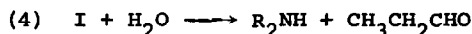# THE MECHANISM OF ANODIC DEALKYLATION OF ALIPHATIC AMINES IN ACETONITRILE
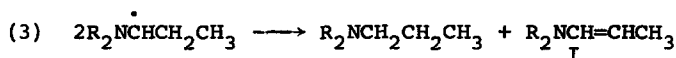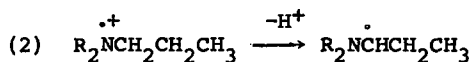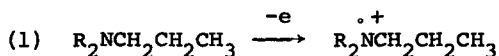
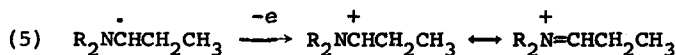Sidney D. Ross
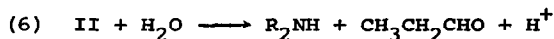Sprague Research and Development Center, North Adams, Massachusetts

In acetonitrile containing water aliphatic amines are smoothly dealky-lated electrochemically at platinum to give an amine of lower order and an alde-hyde. When the oxidation of either tri-n-propylamine or di-n-propylamine was carried out in rigorously dried acetonitrile containing deuterium oxide at a concentration five times greater than the initial amine concentration, the alde-hyde obtained was α-deuteriopropionaldehyde. Mann[1] has proposed the following mechanism, (1) – (4), for this reaction.

$$(1) \quad R_2NCH_2CH_2CH_3 \xrightarrow{-e} R_2\overset{\cdot}{\underset{}{N}}{}^{+}CH_2CH_2CH_3$$

$$(2) \quad R_2\overset{\cdot}{\underset{}{N}}{}^{+}CH_2CH_2CH_3 \xrightarrow{-H^+} R_2\overset{\cdot}{N}CHCH_2CH_3$$

$$(3) \quad 2R_2\overset{\cdot}{N}CHCH_2CH_3 \longrightarrow R_2NCH_2CH_2CH_3 + \underset{I}{R_2NCH{=}CHCH_3}$$

$$(4) \quad I + H_2O \longrightarrow R_2NH + CH_3CH_2CHO$$

Mann recognized that reactions (5) and (6) were possible in this system, but argued that the iminium ion, II, would give undeuterated aldehyde on

$$(5) \quad R_2\overset{\cdot}{N}CHCH_2CH_3 \xrightarrow{-e} R_2\overset{+}{N}CHCH_2CH_3 \longleftrightarrow \underset{II}{R_2\overset{+}{N}{=}CHCH_2CH_3}$$

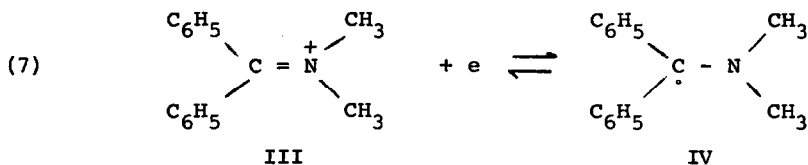$$(6) \quad II + H_2O \longrightarrow R_2NH + CH_3CH_2CHO + H^+$$

hydrolysis and that the enamine, I, was the essential intermediate, which alone could give α-deuteriopropionaldehyde on hydrolysis. He, therefore, concluded that reaction (5), even if possible, was much slower than reaction (3).

