Electrochemical Oxidation of 2,2,6,6-Tetramethylpiperidines in Acetonitrile: Mechanism of *N*-Cyanomethylation

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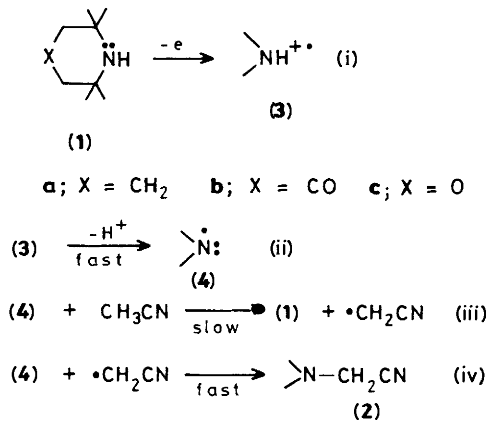
Electrochemical oxidation of 2,2,6,6-tetramethylpiperidine (**1a**), its 4-oxo derivative (**1b**), and 2,2,6,6-tetramethylmorpholine (**1c**) in deoxygenated acetonitrile gave the corresponding *N*-cyanomethylated products (**2**). The process was investigated by cyclic voltammetry, controlled-potential electrolysis, and electrolysis in the cavity of an e.s.r. spectrometer. The sequence of cyanomethylation is proposed to be as follows: one-electron transfer from (**1**) to generate the radical cation, $>\ddot{N}H^{+\bullet}$ (**3**); deprotonation of (**3**) to give the aminyl radical, $>\dot{N}:$ (**4**); hydrogen abstraction by (**4**) from the solvent to afford the cyanomethylene radical; cross-coupling of (**4**) with the solvent-derived radical. The generation of the radical (**4**) was confirmed by the e.s.r. experiments. The decay of the 4-oxopiperidinyl radical (**4b**) obeyed first-order kinetics and exhibited a large primary deuterium isotope effect in [$^2H_3$]acetonitrile, indicating that the hydrogen abstraction is rate-determining. The voltammetric behaviour of (**1**) in oxygen-saturated acetonitrile suggested that the aminyl radical (**4**) is oxidized at a potential more positive than is the starting amine (**1**).

Previously we have reported the *N*-cyanomethylation of 2,2,6,6-tetramethylpiperidine (**1a**) and its 4-oxo derivative (**1b**) by electrochemical oxidation in deoxygenated acetonitrile.[1] Although N–C bond formation is rather exceptional in the electrochemical oxidation of aliphatic amines,†[,2] examples can be seen in the formylation of nortropane (8-azabicyclo[3.2.1]-octane) in wet acetonitrile,[3] in the formation of 2-aminotetrahydrofurans from cyclic secondary amines in tetrahydrofuran,[4] and in the *N*-formylation of primary and secondary phenylalkylamines in methanol.[5] Among several mechanistic possibilities, cross-coupling of the corresponding aminyl radicals with radicals derived from the solvents, cyanomethylene radical[1,3] and tetrahydrofuran-2-yl radicals[4] was suggested.‡ However, no direct evidence was presented to substantiate the mechanism. In this paper, the *N*-cyanomethylation of the amines (**1a**—**c**) has been studied further. On the basis of the results, the process shown in the Scheme is proposed, in which hydrogen abstraction from the solvent by the aminyl radical (**4**) is rate-determining in the reactions following the initial one-electron transfer from the substrate. The advantage of the amines (**1**) as substrates for the mechanistic study is that the absence of α-hydrogen atoms and the steric crowding around the nitrogen atom may exclude the possibilities of oxidative dealkylation[4] and N–N bond coupling of the substrate,[3,4] observed in the other examples of N–C bond formation.

