

## Hydrogenation of 1,10-Phenanthroline

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### Abstract

Hydrogenation of 1,10-phenanthroline with Raney nickel catalyst affords 1,2,3,4-tetrahydro-1,10-phenanthroline and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline.

The recent report by Hensen and Trobs<sup>1</sup> of the chemical reduction of 1,10-phenanthroline to give 1,2,3,4-tetrahydro-1,10-phenanthroline (1) in low yield (10%) prompts us to record at this stage a much better method of preparing this compound by catalytic hydrogenation of 1,10-phenanthroline. There appears to be no other report of the reduction of 1,10-phenanthroline although the reduction of mono-quaternary<sup>2,3</sup> and diquaternary<sup>4</sup> salts of 1,10-phenanthroline has been described (cf.<sup>5</sup>). A reductive dehalogenation of substituted 1,10-phenanthrolines has also been noted.<sup>6,7</sup>

Catalytic hydrogenation of 1,10-phenanthroline with Raney nickel catalyst by a method similar to that adopted by Searles and Warren<sup>8</sup> for the reduction of 4,7-phenanthroline (2) afforded 1,2,3,4-tetrahydro-1,10-phenanthroline (1) in 80% yield when the hydrogenation was carried out at 58 lb/sq in pressure at 20° for 40 h. There was no evidence for the formation of the 5,6-dihydro derivative analogous to (3) although Searles and Warren<sup>8</sup> obtained both (4), in 40% yield, and (3), in 44% yield, from the similar reduction of 4,7-phenanthroline. The structure of (1) was confirmed by elementary analyses and n.m.r. spectroscopy and by characterization of the derived hydrobromide salt. Hensen and Trobs<sup>1</sup> did not analyse compound (1) but characterized it by way of the dihydrochloride salt and the picrate. The tetrahydro-1,10-phenanthroline (1) afforded 1-acetyl-1,2,3,4-tetrahydro-1,10-phenanthroline by

<sup>1</sup> Hensen, K., and Trobs, U., *Chem. Ber.*, 1974, **107**, 3176.

<sup>2</sup> Karrer, P., Pletscher, A., and Manz, W., *Helv. Chim. Acta*, 1947, **30**, 1146.

<sup>3</sup> Karrer, P., and Pletscher, A., *Helv. Chim. Acta*, 1948, **31**, 786.

<sup>4</sup> Summers, L. A., and Pickles, V. A., *Chem. Ind. (London)*, 1967, 619; Summers, L. A., *Nature*, 1967, **215**, 1410; Summers, L. A., *Tetrahedron*, 1968, **24**, 5433; Dickeson, J. E., and Summers, L. A., *J. Sci. Food Agr.*, 1969, **20**, 74; Popp, F. D., and Chesney, D. K., *J. Heterocycl. Chem.*, 1972, **9**, 1165.

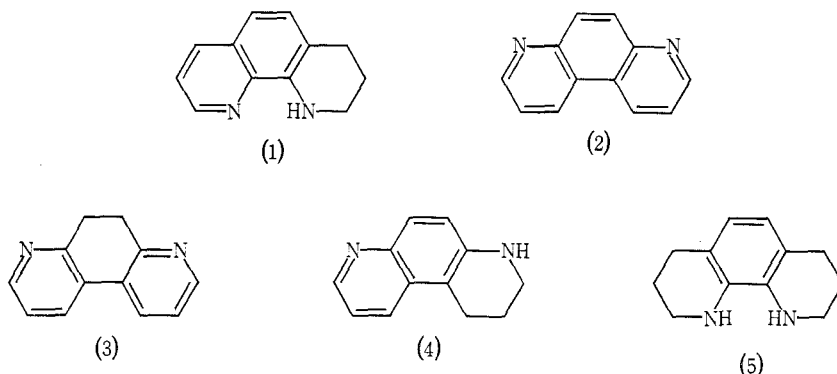
<sup>5</sup> Kermack, W. O., and McKail, J. E., in 'Heterocyclic Compounds' (Ed. R. C. Elderfield) Vol. 7, p. 344 (John Wiley: New York 1961).

<sup>6</sup> Dey, A. S., and Joullie, M. M., *J. Heterocycl. Chem.*, 1965, **2**, 120.

<sup>7</sup> Nyquist, E. B., and Joullie, M. M., *J. Heterocycl. Chem.*, 1967, **4**, 539.

<sup>8</sup> Searles, A. L., and Warren, R. M., *J. Org. Chem.*, 1953, **18**, 1317.

reaction with acetic anhydride. 1,2,3,4-Tetrahydro-1,10-phenanthroline (1) is an amber-coloured liquid which rapidly darkens on standing in air.



When the hydrogenation was performed at 400 lb/sq in for 36 h at 100° an almost quantitative yield of 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (5) was obtained. The structure was confirmed by elementary analyses and by n.m.r. spectroscopy. In less drastic hydrogenation conditions a mixture of (1) and (5) was formed. In more severe conditions, for example at 400 lb/sq in for 48 h at 200°, a complex mixture of products was obtained due to breakdown of the molecule.

