ELECTROCHEMICAL OXIDATION OF 3,3,7,7-TETRAETHYL-PERHYDRO-1,5-DIAZOCINE[1]

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The electrochemical oxidation of 3,3,7,7-tetraethyl-perhydro-1,5-diazocine (I) was investigated at platinum, carbon, nickel, and silver anodes. The former three electrodes gave 3,3,7,7-tetraethyl-1,5-diazabicyclo[3,3,0]octane (II) and 1-(2-ethyl-2-formylbutyl)-4,4-diethyl-4,5-dihydropyrazole (III) in approximately the same yields, while the latter one gave (III) solely.

While electrooxidative N,N-coupling of aromatic amines to the corresponding hydrazines or azo compounds has been performed,[2] that of aliphatic amines has not been reported except for the formation of azo-t-butane from t-butylamine as reported by Blackham et al.[3] Such difficulty in oxidative hydrazine formation from aliphatic amines by the intermolecular N,N-coupling is supposed to be attributable to instability of nitrogen radical intermediates.

In view of the above consideration, we have investigated the intramolecular N,N-coupling by electrochemical oxidation of a cyclic diamine such as (I).

1,5-Diazocine (I) was prepared by reduction of tetraethyltetron with diborane according to the method of Kemp et al.[4]

Electrolyses of (I) were carried out at a constant potential as follows. An H-type cell devided with a sintered glass diaphragm, and platinum, carbon, nickel, and silver plates (2x4 cm) were used as an anode. A platinum anode was treated with conc. nitric acid and the others were carefully polished with an emery paper No. 3000 before electrolysis. The anolyte is 50 ml of 0.1 M Et_4NOTs acetonitrile solution suspending lithium hydroxide powder. To the anolyte was added 1 mmol of (I) and then a current was supplied. The electricity passed was adjusted to about 0.8 F/mol in order to investigate the effect of electrolytic conditions on the yields of products.

After the electrolysis, the anolyte was acidified with hydrochloric acid and acetonitrile

was evaporated under reduced pressure, and then the residual aqueous solution was made strongly

alkaline with sodium hydroxide.   The alkaline solution was extracted repeatedly with ether and

the ethereal extracts were subjected to gas chromatographic analysis (column packing, PEG 20M;

column temperature, 186°C).

Two compounds were detected and one is identified as 3,3,7,7-tetraethyl-1,5-diazabicyclo-

[3,3,0]octane (II) by comparison of the mass fragmentation[5] and the retention time with those

of the independently synthesized authentic sample.[4]   The other one, which could be isolated by

column chromatography on alumina with dichloromethane, was 1-(2-ethyl-2-formylbutyl)-4,4-di-

ethyl-4,5-dihydropyrazole (III).   Its structure was confirmed by means of elemental analysis

(Found: C, 70.44; H, 11.35; N, 11.17%.   Calcd for $C_{14}H_{26}N_2O$: C, 70.54; H, 11.00; N, 11.75%) and

spectral studies.

In the IR spectrum, the characteristic strong absorption of a carbonyl group was observed

at 1740 cm^{-1} and N-H absorption was absent.   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

and other signals supported the structure of (III): δ 0.80 (3H, triplet, ^{d}H,^{f}H), 0.82 (3H, triplet,

^{j}H,^{l}H), 1.50 (8H, multiplet, ^{c}H,^{e}H,^{i}H,^{k}H), 2.78 (2H, singlet, ^{b}H), 2.96 (2H, singlet, ^{g}H), 6.24

(1H, singlet, ^{a}H).   In the mass spectrum, the molecular ion (M^+ 238) was observed together with

the appropriate fragment peaks such as m/e 209 (M^+-CHO and/or M^+-Et) and 139 (M^+-Et_2CCHO).

The compound, (III) thus isolated is neutral colorless oily material and shows positive

Tollen's test.   Such a 1-substituted dihydropyrazole derivative has never been known.

The electrolytic results are summarized in Table.

As shown in the Table, N,N-coupling products were expectedly formed and their current

efficiencies are generally good.

In the case of a platinum anode, both (II) and (III) were formed in approximately the same

yields.   A change in the anode potential resulted no appreciable change in the product yields.

However, the total yield increased slightly in the electrolysis at lower temperatures.   In the

absence of lithium hydroxide, the yield of (II) was reduced to about one half, while that of (III)

increased.   However, the reason has not been clarified yet.   In the presence of 10 equivarents

of lithium hydroxide, about 2F/mol of electricity was consumed and the ratio of (III)/(II) was

doubled.   This observation suggested that the more the electricity passed the higher the yield

of (III).   Carbon and nickel anodes gave (II) in a slightly higher yield than (III).

