# Electrochemical Oxidation of Aromatic Enediamines. A Unique Example of Anodic Double Cyclisation to an Indolo-oxazolidine

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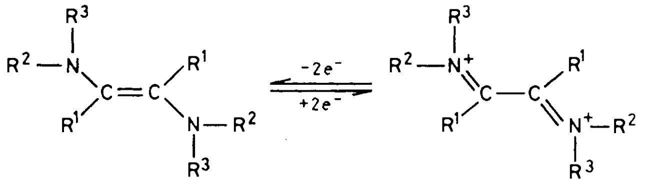
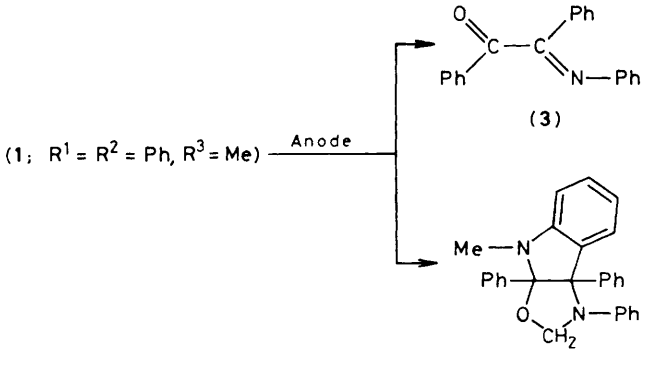
The anodic oxidation of enediamines leads to an unexpected cyclisation involving solvent moisture to give an indolo-oxazolidine in a good yield.

The anodic oxidations of enamines[1] and also enediamines[2,3] are two-electron processes. At a platinum microelectrode iminium and di-iminium salts are obtained respectively. For oxidation of the symmetrical enediamines (**1**) ($R^1$, $R^2$, $R^3 \neq H$), cyclic voltammetry showed a fully reversible anodic process. The nature of $R^1$, $R^2$, and $R^3$ may favour[1] either two reversible one-electron steps or one two-electron step. For example, *trans*-(**1**) ($R^1 = R^2 = Ph$, $R^3 = Me$) was oxidised in a two-electron reversible step in a 0.1 M acetonitrile–$KPF_6$ solution at 0.48 V [*vs.* aqueous saturated calomel electrode (S.C.E.)] at a platinum anode.



(1) *cis* or *trans* (2)

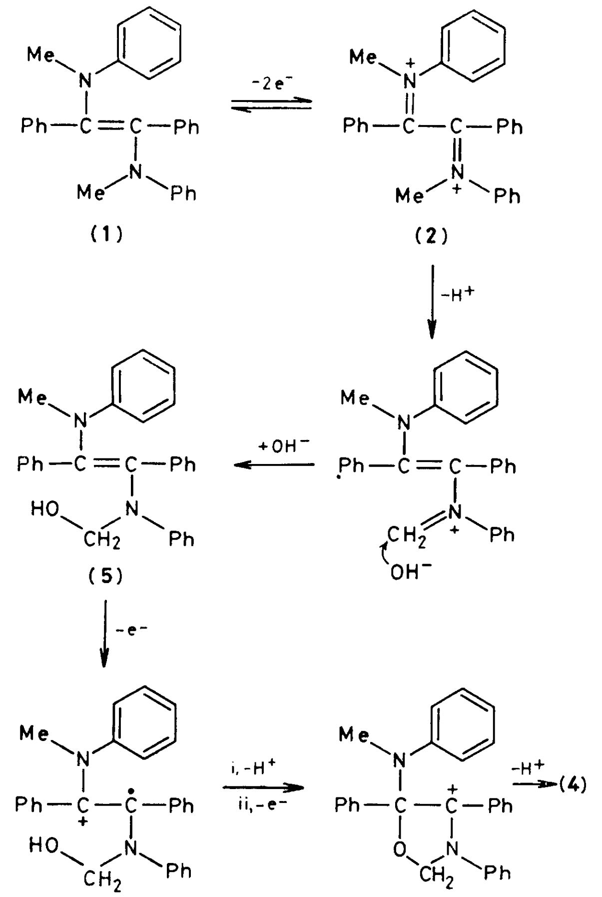
The di-iminium salts (**2**) however, are rather unstable and microcoulometric measurements indicated that the yield of (**2**) in solution could not be higher than 15% and negligible after two or three hours. New anodic peaks appeared in the voltammetry; these were located at more oxidizing potentials



(3)

(4)

and all were irreversible. Macroscale electrolyses (in 0.3 M acetonitrile–$LiClO_4$)† led to two products (3) and (4)‡ the yields of which depended on the nature of the base ($K_2CO_3$ or 2,6-lutidine) present in the anode electrolyte.§



**Scheme 1**

The formation of (3) and (4) occurs *via* attack of solvent moisture either on the central C–C bond or on the methyl ($R^3$) group of the intermediate carbocations. Scheme 1 shows the pathway to the unexpected formation of (4).

Although (5) was not isolated, its formation from (1) would be expected from typical decompositions of iminium salts (*e.g.*, see ref. 6). The intermediate (5), which is readily oxidized at the fixed potential used for the electrolysis of (1), could react further at the anode in a *double* cyclisation. The indolo-oxazolidine (4) was oxidised at 0.9 V and was rather unstable in the electrolysis solution in the presence of $K_2CO_3$ as base; the deep green colour of the solution was due to the chemical degradation of (4); however, in the presence of 2,6-lutidine, (4) appeared to be quite stable and gave a better yield.

The authors thank the centre of diffractometry of the University of Rennes 1 and Dr. L. Toupet for assistance in the determination of structure (4).

*Received, 25th March 1983; Com. 391*

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† Hydrogen cell with G3 frit as separator; platinum anode, $A$ = 16 cm$^2$; graphite rod cathode; applied potential 0.40 V *vs.* S.C.E.; concentration of (1) 4 mM.

‡ (3), m.p. 106—107 °C [lit. (ref. 4), m.p. 103—106 °C]; (4) [structure determined (ref. 5) by an *X*-ray analysis] colourless crystals, m.p. 182 °C (ethanol), $C_{28}H_{24}N_2O$, established by mass spectroscopy; $^1H$ n.m.r. ($CDCl_3$) $\delta$ 2.73 (s, 3H, NMe), 5.04 and 5.56 (2 × d, $^2J$ 2 Hz, 2H, $CH_2$), 6.40—6.70 (m, 3H, aromatic), and 7.00 (br. s, 16H, aromatic); $^{13}C$ n.m.r. ($CDCl_3$) includes $\delta$ 28.85 (q, $NCH_3$) and 80.37 p.p.m. (t, $J_{C-H}$ 155 Hz, $CH_2$).

§ In the presence of $K_2CO_3$ (1.5 g), the electrolyses consumed 3.5 F mol$^{-1}$ and the isolated yields were 56 and 13% for (3) and (4) respectively; when 2,6-lutidine (20 mM) was used as a base, the consumption of electricity was 3.8 F mol$^{-1}$ and the isolated yields were 26% for (3) and 59% for (4).