Results and Discussion

On cyclic voltammetry in deoxygenated acetonitrile, the amines (**1a** and **b**) showed three anodic peaks provided that the voltage sweep rate (v/mV s^{-1}) was properly selected for each compound. Typical voltammograms at 25 °C are illustrated in Figure 1: the peak potentials are 1.00, 1.21, and 1.5 V *vs.* saturated calomel electrode (s.c.e.) for (**1a**) at $v = 100$; and 1.19, 1.37, and 1.58 V for (**1b**) at $v = 50$. At higher values of v, the second anodic peak became obscure while the third peak was enhanced. The second peak for (**1b**) was no longer observed at $v \geqslant 200$, and the third peak for (**1a**) became distinct at $v > 1\,000$ (*cf.* Figure 1). Similar voltammetric results were obtained with the amine (**1c**): peak potentials 1.17, 1.39, and 1.51 V at $v = 100$.



Scheme.

The initial step of the electrochemical oxidation of an aliphatic amine is believed to be one-electron transfer from the substrate to form the corresponding radical cation.[2] Generation of relatively stable radical cations has been demonstrated for bicyclic amines in which deprotonation of the α-carbon atom is prevented by stabilization according to Bredt's rule.[6] Since the amines (**1**) lack α-hydrogen atoms, it was expected that the radical cations (**3**) might exhibit a certain degree of stability. However, no evidence of a reversible process was observed for the first anodic peak of (**1**) even in the voltammetric measurements at −40 °C and $v = 10\,000$, indicating that the deprotonation of (**3**) [step (ii)] is very fast under the present conditions.

Voltammetry of the *N*-cyanomethylated amine (**2**), obtained by controlled-potential electrolysis (see later) of the amine (**1**), showed a well defined but irreversible anodic peak; its peak

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† Oxidative dealkylation is generally observed in the electrochemical oxidation of simple aliphatic amines possessing α-hydrogen atoms in aqueous or in wet acetonitrile.

‡ A different mechanism was proposed for the reaction in methanol (ref. 5).

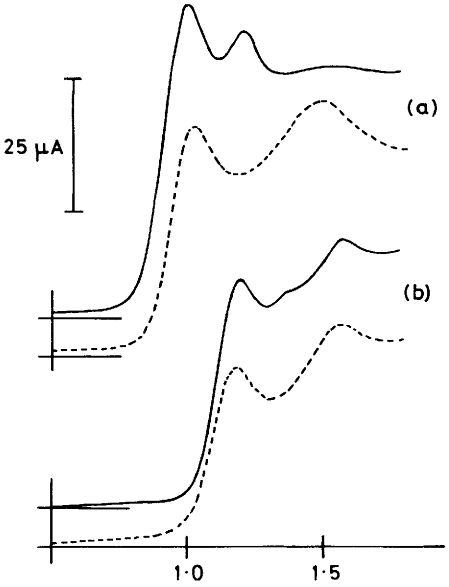

Figure 1. Cyclic voltammograms of the amine (**1**) in deoxygenated acetonitrile (solid line) and [$^2H_3$]acetonitrile (dotted line) containing 0.1M-NaClO$_4$ at a glassy carbon electrode (area 0.071 cm^2) at 25 °C: (a) (**1a**) (5.0 mM), v = 100; (b) (**1b**) (5.0 mM), v = 50. Curves for the reverse sweep are omitted for simplicity: no cathodic peak was observed at least down to 0 V.

potential agreed well with that of the second anodic peak of the amine (**1**) measured under the same conditions. A peak which corresponds to the third anodic peak of (**1**) was not observed in the voltammograms of (**2**).* These results, together with the effects of v on the anodic peaks of (**1**) already mentioned, strongly suggest that the second anodic peak in the voltammetry of (**1**) should be ascribed to the oxidation of the cyanomethylated amine (**2**) produced at the electrode, and the third peak to the oxidation of some intermediate or a by-product formed in the course of conversion of (**1**) into (**2**). Further discussion on the nature of the third peak will be given later.

The voltammograms of (**1**) were also measured in CD$_3$CN and the results compared with those in CH$_3$CN. As shown in Figure 1, the first anodic peak decreased to some extent, the development of the second peak was retarded, and the third peak became clearer in CD$_3$CN. In fact, the second peak for the amine (**1a**) was barely discernible when v was decreased to 50, and that for (**1b**) was not detected at v values as low as 20. In the Scheme, a primary deuterium isotope effect would be expected for hydrogen abstraction by the aminyl radical (**4**) from the solvent [step (iii)], hence the formation of (**2**) as well as the regeneration of (**1**) will be slower in CD$_3$CN. Since the second peak is ascribed to the oxidation of (**2**) and part of the regenerated amine (**1**) will be oxidized at the first peak, the voltammetric results in CD$_3$CN do not conflict with the proposed mechanism.

