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REDUCTIVE RING OPENING OF N-ACYLAZIRIDINES : DIFFERENT OUTCOMES OF CHEMICAL AND ELECTROCHEMICAL REACTIONS

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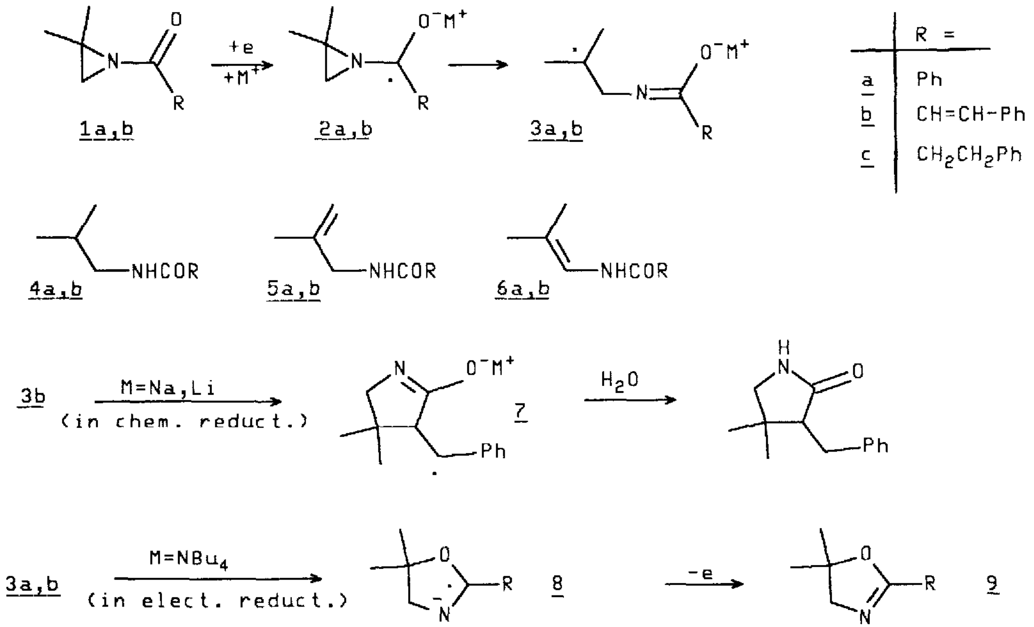
Summary : Main products from electrochemical reduction of two N-acylaziridines are the corresponding oxazolines which are not formed in chemical reduction, probably due to a coordination of the oxygen with a metal counter-ion.

Prompted by ring opening at the more hindered carbon, Stamm *et al.*[1] proposed that the nucleophilic ring opening of (1) may proceed *via* single electron transfer (S.E.T.) to form the ketyl (2) that rapidly homolyses to (3). When (3) (M=Na, Li) could not combine with another radical, it was found to undergo reduction (4), disproportionation (4, 5, 6) or cyclization (3b ---> 7)[2, 3] (Scheme I).



Scheme I

In this paper, we present the subsequent finding : cathodic reduction (Hg pool, THF, $^{+}NBU_4ClO_4^{-}$=0.5 M) of (1a,b)[4] mainly gives oxazolines (9) together with some amounts of (4, 5 and 6). No pyrrolidone (formed *via* 7) could be detected in the runs with (1b). The percentage of isolated products is given in Scheme II.

1a $\xrightarrow{-2.4\text{ V ; }0.98\text{F/mol}}$ 31% 9a + 18% 4a + 14% 5a + 2% 6a

1b $\xrightarrow{-2.2\text{ V ; }0.94\text{F/mol}}$ 25% 9b + 25% 9c + 2% 4b + 3% 6b

1b $\xrightarrow{-2.2\text{ V ; }0.4\text{F/mol}}$ 42% 9b + (32% 1b have not reacted)

Scheme II

Formation of (9) should be electrocatalytic, since step (8 ---> 9) may provide the electron for step (1 ---> 2). Cyclic voltammetry (sweep rate 10 mV/s, 21°C) shows that the reduction of (9a,b) is reversible with peak potentials that suggest a S.E.T from (8) to (1) : E_{pc} = -3.00 V and E_{pa} = -2.75 V for (9a), E_{pc} = -2.50 V and -2.90 V and E_{pa} = -2.25 V for (9b). (9c) is formed by a subsequent reduction of the carbon-carbon double bond of (9b) as is shown by a comparison of the two runs with (1b).

The different behaviour of radicals (3a,b) in chemical and cathodic reduction may be explained in the following way : in cathodic reduction ($M^{+}=N^{+}Bu_4$), the radical center can attack the oxygen and thus easily form the radical anion (8). Cyclizations by radical addition to a carbonyl oxygen are found in the literature[5]. In chemical reduction this process may be prevented by the coordinated counter-ion ($M^{+}=Na^{+}$, Li^{+})[6].

REFERENCES AND NOTES

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4 Cyclic voltammetry : E_p (Ag/Ag^{+}) : -2.5 V for (1a) and 2.2 V (-2.6 V second peak) for (1b).

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6 A referee suggested a base catalyzed chain process from (1) to (9). This alternative is excluded by the following independent reaction : N-acyl 2,2-dimethylaziridines react with potassium hydride (14h, Δ/THF). After hydrolysis by D_2O, no incorporation of deuterium in the ring was observed ; it was only observed on the α carbon of the ketyl group. The alternative process will provide a disfavoured 5 *endo*-trig cyclization.

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