2040 © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53***, *2040—2045 (1980)* [Vol. 53, No. 7

Electrochemical Generation of Unstable Nitrogen Species. Part 4.[1)] Electrochemical and Chemical Oxidation of Cyclic and Open-chain Diamines. The Formation of Cyclic Hydrazine Derivatives

Toshio Fuchigami,* Tomoyasu Iwaoka, Tsutomu Nonaka, and Taro Sekine
Department of Electronic Chemistry, The Graduate School at Nagatsuta,
Tokyo Institute of Technology, Nagatsuta-machi, Midori-ku, Yokohama 227

(Received December 7, 1979)

Intramolecular N,N-coupling by the electrochemical oxidation of cyclic and open-chain diamines such as 3,3,7,7-tetraethylperhydro-1,5-diazocine (**1**) and *N,N*-dimethyl-2,2-diethyl-1,3-diaminopropane (**2**) was investigated with the use of platinum, silver, nickel, and carbon anodes. In the case of **1**, cyclic hydrazine derivatives, 3,3,7,7-tetraethyl-1,5-diazabicyclo[3.3.0]octane and 1-(2-ethyl-2-formylbutyl)-4,4-diethyl-4,5-dihydropyrazole, were formed in high current efficiency. In the case of **2**, the corresponding hydrazines, 1,2-dimethyl-4,4-diethylpyrazolidine and 1-methyl-3,3-diethyl-4,5-dihydropyrazole, were obtained in low current efficiency, because C–N bond cleavage took place before N,N-coupling. A carbon anode was found to be effective for N,N-coupling of such diamines. Chemical oxidative N,N-coupling of **1** and **2** was studied by using sodium peroxodisulfate and lead tetraacetate.

A number of studies have been carried out on the electrochemical oxidation of amines from both electrochemical and organic synthetic viewpoints.[2)] However, only a few papers deal with electrooxidative N,N-coupling reaction. N,N-Coupling is known only in the case of aromatic amines,[3–6)] *e.g.*, the formation of azobenzenes from aniline derivatives.

The initial electrode process of the oxidation of amines is supposed to be one electron transfer from a lone pair of electrons of a nitrogen atom to form a cation radical. In the case of aromatic amines, the life time of the cation radical intermediate thus produced is so long that it can give rise to various intermolecular coupling products.

In the case of aliphatic amines, the cation radical and radical intermediate is so unstable that N,N-coupling is difficult, C–N bond cleavage and/or nucleophilic substitution on an α-carbon supposedly taking place. In their work dealing with anodic N,N-coupling of aliphatic amines, Blackham *et al.*[7)] found that 2,2′-dimethyl-2,2′-azopropane and 2,2′-dimethyl-2,2′-azoxypropane, with a total current efficiency 46%, are formed from *t*-butylamine. Recently, Bauer and Wendt[8)] and Fuchigami *et al.*[9)] found that secondary amines such as dibutylamine and piperidine give the corresponding hydrazine compounds in current efficiency lower than 50%.

In the case of chemical oxidation, no paper dealing with N,N-coupling of aliphatic amines seems to have appeared except for the formation of 1,1′-bipiperidines from piperidines reported by Nomura *et al.*[10)]

We have investigated the intramolecular oxidative N,N-coupling of a cyclic diamine and an open-chain diamine such as **1** and **2**. Intramolecular N,N-coupling seems to occur more easily than intermolecular coupling, since reaction sites in the intramolecular N,N-coupling would be closer to each other. Neither electrochemical nor chemical oxidation of such aliphatic diamines seems to have been carried out so far. The chemical oxidative N,N-coupling of **1** and **2** was studied by using sodium peroxodisulfate and lead tetraacetate as an oxidizing reagent.