Table 1 shows the results of controlled-potential electrolysis of (**1**) in deoxygenated acetonitrile at the potential of the first anodic peak. Electrolyses in a divided cell and in an undivided cell were equally effective in the formation of (**2**) provided that the anode potentials were identical. Thus, the cathode and/or the reactions expected to take place at the cathode will not participate directly in the process to form (**2**): in the undivided cell, the cathode will act as the proton scavenger like K$_2$CO$_3$ suspended in the divided cell (see Table 1, footnote *d*). The yields of (**2**) were improved when the electrolysis was carried out at lower anode potentials, though a longer electrolysis period was required. In the cases of (**1b** and **c**), the products were obtained almost quantitatively.

Table 1. Results of controlled-potential electrolysis of the amine (**1**)^a

Compd.	Cell type^b	Anode potential (V *vs.* s.c.e.)	Yield (%)^c of (**2**)
(**1a**)	H^d	1.07	28
	C	1.07	31
	C	0.95	74
(**1b**)	H^d	1.25	68
	C	1.25	51
	C	1.15	93^e
(**1c**)	C	1.00	98

^{a} In deoxygenated acetonitrile (20 ml) containing 0.1M-NaClO$_4$ at ambient temperature: amount of (**1**), *ca.* 0.5 mmol in all runs. Electrolysis was discontinued when 2.0 F per mol of (**1**) had been consumed. ^{b} H, an **H**-type divided cell; C, cylindrical undivided cell. ^{c} Determined by g.l.c. ^{d} K$_2$CO$_3$ (0.5 g) was suspended in the anode compartment. ^{e} Yield of isolated material.

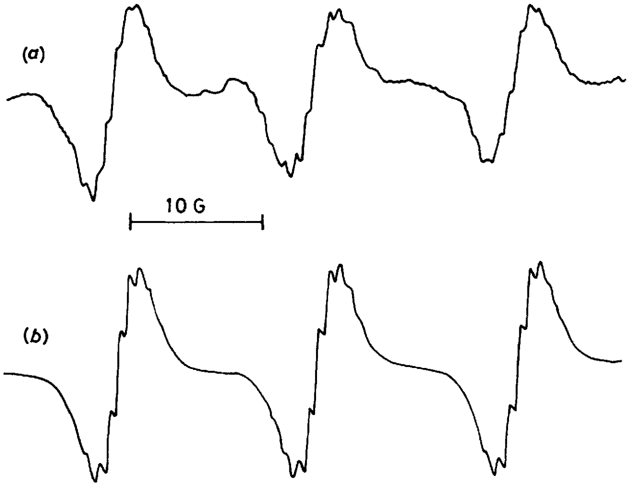

Figure 2. (a) E.s.r. spectrum of an *in situ* electrolysed solution of the amine (**1a**) (20 mM) in deoxygenated acetonitrile (0.1M-NaClO$_4$) at −8 °C; (b) computer-simulated spectrum using the coupling constant given in the text and a linewidth of 1.5 G (Lorentzian lineshape)

The amines (**1a** and **b**) in deoxygenated acetonitrile were subjected to electrolysis in the cavity of an e.s.r. spectrometer in order to detect any of the radical species involved in the proposed mechanism. E.s.r. spectra (Figures 2 and 3) due to the aminyl radicals (**4**) were obtained with the following parameters: for (**4a**) at −8 °C, g = 2.0041, a_1 = 15.1 (1 N), and a_2 = 0.8 G (12 H); for (**4b**) at 20 °C, g = 2.0043, a_1 = 14.95 (1 N), and a_2 = 1.15 G (12 H). These values are closely related to those reported for the same radicals generated by photolysis of the corresponding *N*-chloro-amines in benzene[7] and of 1,1′-azo-(2,2,6,6-tetramethylpiperidine) (**5**) in isopentane.[8] The radical (**4a**) is less stable or more reactive than (**4b**), as indicated by the fact that electrolysis at a lower temperature was required to obtain a resolvable spectrum.

