**Sunao Furukawa and Yukio Kuroiwa : Simplified Preparation
of Pyridine-2- and -4-aldehydes.**

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Preparation of pyridine-2- and -4-aldehyde has been described in the literature, such as the ozone decomposition of stilbazole or vinylpyridine,^{1,2,3)} hydrolysis of ω -dichloropicoline,⁴⁾ air oxidation of picoline using V_2O_5/MoO_3 -mixture as a catalyst,⁵⁾ pyrolysis of picolinyl phenylsulfonyl hydrazide in glycerol,⁶⁾ hydrolysis of picolinic aldehyde acetal, obtained from pyridylmagnesium bromide and orthoformic ester,⁷⁾ and hydrolysis of the picolinic aldehyde diacetate, obtained by the rearrangement of pyridinemethanol 1-oxide with acetic anhydride.⁸⁾ These methods, however, were not satisfactory in respect to the yield or troublesome in procedures.

Previously, Kobayashi and Furukawa⁹⁾ succeeded in preparing 2-pyridinemethanol by the reaction of 2-picoline 1-oxide with acetic anhydride. The present authors attempted the oxidation of pyridinemethanol to pyridinealdehyde, using selenium dioxide as the oxidizing agent, since Weygandt and the others¹⁰⁾ had oxidized benzyl alcohol to benzaldehyde in quantitative yield by selenium dioxide.

In this oxidation, ethanol and dioxane were used as the solvent and the reaction temperature was kept at 80~85°. The yield of pyridinealdehyde was satisfactory both in ethanol and in dioxane, the yield being better in dioxane solution.

Some derivatives of pyridine-2- and 4-aldehyde were prepared through the corresponding pyridinemethanols, which were obtained by the rearrangement of the 1-oxides by the oxidation with selenium dioxide. The relation between the yield and solvent (ethanol, dioxane) was as follows :

Material	Amount (g.)	Yield of corresponding aldehydes	
		EtOH	dioxane
2-Pyridinemethanol	2	1.6 g. (86%)	1.5 g. (95%)
4-Pyridinemethanol	2	1.2 g. (61%)	1.6 g. (81%)
6-Methyl-2-Pyridinemethanol	2	1.6 g. (81%)	1.8 g. (92%)
4-Methyl-2-Pyridinemethanol	2	1.5 g. (76%)	1.8 g. (92%)

As shown in this table, the yield of pyridine-4-aldehyde was poorer than that of pyridine-2-aldehyde.

Thus, pyridine-2- and -4-aldehyde of high purity were prepared from 2- and 4-pyridinemethanol, which were obtained through 1-oxides, with fair ease. The percentage yield of pyridine-2-aldehyde calculated from 2-picoline was 35%, and that of pyridine-4-aldehyde from 4-picoline, 22%.

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Experimental

Preparation of Picolinic Aldehyde from 2-Pyridinemethanol—In EtOH: Two g. of 2-pyridinemethanol was dissolved in 20 cc. EtOH, 1 g. SeO_2 added, and refluxed gently for 2 hrs. After cooling, precipitated metallic Se was filtered, EtOH residue was distilled under a diminished pressure, and the fraction of b.p.₁₃ 63~65° weighed 1.6 g.

ii) In dioxane: Two g. of 2-pyridinemethanol was dissolved in 30 cc. dioxane, 1 g. SeO_2 was added, and the mixture was kept at 80~85° under stirring for 5 hrs. After removing the precipitated Se, dioxane was distilled off under a weakly diminished pressure, and the residue was handled as above; yield, 1.9 g. Phenylhydrazone, m.p. 180~182°, ¹¹⁾ and the thiosemicarbazone, m.p. 210~212°, agreed with their data in the literature.¹²⁾

Preparation of Isonicotinic Aldehyde from 4-Pyridinemethanol—Two g. of 4-pyridinemethanol was dissolved in 30 cc. dioxane, 1 g. SeO_2 added, and the mixture was kept at 80~85° under stirring for 5 hrs. After removing the precipitated Se, dioxane residue was distilled under a diminished pressure, and the fraction of b.p.₁₂ 76~78° weighed 1.6 g. This distillate solidified on standing in the air. The crystals of 4-pyridinealdehyde hydrate, m.p. 78°, agreed with the data in the literature.¹³⁾ Phenylhydrazone, m.p. 178~180°, and thiosemicarbazone, m.p. 234~236°, agreed with the data in the literature.^{12, 13)}

Preparation of 6-Methylpyridine-2-aldehyde from 6-Methyl-2-pyridinemethanol—Two g. of 6-methyl-2-pyridinemethanol was dissolved in 30 cc. dioxane, 1 g. SeO_2 added, and the mixture was kept at 80~85° under stirring for 4 hrs. Dioxane residue was distilled under a diminished pressure and the fraction of b.p. 78~80° weighed 1.8 g. According to Mathes and the others,¹⁴⁾ its phenylhydrazone melts at 199.5°, whereas the phenylhydrazone prepared by the authors formed light yellow needles, m.p. 203~205° (from EtOH). *Anal.* Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_3$: C, 73.87; H, 5.93. Found: C, 73.92; H, 6.20.

Preparation of 4-Methylpyridine-2-aldehyde from 4-Methyl-2-pyridinemethanol—Two g. of 4-methyl-2-pyridinemethanol was dissolved in 30 cc. dioxane, 1 g. SeO_2 added, and the mixture was kept at 80~85° under stirring for 4 hrs. Dioxane residue was distilled under a diminished pressure and the fraction of b.p.₁₅ 94~97° weighed 1.8 g. *p*-Nitrophenylhydrazone: Yellow needles (from MeOH), m.p. 243~245°. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_4$: C, 60.94; H, 4.72. Found: C, 60.73; H, 4.50.

Semicarbazone: White needles (from dil. EtOH), m.p. 204~206°. *Anal.* Calcd. for $\text{C}_8\text{H}_{10}\text{ON}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 51.33; H, 5.88. Found: C, 51.19; H, 5.73.

Thiosemicarbazone: White columnar crystals (from EtOH), m.p. 194~196°. *Anal.* Calcd. for $\text{C}_8\text{H}_{10}\text{N}_4\text{S}$: C, 49.48; H, 5.15. Found: C, 49.23; H, 4.97.

Summary

Some derivatives of pyridine-2- and -4-aldehyde were prepared from 2- and 4-pyridinemethanol derivatives, which were obtained in a good yield through the derivatives of 2- and 4-picoline 1-oxide by oxidation with selenium dioxide, in dioxane or ethanol.

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