mixture was allowed to stand overnight and the precipitates deposited were collected and recrystallized from EtOH-H_2O. The IR spectrum of this product was identical with that of 1-methyl-4-amidinocarbamoyl) pyridinium iodide obtained in i).

1-Methyl- and 1-Ethyl-3-(amidinocarbamoyl)pyridinium Halide——By the method i) described for the synthesis of 1-methyl-4-(amidinocarbamoyl)pyridinium halide.

1-Alkyl-4-(amidinocarbamoyl)pyridinium Bromide——A mixture of 1.6 g. of 4-(amidinocarbamoyl)-pyridine and 0.015 mole of alkyl bromide (alkyl $= C_3H_7$, $C_6H_{13} \sim C_{14}H_{29}$) in 50 ml. of anyhd. BuOH was heated under reflux for 2 hr. After removal of the solvent *in vacuo*, the residue was allowed to stand overnight. The precipitates deposited were collected, washed with ether and recrystallized from EtOH-ether to colorless needles.

1-Benzyl derivative was obtained by the same method using benzyl bromide.

1-Dimethylaminoethyl- and 1-Diethylaminoethyl-4-(amidinocarbamoyl)pyridinium Chloride——A mixture of 0.8 g. of 4-(amidinocarbamoyl)pyridine and 0.8 g. of hydrochloride of dimethylaminoethyl chloride (or 1 g. of hydrochloride of diethylaminoethyl chloride) in 50 ml. of anhyd. BuOH was heated under reflux for 3 hr. After cooling, the precipitates deposited were collected and recrystallized from EtOH-H_2O to colorless needles.

Guanidinium Salt of 1-Methyl-3-carboxypyridinium Iodide——A mixture of ethyl ester of 1-methyl-3-carboxypyridinium iodide and guanidine in anhyd. EtOH was treated by the method ii) described for the synthesis of 1-methyl-(4-amidinocarbamoyl)pyridinium iodide. Recrystallization from EtOH gave yellowish needles. m.p. $185 \sim 187°$. *Anal.* Calcd. for $C_8H_{13}O_2N_4I$: C, 29.64; H, 4.04; N, 17.28. Found : C, 29.85; H, 3.89; N, 17.41. No depression in melting point of this product was observed upon admixture with authentic sample prepared from 1-methyl-3-carboxypyridinium iodide[6] and guanidine, and the IR spectrum of the former was identical with that of the latter.

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Seiji Miyano[*1] : Deoxygenation of Pyridine 1-Oxide by Means of Benzyl Alcohol.

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The reduction of nitro[1] and carbonyl compounds[2~4] by means of hot benzyl alcoholic solutions of potassium hydroxide has been reported by several groups. More recently the reducing properties of the reagent was well demonstrated by Sprinzak who extended the reduction to nitrogen-carbon[5] and some polarized carbon-carbon double bonds.[6]

The present report concerns the extension of this reduction to pyridine and quinoline 1-oxides. For the deoxygenation of N-O bond in pyridine 1-oxides the use of zinc and dilute acid,[7] iron and acetic acid,[8] phosphorus trihalide,[9] triphenyl phosphite,[10] tri-

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phenylphosphine,[11] benzenesulfenyl chloride,[12] sulfur monochloride,[12] sulfur[13~14] and sulfur-containing compounds,[14] and hydrazobenzene[14] has been reported.

When heated with benzyl alcoholic potassium hydroxide pyridine and quinoline 1-oxides underwent exothermic reactions to give pyridine and quinoline in 64.2 and 68.8% yield, respectively. Deoxygenation of pyridine 1-oxide was also effected by 2-pyridinemethanol (I, R=2-pyridyl), in the presence of potassium hydroxide.

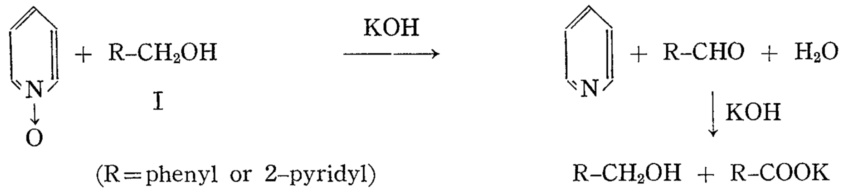

Chart. 1.

The procedure consists of heating benzyl alcohol or 2-pyridinemethanol with N-oxides in the presence of potassium hydroxide. Since the reaction is very exothermic with subsequent loss of the material a solution of N-oxide in benzyl alcohol or 2-pyridinemethanol was added dropwise to benzyl alcoholic or 2-pyridinemethanolic potassium hydroxide at a temperature range of 160~170°. In case of pyridine 1-oxide distillation of pyridine and water as they formed during the reaction was advantageous for the reaction.

