# Amine Oxidation. Part IX.[1] The Electrochemical Oxidation of Some Tertiary Amines: The Effect of Structure on Reactivity

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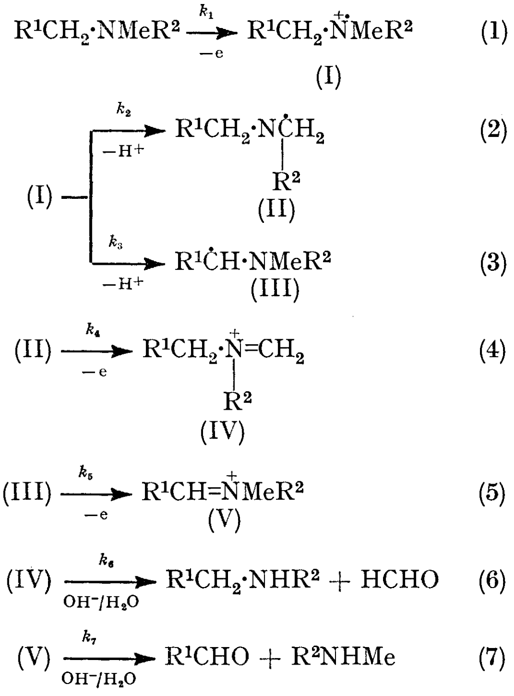
The anodic oxidation of a selection of tertiary alkyl- and aralkyl-amines has been studied by linear sweep voltammetry and controlled potential electrolysis at a glassy-carbon electrode in aqueous alkaline solution. Each amine shows only one oxidation wave. The oxidation peak potentials of a number of substituted *NN*-dimethylbenzylamines have been correlated with the Hammett $\sigma$ values of the substituents ($\rho$ −0.94) and the p$K_a$ values of the amines ($\alpha$ 0.82). The size and magnitude of these values agree well with those from oxidations by one-electron chemical oxidants and are consistent with a potential-determining loss of one electron from the nitrogen of the amine. As expected $\alpha$-deuteriation has little effect on the oxidation peak potential. Structural features in the amines that influence the ease of rehybridisation of the nitrogen ($sp^3 \longrightarrow sp^2$) in the potential-determining step have been studied using a selection of cyclic and bicyclic amines. These show that the transition state in the potential-determining step resembles the aminium radical. The distribution of products is close to that predicted statistically showing that the product-determining $\alpha$-C–H cleavage is very unselective. When coupled with a low primary isotope effect for the deprotonation this suggests that in the transition state the $\alpha$-C–H bond is almost intact and that the transition state resembles the aminium radical more than the $\alpha$-amino-radical.

OUR interest in the oxidation of tertiary amines with the one-electron oxidant alkaline potassium hexacyanoferrate(III)[2] has led us to examine the related electrochemical processes and to compare the influence of structure on reactivity in the two systems. Previously there have been reports on the electrochemical oxidation of amines in anhydrous media (*e.g.* $CH_3CN$ [3] or $CH_3OH$ [4]) or in aqueous alkaline solution[5] by the use of linear sweep voltammetry and controlled potential electrolysis. Simple alkylamines are oxidised irreversibly on platinum or glassy-carbon;[3a,5a] the e.c.e. processes involved in the oxidation in aqueous alkali are outlined in reactions (1)—(7).[5a] It is noteworthy that these reactions are directly analogous to those proposed for these oxidations by chemical one-electron oxidants.[6]



$$R^1CH_2{\cdot}NMeR^2 \xrightarrow[-e]{k_1} R^1CH_2{\cdot}\overset{+\bullet}{N}MeR^2 \quad (1)$$

(I)

$$(I) \xrightarrow[-H^+]{k_2} R^1CH_2{\cdot}N\dot{C}H_2(R^2) \quad (2)$$

(II)

$$(I) \xrightarrow[-H^+]{k_3} R^1\dot{C}H{\cdot}NMeR^2 \quad (3)$$

(III)

$$(II) \xrightarrow[-e]{k_4} R^1CH_2{\cdot}\overset{+}{N}(R^2){=}CH_2 \quad (4)$$

