems hard to explain why the unoxidized form of **1a**, whose concentration must be very small at the electrode, competes for the radical cation **7a** with the large excess of pyridine present in the system. The possibility of a similar ECE mechanism has been taken into account in the electrochemical dimerization of enamino ketones or esters, but was discarded on the basis of the fact that β-β coupled dimers, instead of α-β dimers, were the sole products isolated.[2a]

According to the proposed mechanisms for oxidative dealkylation of aliphatic tertiary amines,[4-6] the results on electrolysis of the amine **5** suggest that the reaction proceeds *via* either the enamine **1a** or the iminium ion, Ph–CH(CN)–CH=N^+Me_2 (**9**), as the principal intermediate.[15] The iminium ion **9** would be rapidly hydrolyzed under the experimental conditions used[8] to give dimethylamine, one of the main products. However, if the enamine **1a** were formed as the intermediate, it would be oxidized further in the electrolysis system because it is stable to hydrolysis, and the electrolysis potential (1.17 V) was more positive than the potential of its second anodic peak. In the electrolysis of **1a** at the same potential, dimethylamine was actually formed, as predicted from Chart 2, but it was accompanied by deep coloration of the electrolysis solution and formation of a considerable amount of tarry materials owing to further oxidation of **2a** and/or **3a** produced along with dimethylamine. On the other hand, the electrolysis of **5** proceeded without such complexity. Thus, the present results also argue against the intermediacy of an enamine in the electrochemical dealkylation of aliphatic amines.

Experimental

Materials——The enamines **1** were prepared by known methods[16] and gave the expected analytical and spectroscopic results. The *Z*-configuration, in which the β-phenyl ring and the amino group are *trans* to each other, is assigned to these enamines.[16,17] The amine **5** was prepared by sodium cyanoborohydride reduction of **1a**, and was purified and stored as the hydrochloride (mp 129—131 °C). In the electrochemical experiments, the required amount of the salt was neutralized with aqueous sodium carbonate and the resulting free base was extracted with chloroform. The chloroform was removed under reduced pressure, and the residue was used as the substrate for voltammetry and controlled potential electrolysis. Sodium perchlorate and acetonitrile were purified as described previously.[18]

Apparatus——Cyclic voltammetry and controlled potential electrolysis were carried out essentially as described previously.[18] Infrared (IR), NMR and mass spectra (MS) were obtained on JASCO A-202, Hitachi R-20A, and Hitachi RMU-6E spectrometers, respectively. HPLC was carried out using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVIDEC-1 spectrophotometer: Bondapack C_{18}-Corasil and 45% aqueous methanol were used. ESR spectra were obtained by the external generation techniques employed previously[19] using a JEOL JES-FElX spectrometer equipped with 100 kHz field modulation.

Identification of Products[20] from Controlled Potential Electrolysis——Electrolysis was carried out at 0 °C in an H-type divided cell. A glassy carbon plate anode was used throughout. A typical example of the procedures used with **1a** to give phenyl-[4-(1-cyano-2-dimethylaminovinyl)phenyl]acetonitrile (**3a**) has been reported previously.[1] The following compounds were obtained by essentially the same procedure, except that the aldehyde 2 was not isolated but the electrolyzed solution was directly treated with aqueous sodium carbonate (see below).

Phenyl-[4-(1-cyano-2-diethylaminovinyl)phenyl]acetonitrile (**3c**), mp 118—119 °C. *Anal.* Calcd for $C_{21}H_{21}N_3$: C, 79.96; H, 6.71; N, 13.32. Found: C, 79.96; H, 6.72; N, 13.28. IR ν_{max}^{Nujol} cm^{-1}: 2260, 2200 (2CN). NMR ($CDCl_3$) δ: 1.27 (6H, t, J=7 Hz, Me), 3.54 (4H, q, J=7 Hz, N–C<u>H</u>$_2$–Me), 5.02 (1H, s, –C(CN)<u>H</u>–), 6.84 (1H, s, =C<u>H</u>–), 7.18 (4H, s, Ar), 7.22 (5H, s, Ar).

Phenyl-[4-(1-cyano-2-pyrroridinovinyl)phenyl]acetonitrile (**3e**), mp 168—169 °C. *Anal.* Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.47; N, 12.83. Found: C, 80.57; H, 6.39; N, 12.86. IR ν_{max}^{Nujol} cm^{-1}: 2260, 2200 (2CN). NMR ($CDCl_3$) δ: 1.69 (6H, m), 3.61 (4H, m, N–C<u>H</u>$_2$), 5.05 (1H, s, –C(CN)<u>H</u>–), 6.82 (1H, s, =C<u>H</u>–), 7.20 (4H, s, Ar), 7.28 (5H, s, Ar).