The possibility that deoxygenation might be caused by thermal decomposition at the above temperature was excluded by the experiment which revealed that no pyridine was obtained on heating pyridine 1-oxide at 170~180° for 20 minutes in the presence of potassium hydroxide*[3]. This indicates that deoxygenation is effected by benzyl alcoholic potassium hydroxide, and not by thermal decomposition under the procedure condition.

Benzaldehyde or 2-pyridinealdehyde as it formed as by-product apparently underwent Cannizzaro reaction in highly basic medium and the potassium benzoate or potassium picolinate separated during the reaction was identified as free acid.

Experimental

Deoxygenation of Pyridine 1-Oxide. By Benzyl Alcohol——A mixture of 9 g. (0.16 mole) of KOH and 51 g. (0.47 mole) of benzyl alcohol was heated in a distilling flask to 140~150° at which most of the KOH came into solution. A solution of 15 g. (0.16 mole) of pyridine 1-oxide in 22 g. (0.2 mole) of benzyl alcohol was added dropwise at 160~170°. The reaction started vigorously and pyridine and H_2O distilled as they formed. Toward the end of the reaction the mixture became so thick that distillation was difficult. The fore-run, b.p. 95~110°, was dried over KOH and combined to the main fraction, b.p. 110~130°. The combined fraction was fractionally distilled to give 8 g. (64.2% based on pyridine 1-oxide) of pyridine, b.p. 113~117°, n_D^{20} 1.5072, reported[15] 1.5092; picrate, m.p. 164~165°, reported[16] 167~168°. The slurry remained in the flask was solved in H_2O, extracted with $CHCl_3$ and the aqueous layer neutrallized with dilute HCl. The benzoic acid separated was filtered, washed with water and dried, yield 6.3 g., m.p. 120~121.5° and no depression of melting point was observed on admixture with authentic sample.

By 2-Pyridinemethanol——The deoxygenation was conducted in a similar manner as described above. Pyridine 1-oxide (3.8 g., 0.04 mole) was reduced by means of 15.3 g. (0.14 mole) of 2-pyridinemethanol and

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*[3] According to Katada deoxygenation of pyridine 1-oxide by thermal decomposition occurred at 210~230° (bath temperature). M. Katada : Yakugaku Zasshi, **67**, 53 (1947); C.A., **45**, 9536 (1951).

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2.3 g. (0.041 mole) of KOH to yield 1.8 g. of pyridine (57% yield based on pyridine 1-oxide). The vigorous reaction was complete in 20 minutes. H_2O was added to the remaining slurry and the mixture was shaken with $CHCl_3$. The aqueous layer was neutrallized with dilute HCl and concentrated. Addition of saturated aqueous solution of $(AcO)_2Cu$ gave Cu-salt of picolinic acid as blue platelets. Hydrogen sulfide was passed into the suspension of Cu-salt in ethanol. Filtration of the resulting mixture and concentration of the filtrate gave 1.2 g. of crude picolinic acid which was purified by vacuum sublimation, m.p. 136~137°, reported[17] 136.5~138°.

Thermal Stability of Pyridine 1-Oxide——A mixture of 10 g. of pyridine 1-oxide and 1.2 g. of KOH placed in a distilling flask was heated to 155~160°, when KOH pellets came into solution. The resulting dark-brown solution was heated at 170~180° and allowed for 20 minutes at the same temperature range. No distillation of pyridine was observed.

Deoxygenation of Quinoline 1-Oxide by Means of Benzyl Alcohol——A mixture of 9 g. (0.062 mole) of quinoline 1-oxide and 19 g. (0.175 mole) of benzyl alcohol was added dropwise to a solution of 3.7 g. (0.066 mole) of KOH in 15 g. (0.139 mole) of benzyl alcohol at 160~170° (bath temperature). As soon as the addition was started, H_2O began to distil with vigorous reaction. H_2O collected amounted to 0.9 ml. After the reaction subsided the resulting slurry was poured into H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was shaken with 10% HCl and the aqueous layer was neutralized with Na_2CO_3 to separate quinoline, which was extracted with $CHCl_3$ and the extract was dried over anhydrous K_2CO_3. Removal of $CHCl_3$ and vacuum distillation of the residue gave 5.5 g. (68.8% based on quinoline 1-oxide), b.p. 137~139°/40 mm., reported[18] 136.7°/40 mm., n_D^{25} 1.62327, reported[18] n_D^{15} 1.62928. Picrate, m.p. 202~203°, reported[18] 203°.

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