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1,4-DIHYDRO-1-METHYLQUINOLINE

John W. Bunting and William G. Meathrel

Department of Chemistry, University of Toronto, Toronto 181, Ontario, Canada

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No successful preparations of 1,4-dihydroquinoline and its N-methyl derivative have been reported. In fact, few simply substituted 1,4-dihydroquinolines have been characterized. The least substituted compounds known in this series seem to be 1,4-dihydro-1-methyl-3-nitroquinoline (1), 1,2-dicyano-1,4-dihydroquinoline (2) and 4-cyano-1,4-dihydro-1-methylquinoline (2).

Reduction of the 1-methylquinolinium ion with lithium aluminium hydride yields mainly 1,2-dihydro-1-methylquinoline (3,4). Claims have been made for the formation of small amounts of the 1,4-dihydro-isomer in this reaction on the basis of indirect evidence; however, this compound was not isolated (3). The reduction of the 1-phenylpyridinium cation with lithium aluminium hydride has been shown to produce 1,2-dihydro-1-phenylpyridine, whereas the use of sodium amalgam in water as the reducing agent resulted in the formation of 1,4-dihydro-1-phenylpyridine (5). In an early study (6) of the reduction of the 1-ethylquinolinium cation with sodium amalgam, only tetrahydro derivatives and trimeric species were obtained. We have now studied the reduction of the N-methylquinolinium cation with sodium amalgam in aqueous solution, and wish to report the formation of 1,4-dihydro-1-methylquinoline in this reaction.

Freshly prepared 1.4% sodium amalgam (27 gm) was added to a solution of N-methylquinolinium iodide (1 gm) in water (50 ml). After 2 minutes, the solution was extracted with chloroform to remove the more highly saturated species (possibly trimeric (6)) that are formed in the early stages of the reaction. The reduction was then allowed to proceed in the aqueous solution for a further 15 minutes. The oil that had formed on the surface of the aqueous solution was extracted into chloroform. The p.m.r. spectrum of this oil (measured on a Varian T-60 spectrometer) is shown in Figure 1. Although there appears to be a small amount of impurity present (in the region δ 3 ppm), this spectrum is readily interpreted as that of 1,4-dihydro-1-methylquinoline. The peaks may be assigned as follows: δ 3.00 - N-CH_3 (singlet, 3H); δ 3.57 - H(4) (doublet, 2H, $J_{3,4}$ = 4 cps); δ 4.36 - 4.61 - H(3) (multiplet, 1H); δ 5.89 - H(2) (doublet with triplet fine structure, 1H, J_{23} = 8 and J_{24} = 1.6 cps); δ 6.57 - 7.2 - aromatic protons (multiplet, 4H). The coupling constants J_{23} and J_{34} are in good agreement with those reported by Bramley and Johnson (2) for several more highly substituted 1,4-dihydroquinolines (J_{23} = 8 ± 0.5 cps; J_{34} = 4.5 ± 1 cps). The chemical shifts for H(2), H(3) and H(4) are in good agreement with values that one would predict for protons in these chemical environments (δ 5.7, 4.9 and 3.4 respectively) (7).

For comparison with Figure 1, the p.m.r. spectrum of 1,2-dihydro-1-methylquinoline, prepared by the lithium aluminium hydride reduction of the N-methylquinolinium cation (3), is shown in Figure 2. The assignment of peaks in this spectrum is: δ 2.72 - N-CH_3 (singlet, 3H); δ 3.99 - H(2) (doublet of doublets, 2H, J_{23} = 4 and J_{24} = 1.8 cps); δ 5.50 - 5.78 - H(3) (multiplet, 1H, J_{23} = 4 and J_{34} = 10 cps); δ 6.1 - 7.2 - aromatic protons + H(4) (multiplet, 5H). These coupling constants and chemical shifts also agree quite closely with those predicted on the basis of the spectra of more highly substituted 1,2-dihydroquinolines (2).

1,4-Dihydro-1-methylquinoline is an unstable yellow oil (as is 1,2-dihydro-1-methylquinoline (3)) which we have not succeeded to date in freeing from the impurities which are responsible for the extraneous peaks in Figure 1. These impurities seem to be the decomposition products of 1,4-dihydro-1-methylquinoline, since the small peaks in the vicinity of δ 3 in Figure 1 increase in intensity with time ($t_{1/2} \sim$ 3 hours at room temperature), and the oil becomes dark red.

