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Studies on Quinolizine Derivatives. XII.[1] Synthesis of Diazacycl[3,3,3]azine Derivatives. (5)

Previously we reported a new cycl[3,3,3]azine derivative, 1,9-diazacycl[3,3,3]azine derivative[2] which was prepared from 1-imino-1H-pyrido[1,2-*c*]pyrimidine derivative and dimethyl acetylenedicarboxylate, and a new synthetic method of 1-azacycl[3,3,3]azine derivatives[3] which were prepared from 6-methyl-4-imino-4H-quinolizine derivatives with ethoxymethylenemalononitrile or acetic anhydride.

In this communication, we wish to report a new method for the preparation of 1,9-diazacycl[3,3,3]azine derivatives (IV, V) by the reaction of 8-methyl-1-imino-1H-pyrido[1,2-*c*]-pyrimidine derivatives (III) with ethoxymethylenemalononitrile or acetic anhydride.

A solution of 6-methyl-2-pyridineacetonitrile (I) and dimethyl cyanamidedithiocarboxylate (IIa) with sodium hydroxide in N,N-dimethylformamide was heated for half an hour on a boiling water bath to give 1-imino-1H-pyrido[1,2-*c*]pyrimidine derivative (IIIa).

A new cycl[3,3,3]azine derivative, 3-cyano-2-methylthio-1,9-diazacycl[3,3,3]azine (IVa) as blue needles, mp 300° (decomp.), Mass Spectrum *m/e* 240 (M^+), IR (KBr), 2180 (C≡N) cm^{-1}, NMR ($CDCl_3$) δ: 7.90 (1H, doublet, J=6 Hz, C_8–H), 6.77 (1H, triplet, J=8 Hz, C_5–H), 6.61 (1H, doublet, J=8 Hz, C_4–H or C_6–H), 5.88 (1H, doublet, J=8 Hz, C_4–H or C_6–H), 5.40 (1H, doublet, J=6 Hz, C_7–H), 2.39 (3H, singlet, SCH_3), was obtained by the reaction of IIIa and ethoxymethylenemalononitrile for 4 hr at 150°.

On the other hand a solution of IIIa and acetic anhydride in the presence of pyridine was heated for 10 hr on a boiling water bath to give 3-cyano-8-methyl-2-methylthio-1,9-diazacycl[3,3,3]azine (Va) as blue needles, mp 290°, Mass Spectrum *m/e* 254 (M^+), IR (KBr), 2180 (C≡N) cm^{-1}, NMR ($CDCl_3$) δ: 7.79 (1H, triplet, J=8 Hz, C_5–H), 5.86 (1H, doublet, J=

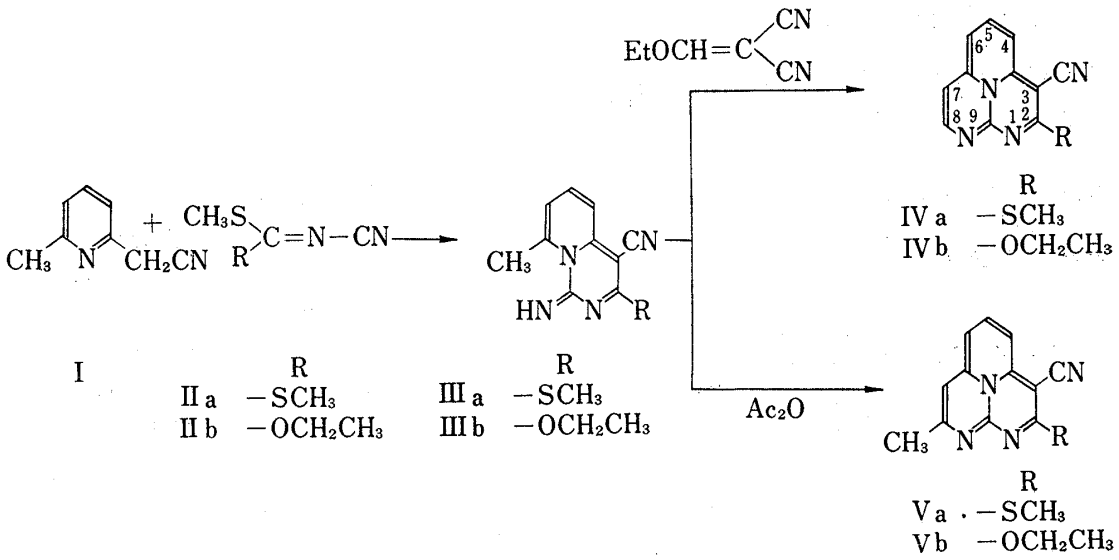

Chart 1

1) Part XI: H. Awaya, C. Maseda, R. Natsuki, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), 22, 1939 (1974).
2) H. Awaya, C. Maseda, Y. Tominaga, R. Natsuki, Y. Matsuda and G. Kobayashi, *Yakugaku Zasshi*, "accepted."
3) H. Awaya, C. Maseda, Y. Tominaga, R. Natsuki, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), 22, 1424 (1974).

Table I

	UV λ_{max}^{EtOH} nm (log ε)		UV λ_{max}^{EtOH} nm (log ε)
IVa	259[a]	IVb	341(4.21)
	315		387(4.20)
	354		392(4.21)
	396		405(4.10)
	409		413(4.22)
	416		620(3.04)
	650		660(3.17)
	710	Vb	239(4.19)
Va	243[a]		250(4.26)
	309		279(4.28)
	396		341(4.25)
	423		390(4.18)
	559		412(4.16)
	690		559(3.24)
IVb	249(4.25)		640(3.29)
	282(4.28)		

a) Concentration is unknown because of insufficient solubility.

8 Hz, C_4–H or C_6–H), 5.65 (1H, doblet, J=8 Hz, C_4–H or C_6–H), 5.40 (1H, singlet, C_7–H), 2.24 (3H, singlet, SCH_3), 1.91 (3H, singlet, C_8–CH_3).

On the similar manner above method, IIIb was obtained from I and O-ethyl S-methyl cyanamidethiocarboxylate (IIb) and then the reaction of IIIb with ethoxymethylenemalononitrile or acetic anhydride gave the corresponding 1,9-diazacycl[3,3,3]azine derivatives (IVb, Vb).

The structures of the products are confirmed by satisfactory elemental analyses, and infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra. The data for the products are summarized in Table I. Further works on the synthesis of the parent compound are in progress.

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