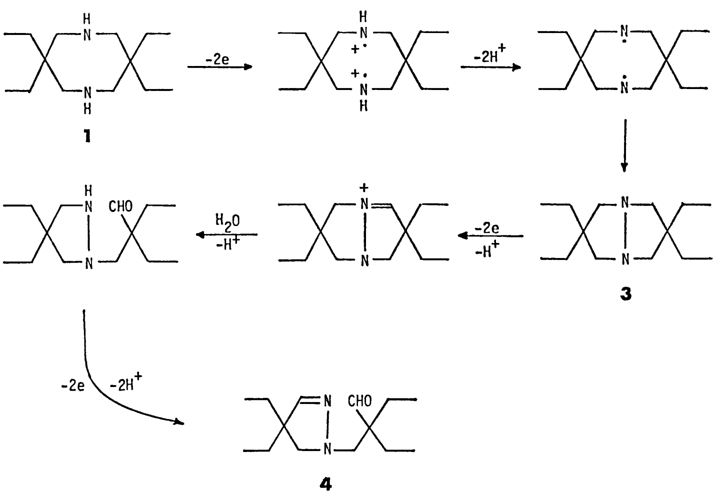
Results and Discussion

Electrochemical Oxidation of 1 and 2. Electrolysis of **1** was carried out in acetonitrile at a constant potential using various anode materials. In order to prevent **1** from becoming inert to oxidation due to the formation of salt during the course of electrolysis,

Table 1. Results of the electrochemical oxidation of 3,3,7,7-tetraethylperhydro-1,5-diazocine (**1**)

Entry	Anode material	Anode potential (V *vs.* SCE)	Temp °C	Molar ratio of LiOH/**1**	Amount of electricity (×10^4 C/mol)	Yields of products[a)] **3**	**4**	Recovery of **1** %
1	Pt	0.8	25	2	7.72	9 (23)	7 (53)	75
2	Pt	1.1	25	2	7.72	7 (18)	8 (60)	83
3	Pt	1.5	25	2	7.72	8 (20)	6 (45)	80
4	Pt	1.1	3	2	8.30	10 (23)	11 (76)	62
5	Pt	1.1	−12	2	7.33	9 (24)	9 (71)	56
6	Pt	1.1	25	0	7.72	4 (10)	10 (75)	89
7	Pt	1.1	25	10	18.14	12 (13)	21 (67)	40
8[b)]	Pt	1.1	25	2	7.91	57[c)]	13 (63)	—
9	C	0.3	25	2	9.07	14 (30)	10 (64)	51
10	Ni	0.7	25	2	8.30	12 (28)	8 (56)	69
11	Ag	0.3	25	2	9.46	trace	11 (67)	66

a) Values in parentheses show current efficiency (%). b) Electrolysis of **3**. c) Recovery of **3**.



Scheme 1.

lithium hydroxide powder was suspended in the anolyte. The electrolytic conditions and results are summarized in Table 1.

Two products were detected by gas chromatography. One was identified as 3,3,7,7-tetraethyl-1,5-diazabicyclo[3.3.0]octane (**3**) by comparison of the mass fragmentation[†] and retention time with those of an authentic sample synthesized separately.[11] The other, isolated by column chromatography on almina with dichloromethane, was identified as 1-(2-ethyl-2-formylbutyl)-4,4-diethyl-4,5-dihydropyrazole (**4**), its structure being confirmed by the following results:

a) The compound shows a positive Tollens test.

b) In the IR spectrum, the characteristic strong absorption of a carbonyl group was observed at 1740 cm^{-1}.

c) In the NMR spectrum measured in CCl_4 with TMS as the internal standard, the characteristic signal of an aldehydic proton was observed at 9.30 ppm, the other signals being explained in terms of the structure of **4**.

d) In the mass spectrum, the molecular ion (*m/e* 238) was observed together with appropriate fragment peaks such as *m/e* 209 (M^+—CHO and/or M^+—Et) and 139 (M^+—Et_2CCHO).

e) The results of elemental analyses of the free base and the 2,4-dinitrophenylhydrazone of **4** agree with the calculated values within normal errors.

The compound thus isolated is neutral colorless oily material; such a 1-substituted dihydropyrazole derivative is unknown so far.

As shown in Table 1, N,N-coupling products were formed as expected, their current efficiency being generally good.

In the case of a platinum anode, both **3** and **4** were formed in approximately equal yields. A change in the anode potential caused no appreciable change in yield. However, the total current efficiency changed with anode potential and electrolytic temperature. N,N-Coupling proceeded efficiently at lower temperature. In the absence of lithium hydroxide, the current decreased more rapidly than in its presence, the yield of **3** being reduced to about one half, while that of **4** increased. The reason for this has not been clarified yet. In the presence of 10 equivalents of lithium hydroxide, *ca.* 193000 C/mol of electricity was consumed and the ratio of **4**/**3** doubled, suggesting that the more the electricity passes, the higher the yield of **4**. Carbon and nickel anodes gave **3** in slightly higher yields than **4**.