It has been reported that the decay of the radical (**4a**), photochemically generated from the tetrazene (**5**) in various hydrocarbon solvents, obeys first-order kinetics.[8] On the basis of large deuterium isotope effects observed in [$^2H_8$]toluene (24 at −10 °C) and in [$^2H_8$]cyclohxane (16 at 22 °C), hydrogen

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* The cyanomethylated amines (**2a** and **c**) showed an additional small ill-defined peak around 1.5 V.

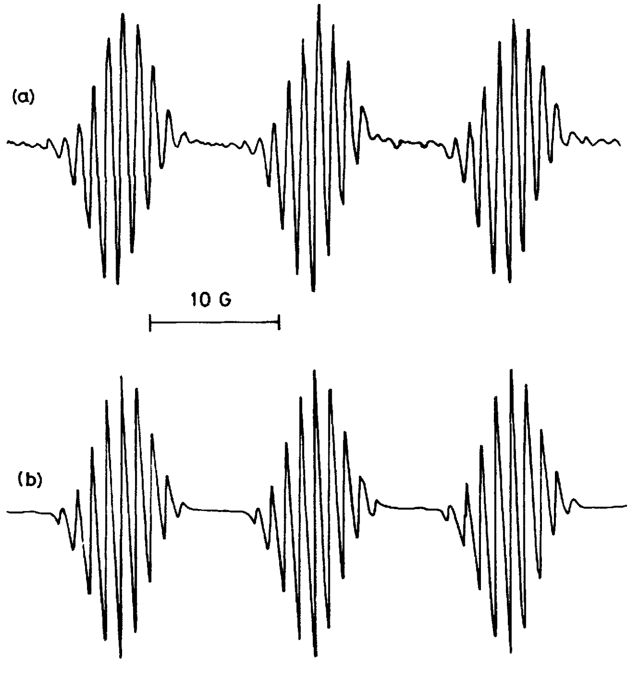
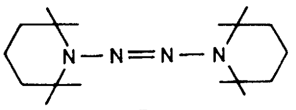


Figure 3. (a) E.s.r. spectrum of an *in situ* electrolysed solution of the amine (**1b**) (10 mM) in deoxygenated acetonitrile (0.1M-NaClO$_4$) at 20 °C; (b) computer-simulated spectrum using the coupling constant given in the text and a linewidth of 0.6 G (Lorentzian lineshape)



(5)

abstraction from the solvent is concluded to be the rate-determining step for the reaction. Open-circuit relaxation experiments[9] were conducted on the observed e.s.r. signal to confirm the kinetic behaviour of the aminyl radical (**4**) under the present experimental conditions. The radical (**4b**) was selected as substrate, because in acetonitrile (**4a**) was too labile to be detected at the temperature of the controlled-potential electrolysis (20—25 °C). A typical example of the relaxation experiments is shown in Figure 4. Good first-order kinetics were observed for up to *ca.* 80% decay of (**4b**). The rate constants obtained under several conditions are given in Table 2. The observation of first-order kinetics is in accord with the observation that the rate of decay was essentially unchanged by the pre-electrolysis period, which would affect the concentration of (**4b**) at the time of circuit opening, that is, the initial concentration. The rate was reduced significantly when the solvent was replaced by CD$_3$CN, and the deuterium isotope effect (k_H/k_D) is calculated to be 38.6, which is unusually large and must be ascribed to tunnelling as discussed by Roberts and Ingold.[8]

Table 2. First-order rate constant (k) for the decay of the aminyl radical (**4b**) at 20 °C

Solvent	t/min[a]	k/s^{-1} [b]
CH$_3$CN	1.5	0.153
	7.0	0.150
	9.0	0.154
CH$_3$CN + 1% H$_2$O[c]	7.0	0.130
CD$_3$CN	4.0	0.003 92
	7.0	0.003 91
	9.0	0.004 02
CD$_3$CN + 1% D$_2$O[c]	7.0	0.003 17

[a] The time of pre-electrolysis (*cf.* Figure 4); for detail, see Experimental section. [b] Average of two or three runs. [c] In the presence of 1% H$_2$O and D$_2$O, respectively.

