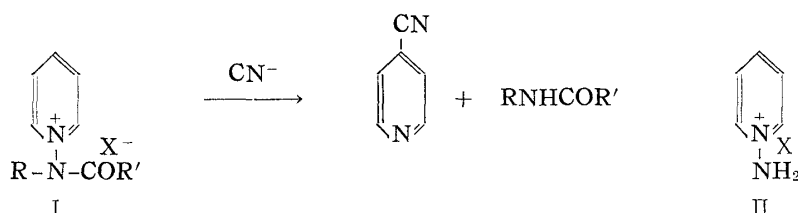
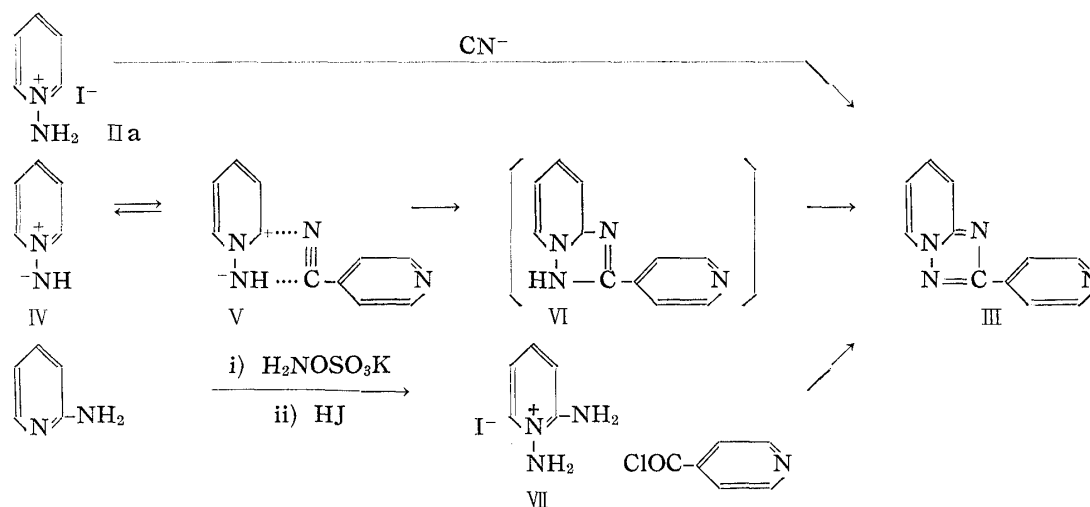


## Reaction of N-Aminopyridinium Salt with Cyanide Ion

In the previous paper,<sup>1)</sup> the reaction of N-acylalkylaminopyridinium salt (I) with cyanide ion has been reported as one of the reactions of N-aminopyridinium salts. 4-Cyanopyridine and amide were obtained as the products of this reaction.



In the present communication, the writers wish to report that a compound containing a novel heterocyclic ring, *s*-triazolo[1,5-*a*]pyridine ring, is produced on reacting N-aminopyridinium salt (II) with cyanide ion. When an aqueous potassium cyanide solution was added to an aqueous solution of N-aminopyridinium iodide (IIa) at room temperature, colorless needles (III) of m.p. 193° (from benzene and chloroform) (*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>4</sub>: C, 67.33; H, 4.11; N, 28.56. Found: C, 67.09; H, 4.48; N, 28.78) separated out in about 25% yield.



The same compound was obtained by dipolar 1,3-cyclic addition\*<sup>1</sup> of 4-cyanopyridine to pyridineimine (IV). Further, the product was also synthesized by condensing isonicotinoyl chloride with 1,2-diaminopyridinium iodide (VII), m.p. 160° (decomp.) (*Anal.* Calcd. for C<sub>6</sub>H<sub>8</sub>N<sub>3</sub>I: C, 25.33; H, 3.40; N, 17.73. Found: C, 25.57; H, 3.48; N, 17.76), which is obtained by treating 2-aminopyridine with hydroxylamine O-sulfonate and then with hydriodic acid. From the latter reaction, dihydro-type structure (VI) for the product should be excluded.\*<sup>2</sup> Thus the structure of the product was definitely proved as

