[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

Tetrahydro-*p*-phenanthroline

BY KONOMU MATSUMURA

In the hope of obtaining the synthetic products desired for test as insecticides, the reduction of *p*-phenanthroline was undertaken, and this paper deals with the preparation of tetrahydro-*p*-phenanthroline. It is notable that regardless of the presence in excess of reducing agent, the sole product isolated was tetrahydro compound and octahydro derivative could not be found in the reaction mixture.

Experimental

Reduction with Sodium in Amyl Alcohol.—Sodium (7 g.) was added in small portions at intervals during one-half hour to the solution of *p*-phenanthroline (2 g.) in amyl alcohol (80 g.) at the boiling temperature. On cooling, ice water was added and amyl alcohol was shaken with dilute hydrochloric acid.

The acid extract, after removal of amorphous matter which separated on carefully neutralizing with sodium carbonate solution, was strongly alkalified with sodium hydroxide and shaken with benzene. On removal of benzene, oil separated which after standing for several weeks turned to a solid (0.8 g.). After two crystallizations from alcohol, it formed light yellow needles, melting at 150–152°, yield 0.5 g. (25% of the theoretical).

Reduction with Tin and Hydrochloric Acid.—Tin (18 g.) was added to a hot solution of *p*-phenanthroline (5.4 g.) in concd. hydrochloric acid (60 cc.) and the solution was refluxed for three hours.

After removing the tin with the aid of hydrogen sulfide, concentrating the filtrate under reduced pressure, and being alkalified with sodium hydroxide, the separated free base was shaken with benzene. On evaporation of the solvent, oil separated which after standing turned to a solid (4.85 g., m. p. 70–130°). On distillation in a diminished pressure (a chief portion distilled at 212–213°, 12 mm.), it gave yellow prisms (3.4 g., m. p. 140–146°).

After two recrystallizations from alcohol, it formed light yellow flat needles, m. p. 152–152.5°; yield, 1.75 g. (32% of the theoretical). The mixed melting point of the specimens prepared by both methods showed no depression.

It is easily soluble in usual organic solvents, but fairly difficultly in petroleum ether and water.

Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.26; H, 6.52; N, 15.21. Found: C, 78.20; H, 6.44; N, 15.17.

TABLE I

DERIVATIVES OF TETRAHYDRO-*p*-PHENANTHROLINE

Derivative	M. p., °C.	Properties
Picrate	220.5	Yellow needles from EtOH
Chloroplatinate	>310	Orange-yellow leaflets from dil. HCl
Benzoyl	183.5	Colorless prisms from EtOH
Dihydrochloride[a]	241	Colorless prisms from ether. Soluble in H_2O
Monohydrochloride[b]	241	Red prisms

Formula		Analyses, % Calcd.	Found
$C_{12}H_{12}N_2 \cdot C_6H_3O_7N_3$	C	52.30	52.22
	H	3.63	3.73
	N	16.95	16.99
$C_{12}H_{12}N_2 \cdot H_2PtCl_6$	Pt	32.87	32.16
$C_{19}H_{16}ON_2$	N	9.72	9.61
$C_{12}H_{12}N_2 \cdot 2HCl$	HCl	28.40	27.06
$C_{12}H_{12}N_2 \cdot HCl$	HCl	16.55	15.86

[a] Obtained by combination of the components in ethereal solution. [b] Dihydrochloride lost one mole of hydrogen chloride on drying at 100°.

I desire to thank Professor Hata for the interest in this work.

Summary

Reduction of *p*-phenanthroline either with tin and hydrochloric acid or with sodium in amyl alcohol gives tetrahydro-*p*-phenanthroline.

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