(IV)

$$(III) \xrightarrow[-e]{k_5} R^1CH{=}\overset{+}{N}MeR^2 \quad (5)$$

(V)

$$(IV) \xrightarrow[OH^-/H_2O]{k_6} R^1CH_2{\cdot}NHR^2 + HCHO \quad (6)$$

$$(V) \xrightarrow[OH^-/H_2O]{k_7} R^1CHO + R^2NHMe \quad (7)$$

## RESULTS

*Linear Sweep Voltammetry.*—For all the amines studied the oxidations were irreversible and showed only one anodic wave.

The peak potentials ($E_p \pm 0.01$ V) of a number of cyclic and bicyclic tertiary amines together with those of triethylamine, *N*-methyl-, and *N*-[$^2H_3$]methyl-di-n-butylamine, and a selection of substituted *NN*-dimethylbenzylamines are recorded in Table 1. This Table also gives the values of $\beta n_a$ and $i_p/ACV^{\frac{1}{2}}$ as defined by the equation $i_p = 3.01 \times 10^5 n(\beta n_a)^{\frac{1}{2}} D^{\frac{1}{2}} ACV^{\frac{1}{2}}$, for an irreversible electron-transfer[7] where $i_p$ is the peak current (amp), $n$ is the total number of electrons transferred per molecule of reactant, $\beta$ is the charge-transfer coefficient, $n_a$ the number of electrons transferred in the rate-determining step, $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $A$ is the area of the anode (cm$^2$), $C$ is the concentration of the reactant (mol cm$^{-3}$), and $V$ is the sweep rate (V s$^{-1}$).

For the substituted *NN*-dimethylbenzylamines good linear correlations are obtained between the measured peak potentials and the Hammett $\sigma$ values of the substituents or the p$K_a$ values of the respective amines from which can be obtained[3c] a Hammett $\rho$ value of −0.94 and a Brönsted $\alpha$ of 0.82.

*Product Studies.*—Tables 2 and 3 summarise the products obtained from some controlled potential electrolyses. The potential used for the oxidation of each amine was between its half-peak and peak potential. Under conditions where the consumption of substrate was kept below 25% to minimise any further oxidation the coulometric value of $n$ was *ca.* 2. All the products could not be recovered quantitatively from the oxidation mixture, however the yields in Tables 2 and 3 have been corrected for the efficiencies of the extraction procedure by the use of standard synthetic mixtures. The g.l.c. analysis of the basic products from

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TABLE 1

Voltammogram parameters for the oxidation of some tertiary amines at 298 K with a potential sweep rate of 33 mV s$^{-1}$; *ca.* 10$^{-2}$M-amine, 10$^{-3}$M-sodium hydroxide, 10$^{-1}$M-sodium perchlorate in 30% methanol in deionised water