Phenyl-[4-(1-cyano-2-pyrroridinovinyl)phenyl]acetonitrile (**3e**), mp 174—176 °C. *Anal.* Calcd for $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.54; H, 6.03; N, 13.40. IR ν_{max}^{Nujol} cm^{-1}: 2260, 2200 (2CN). NMR ($CDCl_3$) δ: 1.91 (4H, m), 3.62 (4H, m, N–C<u>H</u>$_2$), 5.01 (1H, s, –C(CN)<u>H</u>–), 7.09 (1H, s, =C<u>H</u>–), 7.16 (4H, s, Ar), 7.22 (5H, s, Ar).

Phenyl-[4-(1-cyano-2-morpholinovinyl)phenyl]acetonitrile (**3f**), mp 126—128 °C. *Anal.* Calcd for $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76. Found: C, 76.45; H, 5.64; N, 12.78. IR ν_{max}^{Nujol} cm^{-1}: 2250, 2180 (2CN). NMR ($CDCl_3$) δ: 3.69 (8H, m), 5.06 (1H, s, –C(CN)<u>H</u>–), 6.80 (1H, s, =C<u>H</u>–), 7.21 (4H, s, Ar), 7.27 (5H, s, Ar).

3-Chlorophenyl-[4-(1-cyano-2-dimethylaminovinyl)-2-chlorophenyl]acetonitrile (**3j**), mp 150—152 °C. *Anal.* Calcd for $C_{19}H_{15}Cl_2N_3$: C, 64.05; H, 4.24; N, 11.80. Found: C, 63.98; H, 4.10; N, 11.64. IR ν_{max}^{Nujol} cm^{-1}: 2250, 2190

(2CN). NMR ($CDCl_3$) δ: 3.20 (6H, s), 5.50 (1H, s, –C(CN)H–), 6.91 (1H, s, =CH–), 7.22 (7H, m, Ar).

Phenyl-[4-(1-cyano-2-methylaminovinyl)phenyl]acetonitrile (**3b**) was unstable and its exact mp and analytical results were not obtained. However, the spectral data were consistent with the expected structure. IR ν_{max}^{Nujol} cm^{-1}: 2270, 2200 (2CN). NMR ($CDCl_3$) δ: 3.02 (3H, d, J=5 Hz, N–Me), 5.03 (1H, s, –C(CN)H–), 4.90, 5.40 (1H, br NH), 7.01 (1H, s, =CH–), 7.16 (4H, s, Ar), 7.25 (5H, s, Ar).

The enamine **1m** (980 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 0.1 M $NaClO_4$ at 0.83 V at 0 °C. Then 1% aqueous sodium carbonate (300 ml) was added to the electrolyzed solution, and the mixture was extracted with chloroform (3 × 50 ml). The chloroform was removed from the extract under reduced pressure and the residue was recrystallized from acetic acid to give colorless needles (186 mg) [mp 224—227 °C (lit.[21] 234—236 °C)], which were identified as 2,3-bis-*p*-chlorophenyl-succinonitrile (**4m**) with the expected analytical values. IR ν_{max}^{Nujol} cm^{-1}: 2250 (CN). NMR ($CDCl_3$) δ: 4.66 [2H, s, 2 × (–C(CN)H–)], 7.32 (8H, m, Ar). MS *m/e*: 300 (M^+), 302 [$(M+2)^+$], 304 [$(M+4)^+$]. The mother liquor from recrystallization contained another product [MS *m/e*: 355 (M^+)], but it could not be purified.

2,3-Di-*p*-tolyl-succinonitrile (**4n**), which was obtained only in the electrolysis of **1n** in the presence of pyridine, showed mp 185—187 °C. *Anal.* Calcd for $C_{18}H_{16}N_3$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.88; H, 6.11; N, 10.58. IR ν_{max}^{Nujol} cm^{-1}: 2270, 2210 (2CN). NMR ($CDCl_3$) δ: 2.36 (6H, s, 2Me), 4.16 [2H, s, 2 × (–C(CN)H–)], 7.10 (8H, m, Ar). MS *m/e*: 260 (M^+).

Electrolysis of the Amine 5——A typical example is as described below. The amine **5** (65 mg) was subjected to electrolysis in acetonitrile (18 ml) containing 0.1 M $NaClO_4$ at 1.17 V at 0 °C. A cyclic voltammogram of the electrolyzed solution had lost the anodic peak due to the starting amine, but part of the peak was recovered on addition of pyridine, indicating the formation of the protonated starting material. The amount of remaining amine (52%) was determined by HPLC. Dimethylamine was determined as its sulfonamide according to the known method;[22] the yield was 45%.

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