The electrochemical oxidation of **1** proceeded at extremely low potentials in the cases of carbon and silver anodes, the latter giving only **4**, though the current efficiency was relatively low. In the case of a silver anode, the initial electrochemical reaction gives an oxide coating on the electrode surface. This seems to effect the oxidation of **1**. The low current efficiency of **4** in the case of the silver anode can be attributed to the formation of silver oxide, since the corrosion of the silver anode surface was observed during the course of electrolysis. Hampson *et al.*[12–14] also found that platinum and silver anodes give different products in the oxidation of aliphatic monoamines in an alkaline solution. A nickel anode[15] behaves like a silver one, but no such tendency was observed in the present work.

Since **3** can be oxidized at a lower potential than **1**[††] and **4** is formed by electrochemical oxidation of **3**, **4** seems to be formed by further oxidation of **3** produced in the course of the electrochemical oxidation of **1**.

Formation of **3** and **4** might proceed as shown in Scheme 1.

Intramolecular N,N-coupling of the open-chain diamine (**2**) was investigated. Electrochemical oxidation of **2** was carried out at a constant potential in 1 M NaOH solution instead of acetonitrile in the case of **1**, since the anode was passivated in the acetonitrile solution.

Three basic products were detected in the electrolyte by gas chromatography. 1,2-Dimethyl-4,4-diethyl-

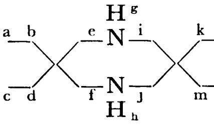
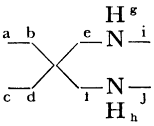
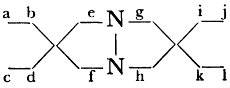
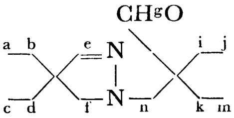
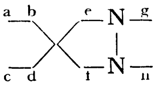
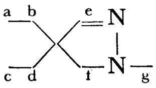
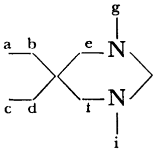
---

[†] The mass spectrum of **3** was measured with a gas chromatograph-mass spectrometer.

[††] This was shown by current density *vs.* anode potential curves of **1** and **3**. Such bicyclic diamines have extremely low oxidation potentials.[16]

pyrazolidine (**5**) was identified to be the authentic sample synthesized separately by gas chromatography and mass spectrometry. 1-Methyl-3,3-diethyl-4,5-dihydropyrazole (**6**) and 1,3-dimethyl-5,5-diethylperhydropyrimidine (**7**) were isolated by column chromatography and preparative gas chromatography, respectively. Their structures were confirmed by means of elemental analyses and spectral studies.

TABLE 2. NMR SPECTRAL DATA

Compound		NMR (δ ppm)[a]
1		0.80 (12H, t, H^a, H^c, H^l, H^n) 1.20 (8H, q, H^b, H^d, H^k, H^m) 1.75 (2H, s, H^g, H^h) 2.53 (s) and 3.36 (s) (8H, H^e, H^f, H^i, H^j)
2		0.78 (6H, t, H^a, H^c) 0.88 (2H, s, H^g, H^h) 1.25 (4H, q, H^b, H^d) 2.30 (4H, s, H^e, H^f) 2.35 (6H, s, H^i, H^j)
3		0.80 (12H, t, H^a, H^c, H^j, H^l) 1.45 (8H, q, H^b, H^f, H^i, H^k) 2.47 (8H, s, H^e, H^f, H^g, H^h)
4		0.80 (6H, t, H^a, H^c) 0.82 (6H, t, H^j, H^l) 1.50 (8H, m, H^b, H^i, H^k) 2.78 (2H, s, H^f), 2.96 (2H, s, H^h) 6.24 (1H, s, H^e), 9.30 (1H, s, H^g)
5		0.80 (6H, t, H^a, H^c) 1.40 (4H, q, H^b, H^d) 2.21 (6H, s, H^g, H^h) 2.38 (4H, s, H^e, H^f)
6		0.80 (6H, t, H^a, H^c) 1.40 (4H, q, H^b, H^d) 2.70 (5H, s, H^f, H^g) 6.25 (1H, s, H^e)
7		0.74 (6H, t, H^a, H^c) 1.32 (4H, q, H^b, H^d) 1.90 (4H, s, H^e, H^f) 2.11 (6H, s, H^g, H^i) 2.62 (2H, s, H^h)

a) Measured in CCl_4 with TMS as an internal standard. s: Singlet, t: triplet, q: qartet, m: multiplet.