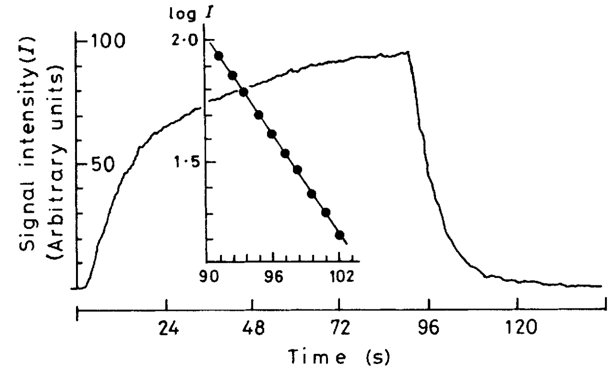


Figure 4. Open-circuit relaxation experiment following the e.s.r. signal of the aminyl radical (**4b**) in deoxygenated acetonitrile (0.1M-NaClO$_4$) at 20 °C: electrolysis of (**1b**) (10 mM) was allowed to proceed for 90 s (for detail see Experimental section)

In the anodic *N*-formylation of nortropane in acetonitrile containing water and suspended sodium hydroxide, it was suggested that hydroxyl radical formed by one-electron transfer from hydroxide ion abstracted a hydrogen atom from the solvent to give cyanomethylene radical.[3] The latter radical was assumed to couple with the aminyl radical generated from nortropane to form an *N*-cyanomethylated intermediate, though this was not isolated. Since it is well known that acetonitrile is unavoidably contaminated by small amounts of water unless purified with special care,[10] a similar mechanism might be considered for the formation of (**2**). However, the rate of decay of (**4b**) decreased to a small extent when water (1%) was added deliberately to the medium (Table 2). An increase in rate would be expected if such a contribution of hydroxyl radical was important in the formation of (**2**).

Since the process for the decay of the aminyl radical (**4**) shown in the Scheme is essentially the same as that proposed for (**4a**) generated photochemically,[8] the results of the relaxation experiments suggest that photochemical formation of the *N*-cyanomethylated amine (**2**) is feasible. Photolysis of the tetrazene (**5**) in deoxygenated acetonitrile actually gave the amine (**2a**) in 15% yield together with the amine (**1a**) (59%). Theoretically, the yield of (**2a**) should be 50% based on (**5**). Although no attempt was made to improve the yield, the photochemical method seems not so effective as the electrochemical oxidation with regard to the formation of (**2**). In the electrolysis the radical (**4**) will be generated locally at the electrode surface, while in the photolysis (**4**) will be distributed homogeneously in the solution. The cyanomethylene radical, formation of which must be rate-determining in both cases, will have more chance of finding (**4**) in the electrolysis than in the photolysis.

In the voltammetry of (**1**) the species giving the third anodic peak remains to be assigned. The protonated form of (**1**) may be a candidate, because the proton liberated from the radical cation (**3**) [step (ii)] will be accepted by an unoxidized molecule of (**1**) diffusing subsequently to the electrode. However, all the three anodic peaks of (**1**) disappeared when the voltammetry was carried out in the presence of perchloric acid equimolar with (**1**).

As already described, the third anodic peak is enhanced under conditions where the second peak due to the oxidation of (**2**)