| | Substrate | $E_p$/ V *versus* s.c.e. | $\beta n_a$ | $i_p/ACV^{\frac{1}{2}}$/ μA s$^{\frac{1}{2}}$ mM$^{-1}$ cm$^{-2}$ $V^{-\frac{1}{2}}$ |
|---|---|---|---|---|
| 1 | *N*-n-Butylaziridine | 1.63 | 0.24 | 612 |
| 2 | *N*-Methylpyrrolidine | 0.68 | 0.53 | 605 |
| 3 | *N*-Methylpiperidine | 0.80 | 0.48 | 512 |
| 4 | *N*-Methylhexamethyleneimine | 0.60 | 0.64 | 752 |
| 5 | *N*-Methylheptamethyleneimine | 0.51 | 0.60 | 705 |
| 6 | 1,2-Dimethylpiperidine | 0.78 | 0.48 | 620 |
| 7 | *cis*-1,2,6-Trimethylpiperidine | 0.77 | 0.48 | 729 |
| 8 | *trans*-1,2,6-Trimethylpiperidine | 0.74 | 0.53 | 853 |
| 9 | 1,2,2,6,6-Pentamethylpiperidine | 0.63 | 0.60 | 977 |
| 10 | 1-Azabicyclo[2.2.2]octane | 0.96 | 0.69 | 1 023 |
| 11 | 1-Azabicyclo[3.3.3]undecane | 0.38 | 0.48 | 643 |
| 12 | *N*-Methyl-di-n-butylamine | 0.65 | 0.60 | 814 |
| 13 | *N*-[$^2H_3$]Methyl-di-n-butylamine | 0.66 | 0.60 | 829 |
| 14 | *NN*-Dimethylcyclopropylamine | 0.78 | 0.30 | 581 |
| 15 | 2-Dimethylaminopropane | 0.73 | 0.53 | 721 |
| 16 | *NN*-Dimethylcyclopropylmethylamine | 0.75 | 0.48 | 822 |
| 17 | Triethylamine | 0.73 | 0.48 | 791 |
| 18 | *NN*-Dimethyl-4-methoxybenzylamine | 0.76 | 0.37 | 698 |
| 19 | *NN*, 4-Trimethylbenzylamine | 0.76 | 0.40 | 682 |
| 20 | *NN*-Dimethylbenzylamine | 0.77 | 0.53 | 674 |
| 21 | *NN*-Dimethyl-4-chlorobenzylamine | 0.78 | 0.34 | 589 |
| 22 | *NN*-Dimethyl-4-bromobenzylamine | 0.78 | 0.37 | 690 |
| 23 | *NN*-Dimethyl-3-trifluoromethylbenzylamine | 0.80 | 0.48 | 543 |
| 24 | *NN*-Dimethyl-3-nitrobenzylamine | 0.81 | 0.47 | 527 |
| 25 | *NN*-Dimethyl-4-nitrobenzylamine | 0.81 | 0.40 | 729 |

TABLE 2

Yields (% based on substrate) of products from the electrochemical oxidation of *N*-methyl- and *N*-[$^2H_3$]methyl-di-n-butylamine for 3 h at 0.60 V *versus* s.c.e. in 10$^{-1}$M-sodium perchlorate

| Solvent | [NaOH]/M | Demethylation | Debutylation | Unchanged substrate | Ratio demethylation : debutylation | *n* * |
|---|---|---|---|---|---|---|
| a *N*-Methyl-di-n-butylamine | | | | | | |
| 30% v/v Dimethoxyethane in deionised water | 10$^{-4}$ | 11.7 | 9.9 | 82.4 | 1.18 | 1.75 |
| 30% v/v Dimethoxyethane in deionised water | 10$^{-3}$ † | 6.1 | 5.4 | 91.1 | 1.15 | 1.78 |
| 30% v/v Dimethoxyethane in deionised water | 0.5 | 9.9 | 8.4 | 76.2 | 1.18 | 2.87 |
| Aqueous buffer pH 11 | | 10.6 | 7.9 | 77.3 | 1.36 | 2.06 |
| b *N*-[$^2H_3$]Methyl-di-n-butylamine | | | | | | |
| 30% v/v Dimethoxyethane in deionised water | 10$^{-3}$ | 4.6 | 6.7 | 78.3 | 0.69 | 1.78 |
| 30% v/v Dimethoxyethane in deionised water | 0.5 | 3.4 | 5.4 | 92.7 | 0.64 | 1.70 |

* Number of electrons transferred per molecule of amine oxidised. † Electrolysis time 2 h.

TABLE 3

Yields (% based on substrate) of products from the electrochemical oxidation of some substituted *NN*-dimethylbenzylamines ($XC_6H_4CH_2NMe_2$) in 10$^{-3}$M-sodium hydroxide and 10$^{-1}$M-sodium perchlorate in 30% v/v methanol in deionised water