In the NMR spectrum of **6**, the characteristic signal of an imino proton was observed at a low magnetic field such as 6.25 ppm; in that of **7**, the signal of N–H protons disappeared and that of singlet methylene protons appeared newly at 2.62 ppm. The compound was further identified by a mixed-melting-point test with a sample prepared from **2** and formaldehyde in an alkaline solution.

The basic products obtained are new. Their NMR spectral data together with those of the starting diamines, **1** and **2**, are summarized in Table 2.

When a large amount of electricity was passed in the electrolysis, a large amount of acidic substances were formed in addition to the basic products, but their structures could not be established.

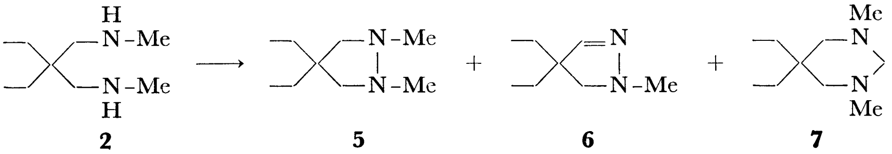
The results of electrolysis of **2** are summarized in Table 3.

The N,N-coupling product, **5**, expected in this reaction, was scarcely formed; it was detected in a very small amount only in the case of using a carbon anode. In addition to **5**, a highly oxidized product, **6**, having a N–N bond was formed in a low yield. **6** was formed at the highest current efficiency 16% at a carbon anode, but scarcely formed at all at platinum and silver anodes. **7** was formed in a considerable yield at anodes other than nickel.

2 as well as **1** can be oxidized at a low potential at a carbon anode.

Since the oxidation of **5** was much easier than that of **2** (Fig. 1)[†††] and **6** was also formed by electrochem-

TABLE 3. RESULTS OF THE ELECTROCHEMICAL OXIDATION OF *N*,*N'*-DIMETHYL-2,2-DIETHYL-1,3-PROPANEDIAMINE (**2**)[a)]

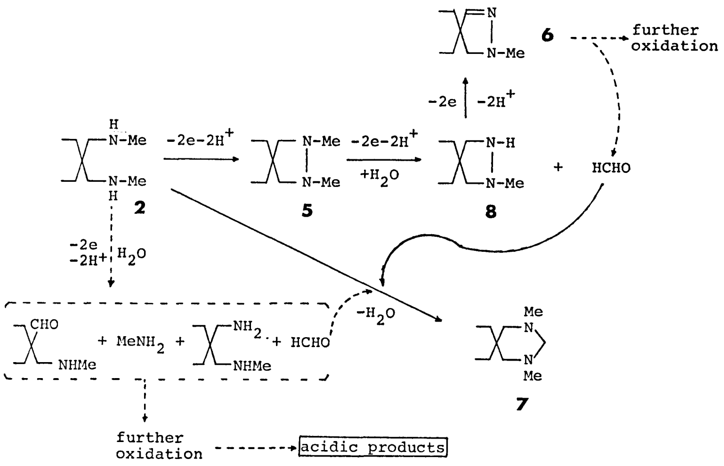


2 **5** **6** **7**

Entry	Anode material	Anode potential (V *vs.* SCE)	Amount of electricity (×10⁴ C/mol)	Yields of products[b)]/% 5	6	7	Recovery of **2** %	Others[c)] mg
12	Pt	1.2	9.65	0	trace	10	58	—
13	Pt	1.2	38.60	0	trace	26	13	60
14	C	0.5	9.65	trace	4(16)	8	65	—
15	C	0.5	38.60	trace	4(4)	23	17	55
16	Ag	0.7	9.65	0	1(4)	4	77	—
17	Ag	0.9	9.65	0	trace	3	80	—
18	Ag	0.9	62.73	0	4(3)	10	51	—
19	Ni	0.55	62.73	0	0	0	80	—
20[d)]	C	0.4	9.65	29[e)]	19(76)	—	—	41

a) **2**: 1 mmol (158 mg). b) Values in parentheses show current efficiency (%). c) Acidic products. d) Electrolysis of **5**. e) Recovery of **5**.