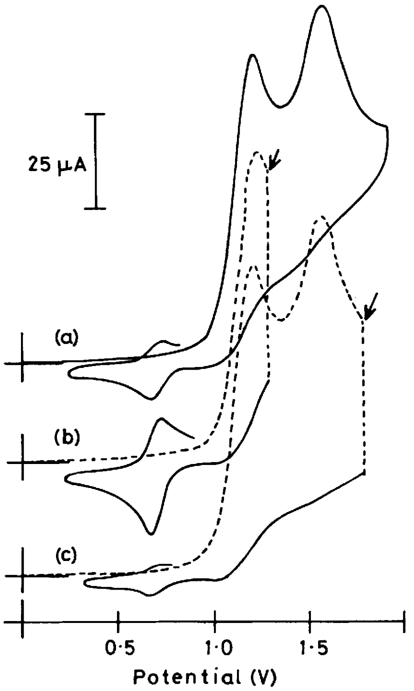


Figure 5. Cyclic voltammograms of the amine (**1b**) (4.8 mM) in oxygen-saturated acetonitrile containing 0.1M-NaClO$_4$ at a glassy carbon electrode (area 0.071 cm^2) at 25 °C: v = 200; in (b) and (c) the initial voltage sweep was stopped at the points shown by arrows, and the current was allowed to decay for 30 s before the subsequent cathodic sweep

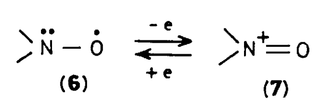
becomes obscure. Thus, the reactions in the Scheme suggest that the oxidation of the aminyl radical (**4**) is responsible for the third peak. It might seem unlikely that an aminyl radical is oxidized at a more positive potential than the amine from which it is derived. Many alkylaminyl radicals have been shown to possess π ground electronic configurations; that is, the unpaired electron resides in the nitrogen 2*p* orbital.[11,12] On the other hand, the lone-pair electrons of alkylamines are in the *sp*^{3}-like orbital. Electron transfer from an aminyl radical [equation (v)] would therefore be easier than from the corresponding amine [equation (vi)].* It has been reported also that the oxidation

$$R_2\dot{N}\!: - e \longrightarrow R_2N\!:^{+} \qquad (v)$$

$$R_2\ddot{N}H - e \longrightarrow R_2NH^{+\bullet} \qquad (vi)$$

potentials of radicals represented by $R_2N\cdots X$ ($X = CR_2$, NR, or O) are usually less positive than those of the corresponding neutral compounds, $R_2\ddot{N}$–Y ($Y = CR_3$, NR_2, or OR).[13] Nevertheless, the assignment of the third peak is supported, as described later, by the voltammetric results for (**1**) in acetonitrile saturated with oxygen.

The voltammograms of (**1**) in the presence of dissolved oxygen lacked the second anodic peak observed in the deoxygenated medium. However, upon reversal of the voltage sweep to the cathodic direction followed by a subsequent anodic sweep, a new redox wave was discernible at a potential less positive than that of the original first anodic peak. A typical example is illustrated in Figure 5. When the initial anodic sweep was stopped at a potential between those of the two anodic peaks (the first and third peaks) for 30 s, the redox couple was markedly enhanced on the subsequent cathodic and anodic sweep [Figure 5(b)]. On the other hand, the redox couple almost disappeared when the initial sweep was stopped beyond the third peak for 30 s [Figure 5(c)]. It has been reported that the aminyl radical (**4a**) reacts with oxygen quantitatively to yield 2,2,6,6-tetramethylpiperidin-1-oxyl (**6a**).[8] A similar reaction of (**4b**) to form the nitroxide (**6b**) (2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl) is also known.[7] In fact, *in situ* electrolysis of (**1a** and **b**) in acetonitrile containing oxygen gave e.s.r. spectra due to (**6a** and **b**): for (**6a**) at −8 °C, g = 2.0058, a = 16.2 G (1 N); for (**6b**) at 20 °C, g = 2.0058, a = 14.8 G (1 N).† The new wave observed in the voltammetry of (**1b**) matched well the voltammogram of an authentic sample of (**6b**) prepared by a known method,[14] and the electrode process may be represented as in equation (vii). Then, at the first anodic peak in the voltammetry of (**1**) in oxygen-saturated acetonitrile, the aminyl radical (**4**) will react with oxygen to form the nitroxide (**6**), which will be oxidized further to the oxoammonium ion (**7**) to afford the redox couple in the subsequent cathodic and anodic sweep [Figure 5(b)].‡ At the potential beyond the third anodic peak, further electron transfer from (**4**) will take place in preference to the reaction with oxygen, and the redox couple will be depressed [Figure 5(c)].



(vii)

Although further evidence would be required to verify the present conclusion about the oxidation potential of the aminyl radical (**4**), we believe that the results described so far have provided convincing proof for the mechanism of the electrochemical N–C bond formation.