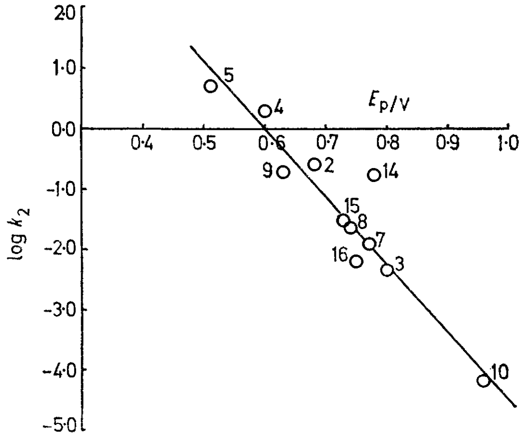
| | | Product | | | | |
|---|---|---|---|---|---|---|
| X | Potential/V *versus* s.c.e. | $XC_6H_4CH_2NHMe$ | $XC_6H_4CHO$ | Unchanged substrate | Ratio demethylation : debenzylation | *n* * |
| 4-OMe | 0.70 † | 10.0 | 4.9 | 80.0 | 2.0 | 1.97 |
| 4-Me | 0.70 † | 12.0 | 4.8 | 79.2 | 2.5 | 2.20 |
| H | 0.70 ‡ | 7.4 | 2.8 | 89.0 | 2.7 | 1.85 |
| 4-Cl | 0.70 † | 5.0 | 1.7 | 83.2 | 3.0 | 2.40 |
| 3-$NO_2$ | 0.75 † | 5.7 | 2.6 | 86.3 | 2.2 | 2.40 |
| 4-$NO_2$ | 0.75 † | 8.8 § | 3.8 | 87.4 | 2.3 | 2.00 § |

* Number of electrons transferred per molecule of amine oxidised. † Electrolysis time 3 h. ‡ Electrolysis time 2 h. § Yield calculated assuming $n = 2.00$ (see text).

the oxidation of *NN*-dimethyl-4-nitrobenzylamine was not satisfactory. To obtain an estimate of the yield of *N*-methyl-4-nitrobenzylamine, the expected total yield of *N*-methyl-4-nitrobenzylamine and 4-nitrobenzaldehyde was obtained by use of Faraday's law assuming $n = 2.0$. Subtraction of the measured yield of 4-nitrobenzaldehyde gave the yield of the secondary amine.

## DISCUSSION

The influence of α-deuteriation of an amine on the ease of formation of its aminium radical is small; the values of $k_H/k_D$ for one-electron transfer to chemical oxidants lie between 1.3 and 9% per deuterium[2,8] (*cf.* the value for the analogous secondary isotope effect for carbonium ion formation is *ca.* 11% per deuterium[9]). The slight difference in $E_p$ values of *N*-methyl- and *N*-[$^2H_3$]methyl-di-n-butylamine confirm that the potential-determining step in electrochemical oxidation is the formation of an aminium radical [reaction (1)] and does not involve the concomitant cleavage of an α-C–H bond.



Plot of logarithm of second-order rate constant for the potassium hexacyanoferrate(III) oxidation of some cyclic tertiary amines at 298 K against the oxidation peak potentials of these amines at a glassy-carbon electrode at 298 K. The numbers in the graph correspond to those in Table 1

The Hammett ρ value (−0.94) and the value of α from the Brönsted catalysis equation (0.82) are consistent with the development of positive charge on the nitrogen atom in the transition state of the potential-determining step and agree well with those reported for chemical one-electron oxidation of these amines in aqueous solution [ρ −0.984 and α 0.99, and ρ −0.924 and α 0.812 for oxidation with potassium hexacyanoferrate(III)[10] and chlorine dioxide[11] respectively]. These similarities despite the large differences in reaction conditions concur with the suggestion of Rosenblatt and his co-workers[3c] that solvation effects on the initial-electron transfer are relatively unimportant.

It is interesting to note that there is a linear relationship (Figure; correlation coefficient $r$ 0.97) between the $E_p$ values of the cyclic amines and the logarithms of their second-order rate constants for oxidation by potassium hexacyanoferrate(III)[2] which again emphasises the similarity between the chemical and electrochemical processes. Similar correlations are seen for the $E_p$ values for the cyclic amines and the logarithms of the first-order rate constants for the $S_N1$ solvolyses of the corresponding 1-methylcycloalkyl chlorides[12] or the pyrolysis of the cycloalkylazonitriles[13] ($r$ 0.89 and 0.99 respectively). In all these processes the hybridisation of the reaction centre in the rate-determining step changes from $sp^3$ to $sp^2$. Applying the same reasoning to the electrochemical data as that used previously[2] the transition state for the potential-determining step occurs late on the reaction profile and resembles the aminium radical rather than the amine.