[†††] At a carbon anode, a negative shift of current *vs.* potential curve was induced in the presence of diamine, **2** (Fig. 1), no shift being observed at a platinum anode. Such a tendency was also observed in the case of **1**.



Scheme 2.

Table 4. Results of chemical oxidation of **1** and **2**

Diamine	Oxidizing reagent	Yields of products/%					Recovery of **1** or **2**
		3	**4**	**5**	**6**	**7**	%
1	$Na_2S_2O_8/Ag^+$ (1 eq./mol)	46	trace	—	—	—	24
1	$Pb(OAc)_4$ (1 eq./mol)	5	24	—	—	—	65
1	$Pb(OAc)_4$ (3 eq./mol)	4	89	—	—	—	0
2	$Na_2S_2O_8/Ag^+$ (1 eq./mol)	—	—	11	14	26	36

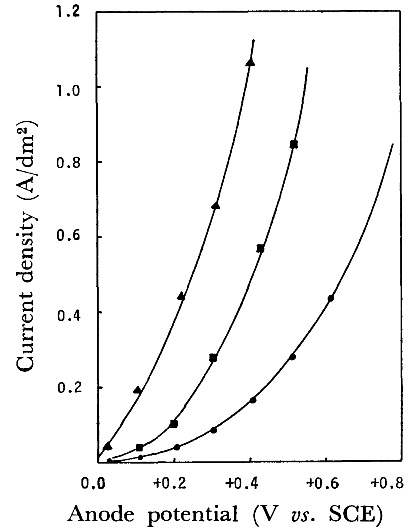


Fig. 1. Current density *vs.* anode potential curves of **2** and **5** in 1M NaOH at a carbon electrode.
—●—: 1 M NaOH (50 ml), —■—: 1 M NaOH (50 ml) + **2** (1 mmol), —▲—: 1 M NaOH (50 ml) + **5** (1 mmol).

ical oxidation of **5** at a lower potential than the oxidation potential of **2**, **6** seems to be formed by further oxidation of **5** produced in the course of the electrochemical oxidation of **2**. Since **7** was formed in a good yield by the reaction of **2** with excess formaldehyde under the same conditions as the electrolysis of **2**, **7** seems to be formed by the reaction of **2** with formaldehyde produced in the course of the electrolysis.

From the results and the formation of 1-methyl-4,4-diethylpyrazolidine (**8**),[††††] detected by a gas chromatography-mass spectrometer, electrochemical oxidation of **2** might proceed as in Scheme 2.

*Chemical Oxidation of **1** and **2**.* Nomura *et al.* found that sodium peroxodisulfate is effective for N,N-coupling of piperidines in the presence of silver ions.[10] We investigated chemical oxidation of **1** and **2** with sodium peroxodisulfate and also lead tetraacetate in order to compare the results with those of electrochemical oxidation. The results are summarized in Table 4.

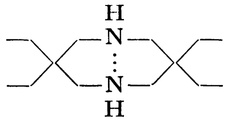
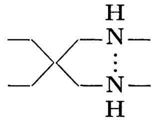
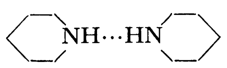
In the oxidation of **1** with sodium peroxodisulfate, the reaction stopped at the initial step of N,N-coupling, **3** being formed as the sole product. On the other hand, oxidation with lead tetraacetate afforded a highly oxidized product, **4**, far exceeding **3** in amount, though one equivalent of the oxidation reagent was employed. **4** was also formed in an excellent yield with use of three equivalents of the reagent.