Experimental

Materials.—The amine (**1a**) was obtained commercially and purified by distillation. The amines (**1b** and **c**) were prepared by known methods,[15,16] and gave the expected analytical results. Acetonitrile was purified by the method of Kiesele.[17] Sodium perchlorate, used as the supporting electrolyte, was recrystallized from ethanol–water and stored over phosphorus pentaoxide under reduced pressure.

Apparatus.—Cyclic voltammetry was carried out either with the combination of a Hokuto Denko HA-104 potentiostat–galvanostat, a Hokuto Denko HB-101 linear scanning unit, and a Riken Denshi X-Y recorder F-5C, or with that of a Fuso potentiostat 315A, a Kawasaki Electronica TM-2520D dual-channel transient memory, and an *X–Y* recorder. Voltammograms were obtained with a three-electrode system consisting of

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* This presumption is consistent with the explanation of the fact that dimethylamine is more basic than dimethylaminyl radical. The lone-pair orbitals, at which protonation takes place, are *sp*^{3} for dimethylamine and *sp*^{2} for the aminyl radical. The higher basicity of the former is ascribed to the smaller *s* character (R. W. Fessenden and P. Neta, *J. Phys. Chem.*, 1972, **76**, 2857).

† The following e.s.r. parameters have been reported for solution in benzene at room temperature: for (**6a**), g = 2.0056, a = 15.0 G; for (**6b**) g = 2.0055, a = 14.3 G (ref. 7).

‡ The nature of the final products of the electrolysis of (**1**) in oxygen-saturated acetonitrile is not yet clear. Only in the case of (**1b**) was formation of the nitro compound $Me_2{=}CHCOCH_2CMe_2NO_2$ (*ca.* 25%) confirmed. This compound has been shown to be formed in the oxidation of the nitroxide (**6b**) by *m*-chloroperbenzoic acid in dichloromethane *via* the oxoammonium ion (**7b**) (J. A. Cella, J. A. Kelly, and E. F. Kenehan, *Tetrahedron Lett.*, 1975, 2869). In fact, the oxoammonium ion (**7b**), produced almost quantitatively by controlled-potential electrolysis of (**6b**) in oxygen-saturated acetonitrile at 0.8 V, was found to be converted into the nitro compound under the influence of light, oxygen, and a base such as the amine (**1b**) itself: the yield could not be improved above 25%.

a glassy carbon working electrode,[18] a platinum wire counter electrode, and an s.c.e. separated by an agar bridge.

Controlled-potential electrolysis was performed in an undivided cylindrical cell (25 × 65 mm) or in an **H**-type divided cell, the anode compartment (22 × 75 mm) of which was separated with methyl cellulose plug and a sintered glass disk, using a Hokuto Denko HA-105 or HA-301 potentiostat–galvanostat with a Hokuto HF-201 coulometer and a Toadempa EPR-108 electronic recorder. A glassy carbon plate, a platinum foil, and an s.c.e. separated by an agar bridge were used as the anode, cathode, and reference electrode, respectively.

E.s.r. spectra were recorded with a JEOL JES-FE 1X spectrometer equipped with 100 kHz field modulation and a ES-UCT-2AX variable-temperature accessory. The electrolysis cell used for internal generation of the radical species was a Pyrex capillary (1 × 100 mm) with a Pyrex reservoir (25 × 35 mm) at the top. The cell was attached to the spectrometer so that the centre region of the capillary was located in the centre of the e.s.r. cavity. A platinum wire anode, covered by polyethylene tubing except at both ends, was inserted into the capillary and a platinum wire cathode was placed in the reservoir.