α-Methylation of *N*-methylpiperidine lowers its oxidation potential; a change which is attributable to the inductive effects of the methyl groups aiding the formation of the aminium radical. Superimposed on this electronic effect is a smaller steric influence. For the two trimethylpiperidines with equivalent electronic effects there is a difference in bond-opposition associated with the formation of the piperidinium radical.[2,14] As the $E_p$ values indicate and as can be shown with models the change is easier for the *trans*- than the *cis*-isomer.

The oxidation peak potentials of the two bicyclic amines, 1-azabicyclo[2.2.2]octane and 1-azabicyclo-[3.3.3]undecane, lie either side that of *N*-methylpiperidine and differ by 0.58 V. The high $E_p$ value of the former is expected since the bicyclo-octane cage structure distorts the aminium radical from its preferred planar configuration thus decreasing its ease of formation. By contrast the $E_p$ value of the azabicycloundecane is the lowest in this study and 0.13 V lower than the next most readily oxidised amine, the corresponding monocyclic compound *N*-methylheptamethyleneimine. The bridgehead bond angles in the azabicycloundecane are distorted from the normal tetrahedral value to between 115—116°.[15] Thus the ease of oxidation arises from relief of angular strain that accompanies the formation of the $sp^2$ hybridised aminium radical. These results complement the unusually high reactivity of the 1-position of 1-chlorobicyclo[3.3.3]undecane in reactions involving $sp^3 \longrightarrow sp^2$ rehybridisation, for example the chlorobicycloundecane is solvolysed $10^4$ times faster than 2-chloro-2-methylpropane.[16]

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The relative rates of oxidation of *NN*-dimethylcyclopropylamine, 2-dimethylaminopropane, and *NN*-dimethylcyclopropylmethylamine with potassium hexacyanoferrate(III) [17] are 27 : 4.8 : 1.0 and their oxidation peak potentials are 0.78, 0.73, and 0.75 V *versus* s.c.e. respectively. The difference in the behaviour of the two systems is illustrated in the Figure where the points for 2-dimethylaminopropane and *NN*-dimethylcyclopropylmethylamine lie close to the line but that of *NN*-dimethylcyclopropylamine deviates.

The cyclopropyl ring has a $-I$ effect due to the hybridisation of the ring carbons [18] but in the cyclopropylmethyl carbonium ion there is a more effective donation of electrons by $\sigma$–$\pi$ overlap between the C–C bonds of the ring and the empty *p*-orbital.[19] The order of reactivity of the three amines to chemical oxidation is readily interpretable in terms of these two effects with the $\sigma$–$\pi$ interaction favouring the formation of the cyclopropylaminium radical. However, in the electrochemical oxidation there can be no substantial $\sigma$–$\pi$ interaction. Although there is no obvious explanation for this difference it is possible that in the electrochemical process the cyclopropyl group interacts with the electrode surface favouring a conformation where interaction with the *p*-orbital is small and the $-I$ effect predominates. The $\sigma$–$\pi$ interaction in the cyclopropylmethyl carbonium ion is known to be dependent on the angle between the cyclopropyl ring and the empty *p*-orbital.[20]