In the oxidation of **2** with sodium peroxodisulfate, **5**, which could scarcely be obtained by electrolysis, was formed in *ca.* 10% yield. However, the highly oxidized product **6** was formed in a greater amount than **5**, though a large amount of the starting material remained. In the case of an open-chain diamine such as **2**, the oxidation reaction did not stop at the initial step of N,N-coupling, differing entirely from that of a cyclic diamine such as **1**. In the oxidation using lead tetraacetate, the analysis of products was difficult because of the formation of a large amount of polymer. Daniels and Martin[17] found that *N,N'*-

---

[††††] Its structure was tentatively determined by a study of the MS fragmentation: *m/e* 142 (M^+), 127 (M^+-Me), 126 (M^+-Me-H), 113 (M^+-Et).

Table 5. Efficiencies of electrochemical and chemical oxidative N,N-coupling

Anode material or oxidizing reagent	Efficiency of N,N-coupling (Current efficiency or yield %)		
			
C	94	16	low
Pt	99	4	low
Ag	67	3	low
Ni	84	0	0
$Na_2S_2O_8/Ag^+$ (1 eq.)	46	25	61[10]
$Pb(OAc)_4$ (1 eq.)	29	—	5

diakyl-1,3-propanediamines affords only unchanged diamines, though the *N,N'*-diaryl derivatives give N,N-coupling products by the oxidation using manganese dioxide.

Comparison of Electrochemical and Chemical Oxidation. Efficiencies of electrochemical and chemical oxidative N,N-coupling of **1** and **2** together with piperidine[10] are summarized in Table 5.

A precise comparison of N,N-coupling efficiencies can not be made because of different reaction conditions. However, points to be noted are as follows. The intramolecular N,N-coupling took place more easily in electrochemical oxidation than in intermolecular oxidation. In the former reaction, N,N-coupling of the cyclic diamine proceeded more readily than that of the open-chain diamine. In the case of the cyclic diamine, current efficiency of the N,N-coupling was good, regardless of anode material. In the case of the open-chain diamine, efficiency changes a great deal with anode material, a carbon anode being most effective for N,N-coupling. A nickel anode was very effective for the oxidation of **1**, but not for **2** and piperidine.

In contrast, the structures of amines did not cause such a large difference in the results in chemical oxidation. Selectivities for the oxidation products differ a great deal in chemical and electrochemical oxidation; *e.g.*, **3** and **4** were formed in higher selectivity by oxidation with sodium peroxodisulfate and lead tetraacetate, respectively, than that in the electrochemical oxidation, selectivity for **7** being higher in the electrochemical oxidation.

Experimental

Materials. *3,3,7,7-Tetraethylperhydro-1,5-diazocine (1) and 3,3,7,7-Tetraethyl-1,5-diazabicyclo[3.3.0]octane (3)*: **1** and **3** were prepared according to a modification of Kemp's procedure.[11] To a stirred solution of 3,3,7,7-tetraethylperhydro-1,5-diazocine-2,4,6,8-tetrone (0.097 mol) in dry THF was gradually added a solution of diborane hexahydride (0.36 mol) in THF at 0—5 °C. Stirring was carried out at 0—5 °C for 1 h and then at room temperature for 1 h. The mixture was refluxed for 24 h. After cooling, 3 M HCl (1 M = 1 mol·dm^{-3}) (200 ml) was added and THF was removed under reduced pressure. The residual solution was refluxed for 1 h. After cooling, the solution was made alkaline and was extracted repeatedly with ether. The extracts were dried over Na_2SO_4 and filtered. Hydrogen chloride gas was passed through the ether solution and the precipitates were collected by filtration. The crystals were treated with methanol at room temperature and insoluble parts were collected by filtration. Recrystallization of the matter from methanol–water (9:1, vol. ratio) gave pure hydrochloride of **1**: mp 231—233 °C (Ref.[11] 219—220 °C). From this salt, the free base of **1** was obtained by treatment with sodium hydroxide and extraction with ether: Yield 36%; mp 31—31.5 °C; *m/e* 226 (M^+). Found: C, 73.78; H, 13.67; N, 12.14%. Calcd for $C_{14}H_{30}N_2$: C, 74.27; H, 13.36; N, 12.37%. The methanolic solution of the filtrate was concentrated to dryness under reduced pressure. The residue was mixed with aqueous sodium hydroxide solution and the solution then extracted with ether. After drying of the ethereal extracts and concentration under reduced pressure, the residual oily substance was distilled under reduced pressure to give a fraction (**3**): Yield 7%, bp 115—116 °C/3 Torr; *m/e* 224 (M^+).

