

## ***N*-Cyanomethylation of 2,2,6,6-Tetramethylpiperidines by Anodic Oxidation in Acetonitrile**

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Anodic oxidation of 2,2,6,6-tetramethylpiperidine and its 4-oxo-derivative in deoxygenated acetonitrile resulted in the formation of *N*-cyanomethylated products.

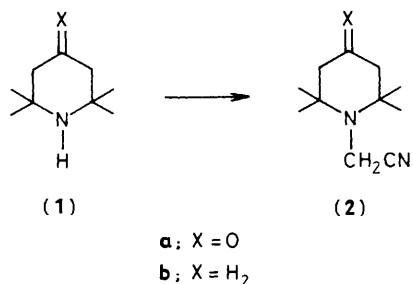
Many papers have reported the anodic addition of acetonitrile to organic compounds, but all of them are concerned with acetamidation *via* nucleophilic attack of the nitrogen atom of acetonitrile on the electrogenerated carbocation and the subsequent reaction with water.<sup>1</sup> The only exception is the reaction reported by Mann and co-workers yielding an *N*-formylated product from 8-azabicyclo[3.2.1]octane,<sup>2</sup> in which they assumed an *N*-cyanomethylated intermediate. Unfortunately, however, they did not detect the intermediate in the electrolysis solution.

In the anodic oxidation of simple aliphatic amines possessing  $\alpha$ -hydrogen atoms in aqueous solution or in wet acetonitrile, oxidative dealkylation is the generally observed pathway,<sup>3</sup> although examples of inter- or intra-molecular N-N coupling<sup>2,4,5</sup> and intramolecular N-C bond formation<sup>5</sup> have

been reported. Generation of relatively stable radical cations has been demonstrated for bicyclic amines in which deprotonation of the  $\alpha$ -carbon is prevented by stabilisation according to Bredt's rule.<sup>6</sup> As a continuation of our studies on the anodic oxidation of aliphatic amines, we have investigated the oxidation of the title amines (**1**), which lack  $\alpha$ -hydrogen atoms, and have isolated the cyanomethylated products (**2**).

As far as we are aware, this is the first unambiguous evidence of participation of acetonitrile at its carbon atom in the anodic oxidation of organic compounds, though cyanomethylation with a cathodically generated cyanomethyl anion has been reported.<sup>7</sup>

Cyclic voltammetry (c.v.) in deoxygenated acetonitrile (0.1 M NaClO<sub>4</sub>) of (**1**) showed three irreversible anodic peaks: 1.19, 1.35, and 1.57 V vs. saturated calomel electrode (s.c.e.)



for (**1a**); 0.99, 1.19, and 1.5 V for (**1b**) (glassy carbon anode, 25 °C, voltage sweep rate, 17 mV s<sup>-1</sup>). The second anodic peak is assigned to the oxidation of (**2**) formed at the electrode. Controlled potential electrolysis of (**1a**) (1.03 mmol) in acetonitrile (50 ml) containing 0.1 M NaClO<sub>4</sub> and suspended K<sub>2</sub>CO<sub>3</sub> (0.3 g) at 1.25 V under an N<sub>2</sub> atmosphere (H-type divided cell; glassy carbon anode and Pt foil cathode) terminated by consuming *ca.* 2 F per mol of the substrate (6.5 h). Work-up of the electrolysis solution [evaporation of the solvent, extraction with chloroform, and preparative thin layer chromatography on silica gel (AcOEt–hexane, 1:3)] gave (**2a**)<sup>†</sup> (132 mg, 68%) and (**1a**) (19 mg, 12%). Electrolysis of (**1b**) similarly afforded (**2b**)<sup>†</sup> but in a lower yield (20%).

Although the products (**2**) are likely to be formed *via* coupling of the radical cation >NH<sup>•+</sup> or the radical >N<sup>•</sup> derived from (**1**) with the cyanomethylene radical, <sup>•</sup>CH<sub>2</sub>CN, at present it is not clear which species abstracts a hydrogen atom from the solvent to give <sup>•</sup>CH<sub>2</sub>CN. The radicals >NH<sup>•+</sup> and >N<sup>•</sup> and the nitrenium ion >N<sup>+</sup>, formed by further oxidation of >N<sup>•</sup> are all possibilities. Reaction of H<sub>2</sub>O with any of >NH<sup>•+</sup>, >N<sup>•</sup>, or >N<sup>+</sup> would give rise to the hydroxyl radical which could then interact with the solvent to give <sup>•</sup>CH<sub>2</sub>CN. The hydroxyl radical is unlikely to be generated by direct electron transfer from the hydroxide ion,<sup>2</sup> because the water content in the medium is small and the suspended K<sub>2</sub>CO<sub>3</sub> is a weak base. C. v. of the solution without the starting amine (**1**) did not show a discernible anodic wave

<sup>†</sup> The products (**2a**) (colourless needles, m.p. 108–109 °C) and (**2b**) (colourless needles, m.p. 35–36 °C) gave the expected analytical results. (**2a**) N.m.r. (CDCl<sub>3</sub>) δ: 1.28 (12H, s), 2.44 (4H, s), 3.65 (2H, s). I.r. (KBr): 2200 (CN), 1710 cm<sup>-1</sup> (CO). *m/z*: 194 (*M*<sup>+</sup>). (**2b**) N.m.r. (CDCl<sub>3</sub>) δ: 1.12 (12H, br.s), 1.50 (6H, br.s), 3.48 (2H, s). I.r. (neat): 2170 cm<sup>-1</sup> (CN). *m/z*: 180 (*M*<sup>+</sup>).

below 1.5 V. This presumption is also supported by the observation that electrolysis of (**1b**) in an undivided cell without K<sub>2</sub>CO<sub>3</sub> gave (**2b**) in 66% yield. Under these conditions the possibility of water contamination is smaller than in electrolysis with a divided cell.

Another plausible route to (**2**) is the reaction of the nitrenium ion with the solvent *via* a mechanism similar to that reported for the nitrenium ion generated from *N*-chloroazacyclononane and a silver ion,<sup>8</sup> where hydride transfer from carbon to nitrogen is suggested. In the present case, however, hydride transfer would be from a carbon atom adjacent to a strong electron withdrawing group, the α-carbon atom of acetonitrile, and therefore seems unlikely.

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