Coulometric studies show that in agreement with reactions (1)—(7) two electrons are consumed for the dealkylation of each molecule of tertiary amine. Comparison of the ratio of demethylation to debutylation in the oxidation of *N*-methyl- and *N*-[$^2H_3$]methyl-di-n-butylamine, 1.17 and 0.67 respectively, gives a kinetic isotope effect $k_2^{H}/k_2^{D}$ of 1.75. [The calculation assumes that reactions (3)—(7) are unaffected by isotopic substitution.] These values are significantly lower than those obtained from the oxidation of these amines by alkaline potassium hexacyanoferrate(III) [2] (demethylation : debutylation 3.1 for the protioamine and 0.86 for the deuterioamine and $k_2^{H}/k_2^{D} = 3.6$). Following the arguments of Westheimer [21] the small isotope effect in the electrochemical studies indicates that in the transition state for proton removal from (I) in reaction (2) either the $\alpha$-C–H bond is virtually intact or it is almost completely broken. (The related transition state in the chemical oxidation must be more symmetrical.) Attempts to alter the symmetry of the transition state and the value of $k_2^{H}/k_2^{D}$ by changing the concentration of base, in the manner described by Lee and Srinivasan [22] for the oxidation of *NN*-dimethylbenzylamine by bromine, or by removing the organic co-solvent proved unsuccessful.

Substituents have a negligible influence on the product distribution from the electrochemical oxidation of the substituted benzylamines, there being a slight preference for loss of the benzyl group but no overall trend with the electronic properties of the substituents. These results agree with the non-selective product-determining step in the chlorine dioxide oxidation of some substituted *NN*-dimethylbenzylamines [11] and the near statistical distribution of products in the electrochemical oxidation of *NN*-dimethylbenzylamine in alkaline methanol,[4d] but are in conflict with other studies where the acidity of the $\alpha$-protons in the aminium radical is considered partly responsible for determining the direction of dealkylation.[5b,10]

The results from this study can be rationalised with a slow potential-determining one-electron transfer to the anode [reaction (1)] followed by a fast exothermic deprotonation of the aminium radical in reactions (2) and (3). Further we postulate a smaller amount of $\alpha$-C–H bond cleavage in the transition states for deprotonation in the electrochemical than in the hexacyanoferrate(III) oxidation accounting for the near statistical distribution of products and the low kinetic isotope effect in the former oxidations.

## EXPERIMENTAL

The spectroscopic and analytical methods were the same as those reported previously.[2]

*Materials.*—Sodium hydroxide, sodium perchlorate, methanol, diethyl ether, and 1,2-dimethoxyethane were research grade or AnalaR reagents. *N*-Methyl-pyrrolidine and -piperidine, *N*-ethylpiperidine, and *NN*-dimethylbenzylamine (Koch–Light Ltd.) were purified by distillation and dried over molecular sieve (type 4A, B.D.H. Ltd.). 1-Azabicyclo[2.2.2]octane (Ralph N. Emanuel Ltd.) was purified by sublimation. The following tertiary amines were prepared by methylation of the commercially available primary or secondary amine by the method of Clarke *et al.*; [23] *N*-methylhexamethyleneimine, b.p. 138—140° (lit.,[24] 140°); *N*-methylheptamethyleneimine, b.p. 160—162° (lit.,[25] 157—160°); 1,2-dimethylpiperidine, b.p. 126—127° (lit.,[26] 126—127°); *cis*-1,2,3-trimethylpiperidine, b.p. 146—148° (lit.,[24] 143° at 744 mmHg); 1,2,2,6,6-pentamethylpiperidine, b.p. 183—185° (lit.,[24] 183°); 2-dimethylaminopropane b.p. 65—66° (lit.,[27] 67—67.5°); *NN*-dimethylcyclopropylamine (Found: C, 49.5; H, 9.9; N, 11.4. Calc. for $C_5H_{11}N,HCl$: C, 49.4; H, 10.0; N, 11.5%); *N*-methyl-di-n-butylamine, b.p. 160—162° (lit.,[28] 161—162°). The substituted *NN*-dimethylbenzylamines, except for *NN*-di-