N,N'-Dimethyl-2,2-diethyl-1,3-propanediamine (2): The compound was prepared as a dihydrochloride by reduction of *N,N'*-dimethyl-α,α-diethylmalonamide with diborane by a procedure approximately the same as in the preparation of **1**. Recrystallization from methanol–ethanol (10:1, vol. ratio) gave pure dihydrochloride: Yield 45%; mp 265—267 °C. Found: C, 46.45; H, 10.94; N, 12.18%. Calcd for $C_9H_{24}N_2Cl_2$: C, 46.75; H, 10.46; N, 12.18%. The free base of **2** was obtained as an oil substance from the dihydrochloride: *m/e* 158 (M^+).

1,2-Dimethyl-4,4-diethylpyrazolidine (5): Using approximately the same procedure as above, **5** was prepared from 1,2-dimethyl-4,4-diethylpyrazolidine-3,5-dione.[18] Purification by column chromatography on alumina with hexane–ether (3:1, vol. ratio) gave **5** as an oily substance: *m/e* 156 (M^+), 141 (M^+-Me). Monohydrochloride of **5**: mp 165.5—167.5 °C (from hexane). Found: C, 56.31; H, 11.36; N, 14.54%. Calcd for $C_9H_{21}N_2Cl$: C, 56.08; H, 10.99; N, 14.53%.

1,3-Dimethyl-5,5-diethylperhydropyrimidine (7): The dihydrochloride of **2** (0.5 mmol) was dissolved in 20 ml of 1 M sodium hydroxide, and then 1 ml of 37% aq formaldehyde was added. After stirring for 2 h, the solution was extracted repeatedly with ether. Thorough evaporation of the ethereal extract, dried over anhydrous sodium sulfate under reduced pressure gave **7** as an oily substance: Yield 86%; *m/e* 170 (M^+), 155 (M^+-Me), 126 ($M^+-Me-Et$). Dihydrochloride of **7**: mp 217—218 °C (from isopropyl alcohol).

General Electrolytic Procedures. Electrolysis was carried out at a constant potential as follows. An H type cell divided with a sintered glass diaphragm was used. Platinum, carbon, nickel, and silver plates (2×4 cm) were used as an anode. A platinum anode was treated with concd nitric acid and the others were carefully polished with an emery paper No. 3000 before electrolysis. 0.1 M Et_4NOTs acetonitrile solution (50 ml) suspending lithium hydroxide powder and 1 M NaOH (50 ml) were used as an anolyte for electrolysis of **1** and **2**, respectively. To the anolyte was added 1 mmol of diamine (**1** and **2**) and then a current was applied.

Analysis of Products. *Electrolysis of **1***: After electrolysis, the anolyte was acidified with hydrochloric acid. Acetonitrile was evaporated under reduced pressure, the residual aqueous solution being made strongly alkaline with sodium hydroxide. The alkaline solution was extracted repeatedly with ether and the ethereal extracts were subjected to gas chromatography (column packing, PEG 20 M, column temperature, 186 °C).

1-(2-Ethyl-2-formylbutyl)-4,4-diethyl-4,5-dihydropyrazole (**4**) was isolated as an oily substance by column chromatography on almina with dichloromethane: *m/e* 209 (M^+). Found: C, 70.44; H, 11.35; N, 11.71%. Calcd for $C_{14}H_{26}N_2O$: C, 70.54; H, 11.00; N, 11.75%.

*Electrolysis of **2***: After salting-out with sodium chloride, the anolyte was extracted repeatedly with ether and the ethereal extracts were subjected to gas chromatography. Analysis for **5**, **6**, and **7** was carried out on a PEG 20 M column and that for **2** on Chromosorb 103.

In the case of a low material balance between the starting diamine and the products, the above alkaline solution, which was extracted with ether, was acidified with hydrochloric acid. After the acidic solution had been extracted repeatedly with ether, the ethereal extracts were concentrated, the acidic polymer obtained being weighed.