The mass spectrum has a molecular ion peak at 145 (the calculated molecular weight) and also a peak for the N-methylquinolinium ion at 144. The ultraviolet spectrum in chloroform has maxima at 254 and 303 mμ. This spectrum compares favourably with that of 4-cyano-1,4-dihydro-1-methylquinoline (2,8) in

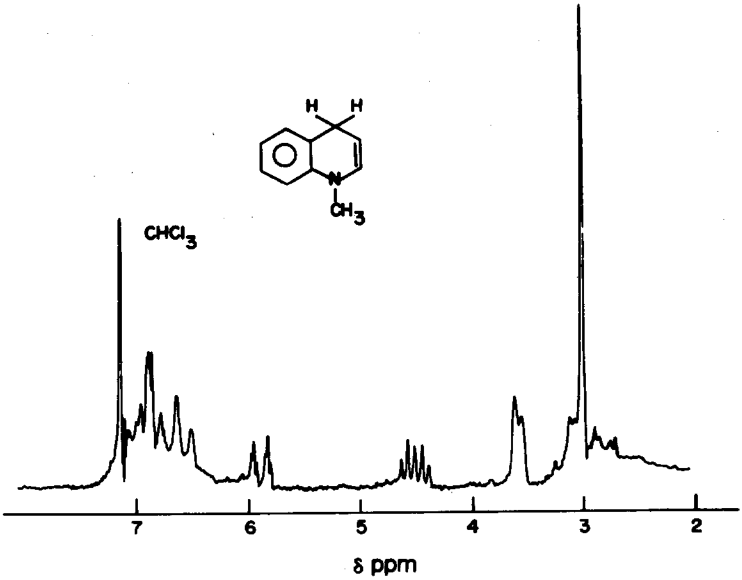

Figure 1. P.m.r. spectrum (60 Mc) of 1,4-dihydro-1-methylquinoline in $CDCl_3$ with tetramethylsilane as internal standard.

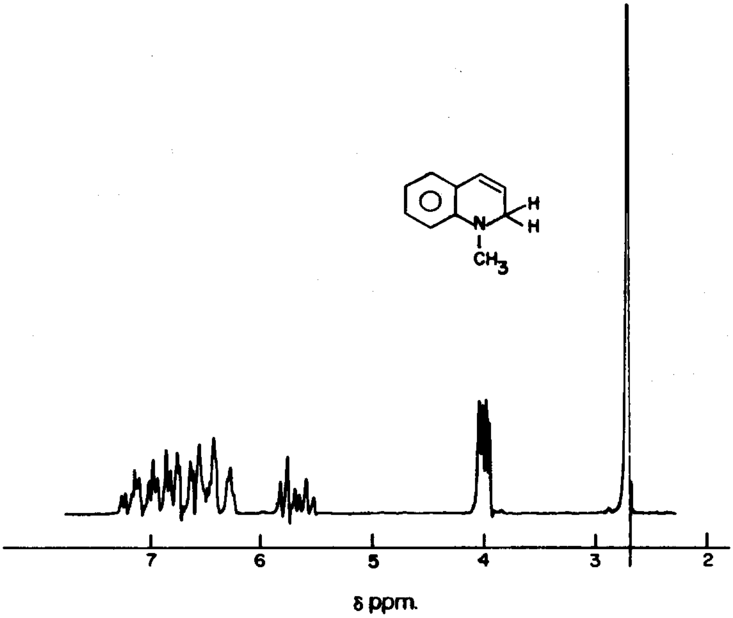

Figure 2. P.m.r. spectrum (60 Mc) of 1,2-dihydro-1-methylquinoline in $CDCl_3$ with tetramethylsilane as internal standard.

chloroform (λ_{max} = 303 mμ, inflexion at 250 mμ) and also with the spectra of a number of more highly substituted N-methyl-1,4-dihydroquinolines (λ_{max} = 312 mμ in 95% ethanol (9)). As expected, there is no absorption maximum in the vicinity of 345 mμ as is observed for 1,2-dihydroquinolines (3,4,10).

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