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methyl-3-trifluoromethylbenzylamine, were prepared from the corresponding benzyl bromide and dimethylamine by the method of Eliel *et al.*;[29] *NN*-dimethyl-4-methoxybenzylamine, b.p. 100—101° at 9 mmHg (lit.,[29] 105—111° at 10 mmHg); *NN*,4-trimethylbenzylamine, b.p. 80—81° at 13 mmHg (lit.,[29] 196—197°); *NN*-dimethyl-4-chlorobenzylamine, b.p. 88—90° at 11 mmHg (lit.,[29] 90—95° at 9—11 mmHg); *NN*-dimethyl-4-bromobenzylamine, b.p. 114—115° at 16 mmHg (lit.,[30] 121—122° at 20 mmHg); *NN*-dimethyl-3-nitrobenzylamine, b.p. 140—142° at 14 mmHg (lit.,[31] 112—114° at 3.5 mmHg); and *NN*-dimethyl-4-nitrobenzylamine, b.p. 136—137° at 11 mmHg (lit.,[30] 140—146° at 13—14 mmHg). The preparations of *N*-butylaziridine, *N*-[$^2H_3$]methyl-di-n-butylamine, and *trans*-1,2,6-trimethylpiperidine have been reported.[2] 1-Azabicyclo[3.3.3]undecane was prepared by the method of Coll *et al.*[15] (Found: C, 63.6; H, 10.5; N, 7.7. Calc. for $C_{10}H_{19}N,HCl$: C, 63.3; H, 10.6; N, 7.4%). *NN*-Dimethylcyclopropylmethylamine was prepared from cyclopropylacetyl chloride following Blomquist and Connolly[32] and had b.p. 96° (lit.,[32] 99—100°). *NN*-Dimethyl-3-trifluoromethylbenzylamine was prepared by treating 3-trifluoromethylbenzoyl fluoride (Ralph N. Emmanuel Ltd.) with dimethylamine and reducing the product ($LiAlH_4$) to give a material with b.p. 71—73° at 14 mmHg (lit.,[33] 104—107° at 60 mmHg) (Found: C, 50.0; H, 5.6; N, 5.8. Calc. for $C_{10}H_{12}F_3N,HCl$: C, 50.1; H, 5.5; N, 5.8%).

The water used was distilled and deionised (conductance $< 1.0\ \mu\Omega^{-1}$). Nitrogen (British Oxygen Co.; white spot) was used to deoxygenate solutions for controlled potential electrolysis.

*Apparatus and Methods.*—The electrolyses were performed with a Chemical Electronics TR40-2A potentiostat and linear sweep generator. The reference electrode was a saturated calomel electrode (E.I.L. Ltd.). Linear sweep voltammograms were recorded on a Bryans 21005 X-Y recorder and the current flowing in controlled potential electrolyses was measured with a Goerz Servoscribe RE 511 recorder.

The cells used for linear sweep voltammetry and controlled potential electrolysis were of the conventional U shape with the anode and cathode compartments separated by a glass frit (porosity 4). The electrodes for voltammetry were made from glassy-carbon rod (diameter 3 mm) (Vitreous Carbon Ltd.); for the controlled potential electrolyses the glassy-carbon electrodes were 20 cm square. Electrical contact between the reference electrode and the working electrode was made by means of an agar-agar–saturated potassium chloride bridge.[34]

The electrode surfaces were prepared following the procedure of Giles *et al.*[35] To obtain reproducible results, it was found necessary to leave the working electrode after each potential sweep in concentrated chromic acid solution for 10 min followed by washing with plenty of water. Using this procedure the working electrodes gave repeatable results after over two years of continuous use.

*Linear Sweep Voltammetry.*—The required amount of amine was added to a graduated flask and this was made up to 50 ml with the solvent. A portion of this solution (30 ml) was placed in the cell, the electrodes were inserted and the cell was placed in a thermostatted bath (±0.2°). After temperature equilibration the cyclic voltammogram was recorded. Three or four voltammograms were recorded with each of two working electrodes for each solution.

*Controlled Potential Electrolysis.*—The solvent (70 ml) was placed in both compartments of the cell and deoxygenated with nitrogen. The amine was then added and electrolysed at room temperature in an atmosphere of nitrogen at the required potential. The extraction procedure used for all but the substituted benzylamines has been reported.[2] For the latter amines simple ether extraction was replaced by continuous ether extraction for 3—5 h using a Soxhlet apparatus.

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