

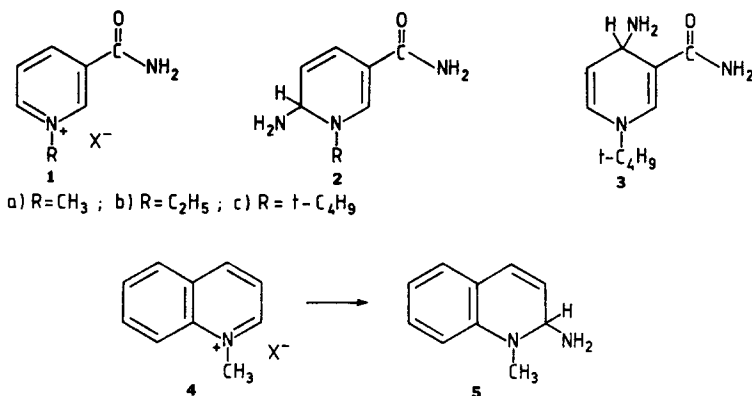
IMINATION OF PYRIDINIUM AND QUINOLINIUM SALTS

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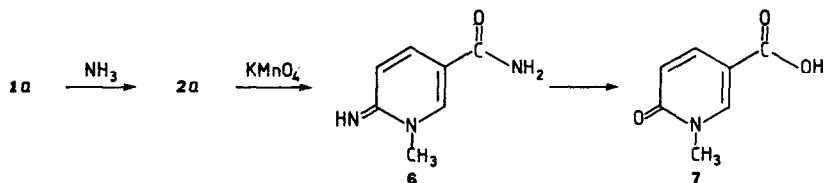
Abstract: A new method for imination of N-alkyl pyridinium- and quinolinium salts is described. It involves a low temperature oxidation of a solution of appropriate substrates in liquid ammonia with potassium permanganate.

It has recently been found¹ that 1-R-3-carbamoylpyridinium salts (1a-b) undergo covalent amination into the corresponding σ -adducts 6-amino-3-carbamoyl-1,6-dihydropyridines (2a-b), when dissolved in liquid ammonia. The 1-t-butyl derivative (1c) gives besides the 1-6 adduct 2c, the 4-amino-3-carbamoyl-1,6-dihydropyrimidine (3) ratio 2c:3 is 6:4. Analogously, the 1-methylquinolinium salt (4) gives with liquid ammonia 2-amino-1,2-dihydro-1-methylquinoline (5).

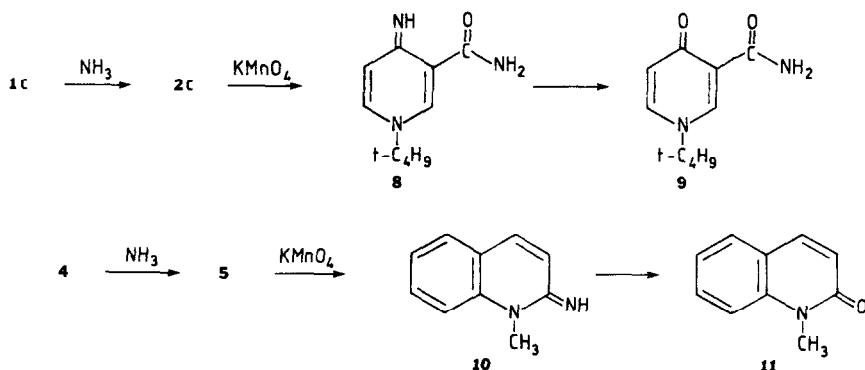


In this paper we wish to report that treatment of a solution of 1a in liquid ammonia with potassium permanganate² gives a compound, which structure was proved to be 3-carbamoyl-1,6-dihydro-6-imino-1-methylpyridine (6), yield 75-80%; ¹H-NMR (D₂O): H-2, δ 8.32 (d, J_{2,4} = 2.0-2.2 Hz); H-4 δ 8.00 (dd, J_{2,4} = 2.0-2.2 Hz, J_{4,5} = 9.0 Hz); H-5 δ 7.00 (d, J_{4,5} = 9.0 Hz); CH₃ δ 3.87 (s), mass spectrum (exact mass observed 151.0748, calc. for C₇H₉N₃O: 151.0746). Especially the doublet structure of H-5 and the magnitude of its coupling constant (J_{4,5} = 9 Hz) are of diagnostic value for the structure assignment³. This structure assignment was confirmed by conversion of 6 into the known compound 1-methyl-1,6-dihydro-6-oxo-pyridine-3-carboxylic acid (7) by prolonged alkaline treatment and subsequent acidification⁴.

It is very likely that the formation of 6 occurs by dehydrogenation of intermediate 2a. Interestingly enough, treatment of a solution of the 1-t-butyl derivative 1c in liquid ammonia with potassium permanganate gave as main product 3-carbamoyl-1,4-dihydro-4-imino-1-t-butylpyridine (8), yield about 60%; ¹H-NMR (CD₃OD): H-2 δ 8.77 (d, J_{2,6} = 1.8 Hz); H-5 δ 7.10



(d, $J_{5,6} = 7.5$ Hz); H-6 δ 8.49 (dd, $J_{5,6} = 7.5$ Hz, $J_{2,6} = 1.8$ Hz); t -C₄H₉, δ 1.72 (s). The magnitude of $J_{5,6} = 7.5$ Hz indicates³ that the imino group has been introduced at C-4. Compound 8 was converted by treatment with an alkaline solution into the corresponding 4-oxo compound 9. Mass spectrometry (exact mass observed 193.1220 calc. for C₁₀H₁₅N₃O: 193.1215).



In the imination of 1c no indication for the formation of the 2-imino compound was found, although, as we have noted before, 2c is also formed, when 1c is dissolved in liquid ammonia. Apparently the presence of the bulky t -butyl substituent on nitrogen, adjacent to the carbon at C-6, where the dehydrogenation has to take place, prevents or at least hampers the approach of the permanganate ion.

The occurrence of an oxidative imination in the α - or γ -position of the pyridinium ring could also be extended to the quinolinium ring system. Treatment of a solution of 4 in liquid ammonia with potassium permanganate gives 1,2-dihydro-2-imino-1-methylquinoline (10) ¹H-NMR (CD₃OD): H-3 δ 8.10 (d, $J_{3,4} = 8.4$ Hz; H-4 δ 7.03 (d, $J_{3,4} = 8.5$ Hz); H-5,6,7,8 δ 7.7 (m); CH₃ δ 3.80 (s). Mass spectrometry (exact mass observed 158.0846, calc. for C₁₀H₁₀N₂: 158.0844). Heating of 10 with an aqueous solution of potassium hydroxide gives N-methylquinolone-2 (11).

In conclusion it is shown that liquid ammonia/potassium permanganate is a very efficient reagent for the introduction of an imino group in N-alkylpyridinium and quinolinium salts. The procedure forms a useful extension of the method generally applied alkylation of aminopyridines or -quinolines.

References

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