It is noticeable that the electrochemical oxidation of (I) proceeded at relatively low

potentials in the cases of carbon and silver anodes and also the latter anode gave (III) solely

even though the current efficiency was relatively low.[6]   Reasonable explanations for these facts

Table. Results for The Electrochemical Oxidation of 3,3,7,7-Tetraethyl-perhydro-1,5-diazocine (I)

Run	Anode material	Anode potential (V vs. SCE)	Temp ($^{\circ}$C)	Molar ratio of LiOH/(I)	Amount of electricity (F/mol)	Yields of products (Current efficiency %)		Recovery of (I) (%)
						(II)	(III)	
1	Pt	0.8	25	2	0.80	9 (23)	7 (53)	75
2	Pt	1.1	25	2	0.80	7 (18)	8 (60)	83
3	Pt	1.5	25	2	0.80	8 (20)	6 (45)	80
4	Pt	1.1	3	2	0.86	10 (23)	11 (76)	62
5	Pt	1.1	-12	2	0.76	9 (24)	9 (71)	56
6	Pt	1.1	25	0	0.80	4 (10)	10 (75)	89
7	Pt	1.1	25	10	1.88	12 (13)	21 (67)	40
8*	Pt	1.1	25	2	0.82	57**	13 (63)	-
9	C	0.3	25	2	0.94	14 (30)	10 (64)	51
10	Ni	0.7	25	2	0.86	12 (28)	8 (56)	69
11	Ag	0.3	25	2	0.98	trace	11 (67)	66

* Electrolysis of (II).   ** Recovery of (II).

Scheme 1.
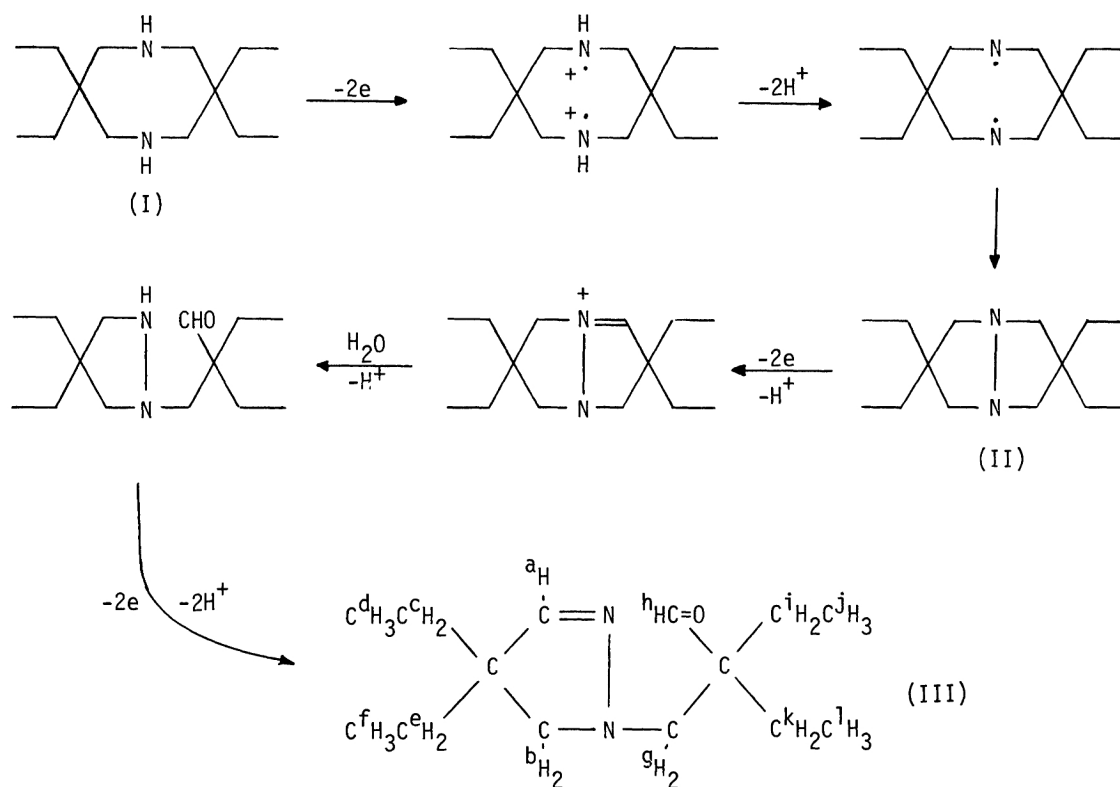
can not be shown in the present.   However, in the case of a silver anode, the initial electro-
chemical reaction generates an oxide coating on the electrode surface, and this electrochemically
generated oxide then seems to effect the oxidation of (I).   The low current efficiency of (III)
in the case of a silver anode may be attributable to such formation of silver oxide because the
corrosion of the silver anode surface was observed in the course of the electrolysis.

Since (II) can be oxidized at a lower potential than (I)[10] and (III) was also found to be
formed by electrochemical oxidation of (II), (III) seems to be formed by further oxidation of (II)
produced in the course of the electrochemical oxidation of (I).

The formation of (II) and (III) might proceed as in Scheme 1.

References and Notes

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5) The mass spectrum of (II) was measured by a gas chromatograph-mass spectrometer.

6) Hampson et al.[7-9] also found that platinum and silver anodes give different products in the

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10) Such bicyclic diamines are known to have extremely low oxidation potentials.[11]

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