Identification and Determination of the Cyanomethyl Derivatives (**2**) *from Controlled-potential Electrolysis.*—Typical examples of the procedure are described here. A solution of the amine (**1b**) (78 mg) in acetonitrile (20 ml) containing 0.1M-$NaClO_4$ was deoxygenated in the undivided cell (see before) by bubbling N_2 gas, which had been dampened with the solvent, for 30 min. The solution was subjected to electrolysis at 1.15 V at ambient temperature until the value of the current became $< 3\%$ of the initial value (8 h): 96.7 C, corresponding to $n = 2.0$, were found to be consumed. During the electrolysis a slow stream of N_2 gas was passed over the solution. The electrolysed solution was evaporated almost to dryness under reduced pressure, and then diluted with water (30 ml). The resulting mixture was extracted with chloroform (3 × 30 ml), and the extract was washed and dried. The chloroform was removed under reduced pressure and the residue was subjected to preparative t.l.c. on neutral alumina with ethyl acetate–hexane (1:3) as developing solvent. 1-*Cyanomethyl*-2,2,6,6-*tetramethyl*-4-*oxopiperidine* (**2b**) (91 mg, 93%) was separated and recrystallized from hexane as colourless needles, m.p. 108—109 °C (Found: C, 68.0; H, 9.5; N, 14.3. $C_{11}H_{18}N_2O$ requires C, 68.0; H, 9.3; N, 14.4%); the spectroscopic data (i.r., ^1H n.m.r., and mass spectra) have been reported.[1] The other two cyanomethylated products were obtained similarly. 1-*Cyanomethyl*-2,2,6,6-*tetramethylpiperidine* (**2a**) (colourless needles from hexane) had m.p. 35—36 °C (Found: C, 73.45; H, 11.25; N, 15.3. $C_{11}H_{20}N_2$ requires C, 73.3; H, 11.2; N, 15.5%); the spectroscopic data have been reported.[1] 1-*Cyanomethyl*-2,2,6,6-*tetramethylmorpholine* (**2c**) (colourless needles from hexane) had m.p. 99—100 °C (Found: C, 66.0; H, 10.4; N, 15.35. $C_{10}H_{18}N_2O$ requires C, 65.9; H, 9.95; N, 15.4%); $\nu_{max.}$(KBr) 2 210 cm^{-1} (CN); $\delta(CDCl_3)$ 1.13 (12 H, s), 3.39 (4 H, s), and 3.47 (2 H, s); m/z 182 (M^+).

The amine (**1a**) (70.3 mg) was subjected to electrolysis at 0.95 V as already described. The electrolysis was discontinued when 2.0 F per mol of (**1a**) had been consumed (6 h): the value of the current had decreased to 2.5% of the initial value. The solution from electrolysis was adjusted to 25.0 ml in a volumetric flask with acetonitrile, and the resulting solution was subjected to g.l.c. to estimate the yield of (**2a**) by using a JEOL JGC-20K gas chromatograph {PEG 6 000 + 10% KOH (2 m); ethyl *p*-methoxybenzoate as internal standard [also used in the determination of (**2c**): *p*-methoxybenzaldehyde was used for (**2b**)]}.

E.s.r. Experiments.—A typical example is as follows. A solution of the amine (**1b**) (10 mM) in acetonitrile containing 0.1M-$NaClO_4$ was deoxygenated in the reservoir by flushing with N_2 gas, and then introduced into the capillary. After thermal equilibrium was attained, the solution was subjected to constant-current electrolysis (10 μA), performed with a Hokuto Denko HA-111 potentiostat–galvanostat, and the e.s.r. spectrum was monitored. During the electrolysis, N_2 gas was passed over the solution. The g value was determined by comparing the spectrum with that of aqueous peroxylamine disulphonate ($g = 2.0055$). Computer simulation of the spectrum was carried out with a JEOL EC-100 computer system.

In the open-circuit experiments, the same procedure was applied to generate the aminyl radical (**4b**). The electrolysis was discontinued after a suitable period (Table 2) and (**4b**) was allowed to decay. The change of intensity of the e.s.r. signal, obtained with a modulation width of 5 G, was monitored from the beginning of the electrolysis at an appropriate magnetic field.

Photolysis of the Tetrazene (**5**).—A solution of (**5**) (148 mg) in acetonitrile (3 ml), after being deoxygenated by N_2 gas, was irradiated with a 100 W high-pressure mercury lamp in a sealed quartz vessel (10 × 100 mm) until (**5**) had disappeared (9 h). The volume of the mixture was adjusted to 10.0 ml with acetonitrile, and the resulting solution was analysed by g.l.c.

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