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Experimental

Material — 3-Ethyl-, 4-ethyl-, and 4-ethyl-2-methyl-pyridine were respectively prepared by the method of Fand,[5] Frank,[6] and Wawzonek.[7] 2-Ethyl- and 2,4-diethylpyridines were synthesized by the method of Ladenburg,[8] heating pyridine and EtI in a sealed tube at 280～300°. By the same method, 2-ethyl-6-methylpyridine was synthesized from α-picoline, and 2-ethyl-4-methylpyridine[9] from γ-picoline. The mixture of basic substances obtained from these procedures was fractionally distilled and the picrate of each fraction was recrystallized until constant melting point was obtained. The pure base was obtained from the picrate.

Method—The absorption spectra were determined with a Shimadzu Spectrophotometer type QB-50, with a quartz cell of 10 mm. optical depth, in the region of 220～290 mμ. Density measurements were never made at intervals of more than 2 mμ, while in the neighborhood of the maxima, the interval was decreased to 0.5 mμ. The concentration of the solutions varied from 0.2 m*M* to 0.05 m*M*. The temperature was at 20°±2°.

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Tsukasa Kuraishi : Synthesis of 4-Aminopyridazine.

(*Pharmaceutical Faculty, University of Nagasaki**)

The synthesis of 4-aminopyridazine (I) has not yet been reported in literature. The writer obtained (I) quantitatively from 4-amino-3,6-dichloropyridazine by catalytic reduction, and comparison of the ultraviolet absorption spectra of 4-aminopyridazine and 3-aminopyridazine[1] is presented here.

Basskakow and Melnikow[2] obtained 1,2-dihydro-4-chloropyridazine-3,6-dione by heating chloromaleic anhydride with hydrazine sulfate in aqueous solution and Druey *et al.*[3] reported the absorption maxima of 3,4,6-trichloropyridazine. 4-Amino-3,6-dichloropyridazine (II) was obtained by heating 3,4,6-trichloropyridazine (III) with dehydrated ethanolic ammonia solution for 5 hours at 100～105°.

4-Aminopyridazine was obtained from the aminodichloropyridazine by reduction with palladium-charcoal as a catalyst.

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2) Ju. A. Basskakow, U. N. Melnikow : Chem. Zentr., **126**, 8384(1955).
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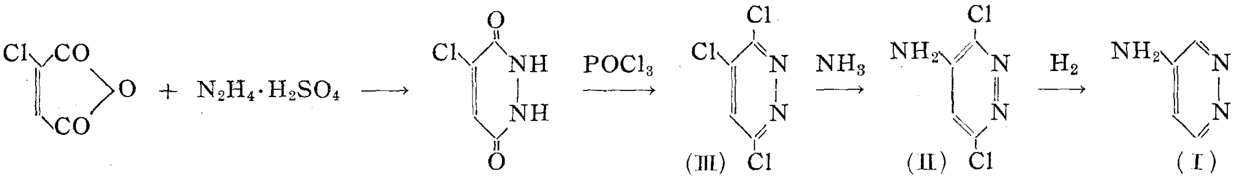
Measurement of the ultraviolet absorption spectra were limited to the region of 220~320 mμ. As to the spectra of these diazine compounds, it has been known[4] that the n–π^* transition appears weakly as well as π–π^* transition at a longer wave length side.

In this experiment for aminopyridazine, an intense band was observed at about 250 mμ and a weak band at 300 mμ. These absorption bands are regarded as π–π^* for the former and the n–π^* transition for the latter. 4-Aminopyridazine : λ_{max}^{EtOH} 252 mμ (ε 11350) and 281 (3690). 3-Aminopyridazine : λ_{max}^{EtOH} : 234 mμ (9200) and 301~302 (2400). 4-Amino-3,6-dichloropyridazine : λ_{max}^{EtOH} 256 mμ (9800) and 294~295 (4500). The reaction route was as follows :



Full details will be reported later.

The author would like to express sincere thanks to Prof. M. Yanai for his helpful suggestions.

Experimental

(All m.p. are uncorrected)

4-Amino-3,6-dichloropyridazine (II)—Twenty g. of trichloropyridazine (III) was placed in a sealed tube with dehyd. EtOH saturated with NH_3, and heated in an oil bath at 100~105° for 5 hrs. After removal of the solvent completely *in vacuo*, the residue was recrystallized from water giving white thin crystals, m.p. 203°; yield, 7 g. *Anal.* Calcd. for $C_4H_3N_3Cl_2$: C, 29.28; H, 1.83. Found. C, 29.61; H, 1.77.

4-Aminopyridazine (I)—A mixture of 2 g. of (II), 1.0 g. NaOH, 30 cc. MeOH, and 1.2 g. Pd-C (8.5%) was placed in a shaking flask and hydrogenated under atmospheric pressure. After removal of the solvent on a water bath, the residue was extracted with 20 cc. AcOEt. 4-Aminopyridazine, m.p. 129~131°, deposited on standing at room temperature. Yield, 1.0 g. *Anal.* Calcd. for $C_4H_4N_2$: C, 50.53; H, 5.26. Found. C, 50.83; H, 5.04.

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