1-Methyl-3,3-diethyl-4,5-dihydropyrazole (**6**) was isolated by column chromatography on almina with dichloromethane: *m/e* 140 (M^+), 111 (M^+-Et). Picrate of **6**: mp 129—130 °C. Found: C, 45.37; H, 5.07; N, 18.91%. Calcd for $C_{14}H_{19}N_5O_7$: C, 45.53; H, 5.18; N, 18.96%. 1,3-Dimethyl-5,5-diethylperhydropyrimidine (**7**) was isolated by preparative gas chromatography: *m/e* 170 (M^+). Dihydrochloride of **7**: mp 217—218 °C. Found: C, 50.05; H, 10.11; N, 11.33%. Calcd for $C_{10}H_{24}N_2Cl_2$: C, 49.39; H, 9.95; N, 11.52%.

Chemical Oxidation. *Oxidation of **1** and **2** with Sodium Peroxodisulfate*: To a stirred mixture of **1** (1 mmol), 0.5 M NaOH–acetone (8—10 ml), and a catalytic amount of silver nitrate (0.02 mmol), was added dropwise a solution of sodium peroxodisulfate (2 mmol) in water (2 ml) at 0 °C. After stirring at 0 °C for 2 h, a small amount of silver oxide was filtered off and the filtrate was extracted repeatedly with ether. The ethereal extracts were subjected to gas chromatography.

Oxidation of **2** with sodium peroxodisulfate was carried out without acetone as a co-solvent in a similar way to that above.

*Oxidation of **1** with Lead Tetraacetate*: To a stirred solution of **1** (1 mmol) in dry benzene (15 ml) was added lead tetraacetate (1 mmol) in a nitrogen atmosphere. After stirring at room temperature for 1 h, the precipitated lead acetate was filtered off. The filtrate of benzene was washed with 1 M NaOH, dried over Na_2SO_4, and then filtered. The filtrate was subjected to gas chromatography.

Oxidation of Piperidine with Lead Tetraacetate: Piperidine was oxidized in a similar way to that above. Analysis of the product, 1,1′-bipiperidine, was carried out in a similar manner to that described previously.[9]

This work was supported by a grant from the Kawakami Memorial Foundation.

References

1) Part 3: T. Fuchigami, T. Iwaoka, T. Nonaka, and T. Sekine, *Chem. Lett.*, **1978**, 1437.

2) a) V. D. Parker, "Organic Electrochemistry," ed by M. M. Baizer, Marcel Dekker, Inc., New York (1973), p. 315; b) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York (1970), p. 259.

3) S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, **114**, 1025 (1967).

4) A. G. Hudson, A. E. Pedler, and J. C. Tatlow, *Tetrahedron Lett.*, **1968**, 2143.

5) G. Cauquis, J. P. Cognard, and D. Serve, *Tetrahedron Lett.*, **1971**, 4645.

6) G. Cauquis, J. P. Coquand, and J. Rigaudy, *C. R. Acad. Sci., Paris, Ser. C*, **268**, 2265 (1969).

7) A. U. Blackham, S. Kwah, and J. L. Palmer, *J. Electrochem. Soc.*, **122**, 1081 (1975).

8) R. Bauer and H. Wendt, *Angew. Chem.*, **90**, 214 (1978).

9) T. Fuchigami, T. Toki, T. Iwaoka, and T. Nonaka, *J. Electrochem. Soc. Jpn.*, **47**, 627 (1979).

10) Y. Nomura, K. Ogawa, Y. Takeuchi, and S. Tomoda, *Chem. Lett.*, **1978**, 271.

11) D. S. Kemp, J. P. Chabala, and S. A. Marson, *Tetrahedron Lett.*, **1978**, 543.

12) N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *Can. J. Chem.*, **47**, 3729 (1969).

13) N. A. Hampson, J. B. Lee, J. R. Morley, K. I. MacDonald, and B. Scanlon, *Tetrahedron*, **26**, 1109 (1970).

14) N. A. Hampson, J. B. Lee, and K. I. MacDonald, *Electrochim. Acta*, **17**, 921 (1972).

15) B. Fleishmann, K. Korinek, and D. Pletcher, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1396.

16) S. F. Nelsen and P. J. Hinz, *J. Am. Chem. Soc.*, **94**, 7108 (1972).

17) R. Daniels and B. D. Martin, *J. Org. Chem.*, **27**, 178 (1962).

18) H. H. Hatt, *Org. Synth.*, Coll. Vol. II, 208.