

1,4-DIHYDROQUINOLINE.<sup>1</sup>

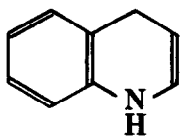
A.J. Birch and P.G. Lehman\*

Research School of Chemistry, Australian National University,

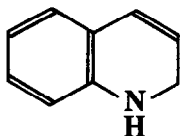
P.O. Box 4, Canberra, ACT 2600, Australia.

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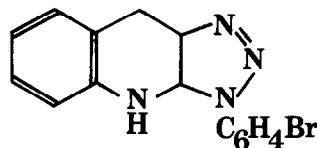
We wish to report the preparation and characterization of 1,4-dihydroquinoline [I], hitherto believed<sup>2</sup> to be unknown, although the isomeric compound, 1,2-dihydroquinoline [II], is already well documented.<sup>3</sup>



[I]



[II]



[III]

Recently we described<sup>4</sup> a new preparative method for 1-alkyl-1,4-dihydroquinolines, via reductive alkylation of the parent aza-aromatics. Since the mechanism<sup>4,5</sup> of this reaction involves a dianionic intermediate which is protonated by ammonia at C-4 to yield a stable nitranion, we anticipated that compound [I] should now also be accessible.

Treatment of quinoline with 2.0 equiv. of lithium in anhydrous ammonia at  $-33^{\circ}$ , followed by quenching with  $\text{NH}_4\text{Cl}$ , gave as the only observable product a solid<sup>6</sup>, which crystallized from ether/petroleum as plates, m.p.  $46-47^{\circ}$ . U.v. (EtOH)  $\lambda_{\text{max}}$  298 nm, c.f. 303 nm for the N-Me derivative of [I]<sup>4</sup> and 343 nm for [II]<sup>3</sup>. I.r. ( $\text{CH}_2\text{Cl}_2$ )  $3420\text{ cm}^{-1}$  (N-H) and  $1660\text{ cm}^{-1}$  (C=C), c.f.  $1660\text{ cm}^{-1}$  for the N-Me derivative of [I]<sup>4</sup>. P.m.r. (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.15-6.34, m (4H) aromatic; 5.99, m (1H) H-2; 5.13, br. s. (1H) N-H; 4.46, m (1H) H-3; 3.49, d (2H)  $J_{3,4}$  4Hz, H-4. Addition of  $\text{D}_2\text{O}$  eliminated the N-H resonance and simplified the multiplicities of H-2 and H-3, c.f. ref.<sup>4</sup>; H-2 d of t,  $J_{2,3}$  8Hz,  $J_{2,4}$  1.5Hz and H-3 quint.

The spectral data are consistent only with the heterocyclic enamine structure [I]. Furthermore, cycloaddition of p-bromophenyl azide, a typical enamine reaction, gave a

triazoline derivative, m.p. 151-152<sup>o</sup>, which from spectral and analytical evidence has the structure [III].

It has been claimed previously<sup>7</sup> that reduction of quinoline with sodium in ammonia at -65<sup>o</sup>, followed by NH<sub>4</sub>Cl, produces 1,2-dihydroquinoline [II]. Repetition of this experiment, with strict adherence to the published conditions, gave a compound, m.p. 46-47<sup>o</sup>, spectrally identical with ours. The m.p. of authentic<sup>3</sup> [II] is 72-74.5<sup>o</sup>.

We conclude that the earlier assignment<sup>7</sup> of structure [II] to the reduction product, which has frequently been cited without question, is unfounded and that reduction of quinoline with either lithium or sodium in ammonia produces only 1,4-dihydroquinoline [I].

#### References.

1. Part II in the series, Metal-Ammonia Reduction of Aromatic Nitrogen Heterocycles.
2. J.W. Bunting and W.G. Meathrel, *Tetrahedron Letters*, 133 (1971); J.A. Joule and G.F. Smith, "Heterocyclic Chemistry", Van Nostrand Reinhold, 1972, p.95.
3. W.S. Johnson and B.G. Buell, *J. Amer. Chem. Soc.*, 74, 4517 (1952); F. Bohlmann, *Chem. Ber.*, 85, 390 (1952); K.W. Rosenmund and F. Zymalkowski, *Chem. Ber.*, 86, 37 (1953); R.F. Collins, *J. Chem. Soc.*, 1954, 3641; W.P. Neumann, *Ann.*, 618, 90 (1958).
4. A.J. Birch and P.G. Lehman, *J.C.S. Perkin I*, 1973, 2754.
5. A.J. Birch and P.G. Lehman, part III, to be published.
6. All manipulations were carried out under dry N<sub>2</sub> in glassware prewashed with aq. alkali. The solid was unstable at r.t. but dilute ether solutions could be stored for 24 hr at -15<sup>o</sup>. Physical measurements utilized freshly isolated material.
7. W. Hückel and L. Hagedorn, *Chem. Ber.*, 90, 752 (1957).