Of the three aromatic rings in 1,10-phenanthroline it is evident therefore that the two pyridine rings are much more susceptible to hydrogenation using Raney nickel catalyst. This result is in accord with expectations since usually, but not always (e.g.<sup>8,9</sup>), pyridine rings are more readily hydrogenated than benzene rings in aromatic polynuclear systems.

### Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. U.v. absorption measurements were taken with approximately 0.0001M solutions. N.m.r. spectra (60 MHz) were determined for 10% w/v solutions with tetramethylsilane as internal standard. Light petroleum as solvent refers to the fraction of b.p. 60–80°.

#### Hydrogenation of 1,10-Phenanthroline

(A) Sodium (1 g) was dissolved in ethanol (200 ml). 1,10-Phenanthroline hydrate (5 g) was added, followed by Raney nickel sludge<sup>10</sup> (2 ml). The suspension was shaken in an atmosphere of hydrogen at 20° under 58 lb/sq in pressure for 40 h. The mixture was then filtered. The filtrate was neutralized with conc. hydrochloric acid and then made slightly alkaline with dilute ammonium hydroxide solution. The solvent was removed under vacuum. The residual brown oil was chromatographed on an alumina column using chloroform–benzene (1 : 1) as eluent. After removal of the solvent the residual liquid was distilled to give 1,2,3,4-tetrahydro-1,10-phenanthroline (1) as an amber liquid, b.p. 136–138°/0.5 mm (yield 80%) (Found: C, 78.3; H, 6.8; N, 15.0. C<sub>12</sub>H<sub>12</sub>N<sub>2</sub> requires C, 78.3; H, 6.5; N, 15.2%). The u.v. spectrum in ethanol showed  $\lambda_{\max}$  261, 344 and 374 nm (log  $\epsilon$  4.31, 3.41, 3.43). The n.m.r. spectrum (cf.<sup>1</sup>) in deuteriochloroform consisted of a quintet at  $\delta$  1.80–2.18 (C3–H<sub>2</sub>), a triplet at 2.76–2.98 (C4–H<sub>2</sub>), a triplet at 3.38–3.56 (C2–H<sub>2</sub>), a broad signal centred at about 5.75 (NH), a multiplet at 6.85–7.32 (H 5,6,8), a doublet at 7.89–8.04 (H 7) and a doublet at 8.64–8.74 (H 9).

<sup>9</sup> Vierhapper, F. W., and Eliel, E. L., *J. Amer. Chem. Soc.*, 1974, **96**, 2256.

<sup>10</sup> Mozingo, R., *Org. Synth.*, 1955, Coll. Vol. III, p. 181.

When 1,2,3,4-tetrahydro-1,10-phenanthroline was dissolved in ethanol and conc. hydrobromic acid added a red precipitate of the *hydrobromide* was obtained. It crystallized from ethanol as red needles, m.p. 249° (Found: C, 54.6; H, 5.2; N, 10.3.  $C_{12}H_{13}BrN_2$  requires C, 54.3; H, 4.9; N, 10.6%).

1,2,3,4-Tetrahydro-1,10-phenanthroline was refluxed with excess acetic anhydride for 1 h. The solvent was then removed under vacuum. The residual brown oil was chromatographed on an alumina column with chloroform as the eluent. The solid obtained on removal of the chloroform was crystallized from light petroleum-benzene to afford 1-acetyl-1,2,3,4-tetrahydro-1,10-phenanthroline as almost colourless crystals, m.p. 111° (Found: C, 74.0; H, 6.2; N, 12.4.  $C_{14}H_{14}N_2O$  requires C, 74.3; H, 6.2; N, 12.4%). The i.r. spectrum (KBr disc) showed a band at  $1640\text{ cm}^{-1}$  (CO).

(B) When the hydrogenation was conducted at 100° with 400 lb/sq in pressure for 36 h using the procedure as in (A) a brown solid was obtained after chromatography on an alumina column using benzene as eluent. The solid crystallized from light petroleum to afford 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (5) as colourless crystals, which darken on standing, m.p. 70° (yield 92%) (Found: C, 76.5; H, 8.6; N, 14.7.  $C_{12}H_{16}N_2$  requires C, 76.6; H, 8.5; N, 14.9%). The u.v. spectrum in ethanol containing a trace of hydrochloric acid showed  $\lambda_{\text{max}}$  255 and 299 nm ( $\log \epsilon$  3.94, 3.48). The n.m.r. spectrum in trifluoroacetic acid consisted of a quintet at  $\delta$  2.10–2.50 (C3,8-H<sub>2</sub>), a triplet at 2.96–3.18 (C4,7-H<sub>2</sub>), a triplet at 3.78–3.96 (C2,9-H<sub>2</sub>) and a singlet at 7.45 (H5,6).

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