Since both benzyldimethylamine and dibenzylmethylamine, where enamine formation is not possible, dealkylate to give benzaldehyde, the mechanism involving generation and hydrolysis of the iminium ion must be operable in other systems, even if it is unfavorable in the case of the n-propylamines. In fact, Andrieux and Saveant[2] have fully documented the formation of the cation, III, in acetonitrile at platinum. Cyclic voltammetry of the benzhydryldimethylamine at a sweep rate of 10 Vsec^{-1} shows an irreversible anodic wave and a reversible wave at a cathodic potential corresponding to reduction of III to the blue-violet radical, IV, according to (7).

$$(7) \quad \begin{array}{c} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{array} C \overset{+}{=} N \begin{array}{c} \diagup CH_3 \\ \diagdown \\ CH_3 \end{array} + e \;\rightleftharpoons\; \begin{array}{c} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{array} \overset{\cdot}{C} - N \begin{array}{c} \diagup CH_3 \\ \diagdown \\ CH_3 \end{array}$$

$$\qquad\qquad\qquad III \qquad\qquad\qquad\qquad\qquad IV$$

Mann also recognized that in basic solution II would be expected to be in equilibrium with I according to (8). The proton transfer shown in (8) is not only a more probable route to the enamine, I, but perhaps the only possible route,
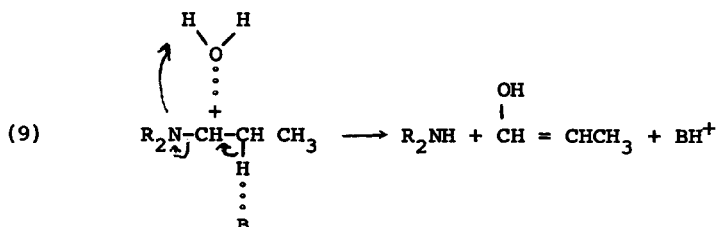
$$(8) \qquad II + B \rightleftharpoons I + BH^+$$
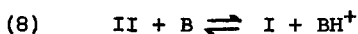
since Cohen[3] has shown that the amine radical intermediates in the photoreduction of aromatic ketones do not disproportionate. Thus, photoreduction by optically active 2-butylamine and N,N-dimethyl-2-butylamine leads to no racemization in the recovered amine. However, if the equilibrium represented by (8) is attained in the presence of a large excess of deuterium oxide, II would be dideuterated and I would be monodeuterated, and both, on hydrolysis, would give α,α-dideuterio-propionaldehyde rather than the observed α-monodeuteriopropionaldehyde.

Di-n-propylamine is oxidized at +0.92 V and tri-n-propylamine at +0.64 V, both vs. Ag/Ag$^+$ (0.1 M).[4] Polarographic data are not available for the

simple enamines, but reported half-wave potentials[5,6] for enediamines suggest that the enamines of present concern will be oxidized at significantly lower potentials than the saturated amines. 1,2-Bis(dimethylamino)ethylene, for example, is oxidized in acetonitrile at a half-wave potential of -0.31 V vs. SCE.[6]

Mann has also argued that the forward reaction of (8) cannot be the source of the enamine, since the enamine would be the strongest base in the system and would end up as a final product in its protonated form. If, indeed, the enamine is the strongest base present and available in significant concentration, it will also be the proton acceptor in (2). The available experimental facts, therefore, require a mechanism in which the enamine is either absent or present in a concentration too trivial to be effective in proton abstraction.

A mechanism involving the reaction sequence, (1), (2), (5), (8) and (4), with (4) rapid compared to the forward reaction of (8), meets this requirement, but is highly improbable. It is a better possibility that hydrolysis of II is a concerted, base-catalyzed reaction, as shown in (9), giving propionaldehyde in the enolic form as the hydrolysis product. Reaction (9) can also proceed in

(9)

$$R_2N-CH-CH\ CH_3 \longrightarrow R_2NH + CH = CHCH_3 + BH^+$$

(with structure showing $H\ H$ on O, and H on B, and OH on product)

two steps, reaction of II with water to form the carbinolamine followed by elimination of amine to afford the enol. In either case, the result is cleavage of the C-N bond and formation of the enol. The reaction sequence is (1), (2), (5) followed by (9). This would result in the monodeuterio-aldehyde, and the enamine would not be a discrete intermediate.

References

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4. C. K. Mann, Anal. Chem., 36, 2424 (1964).

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