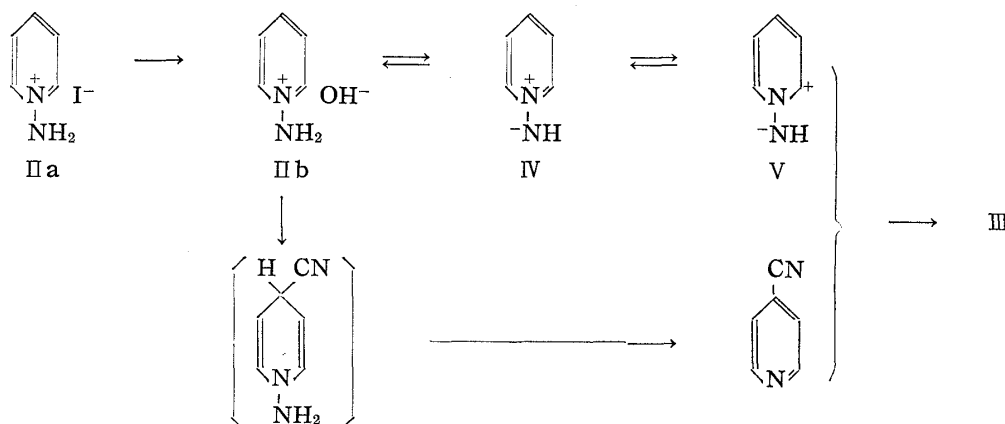
1) T. Okamoto, M. Hirobe, C. Mizushima, A. Osawa: This Bulletin, 11, 780 (1963).

\*<sup>1</sup> As for the conception of the dipolar 1,3-cyclic addition: cf. R. Huisgen: Proc. Chem. Soc., 357 (1961).

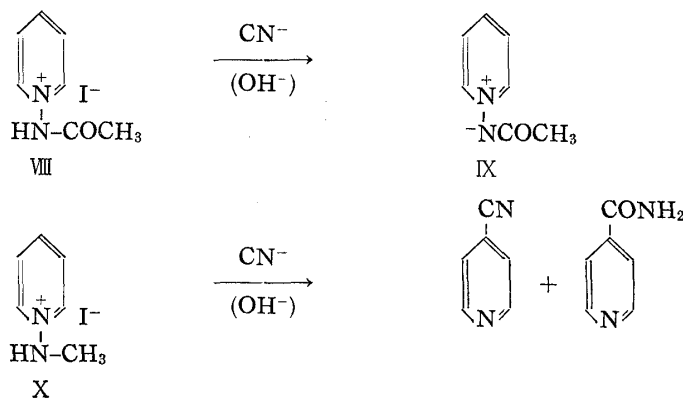
\*<sup>2</sup> The products of 1,3-dipolar addition of pyridineimine with "dipolarphils" generally have 1,2-dihydropyridine-type structures but several cases in which secondary dehydrogenation is observed during the addition reaction have been reported. cf. R. Huisgen, R. Grashey, R. Krischke: Tetrahedron L., 1962, 387, No. 9, May.

2-(4-pyridyl)-s-triazolo[1,5-*a*]pyridine (III).

When the N-aminopyridinium salt (II) is mixed with potassium cyanide in aqueous solution, it should exist as an equilibrium mixture of IIb, IV, and V in the reaction solution. The quaternary hydroxide (IIb) reacts with cyanide ion to give 4-cyanopyridine, which is then condensed with the 1,3-dipolar form (V) of pyridineimine (IV) by means of dipolar 1,3-cyclic addition to produce the final product (III).



On the contrary, N-acetamidopyridinium iodide (VIII)<sup>2)</sup> gave only its ylide compound (IX)<sup>2)</sup> and N-methylaminopyridinium iodide (X)<sup>2)</sup> resulted in 4-cyanopyridine and isonicotinamide in the reaction with cyanide ion. These facts mean that the latter should exist mostly as its quaternary hydroxide in the reaction solution because of stronger basicity of the ring nitrogen.



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2) *Idem*: Yakugaku Zasshi, 83, 309 (1963).