UV λ_{mxa} (nm): pH 1, 276; pH, 7, 281; pH 13, unstable. This fact is a further confirmation of the structural identity of the rearrangement product.

It is worth noting that 6-hydrazinopurine riboside which might have been expected to be the Dimroth rearrangement product of Ia, did not convert to IIa under the reaction conditions chosen in the present study. It is considered that the rearrangement was initiated by hydrolytic cleavage of 1,2-bond, followed by migration of the formyl group to N-amino group and then, by dehydrative ring-closure to give II. Details are to be described in a forthcoming paper.

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Studies on Quinolizine Derivatives. XI.[1] Synthesis of Azacycl[3,3,3]azine Derivatives. (4)

As an extension of our studies on azacyclazine derivatives, we have investigated the syntheses of 1-azacycl[3,3,3]azine derivatives (I).[2] In this communication, we wish to describe that the stable salt of 2-methyl-1-azacycl[3,3,3]azine hydrobromide (IV) and its unstable free base (V) are prepared by the degradation from methyl 9-cyano-2-methyl-1-azacycl[3,3,3]-azine-7-carboxylate (I).

A mixture of I in polyphosphoric acid (PPA) was heated on a boilling water bath for 4 hr to give corresponding 9-carboxamide derivative (II), mp 277—278°. While a mixture of I in PPA was heated at 150° for 4 hr to give decarboxylated 9-carboxamide derivative (III), mp 237°.

Then a mixture of II or III in 48% hydrobromic acid was refluxed for 4 hr to give 2-methyl-1-azacycl[3,3,3]azine hydrobromide (IV), mp>300°. Mass Spectrum *m/e*: 182 (M^+). UV λ_{max}^{EtOH} mμ (log ε): 228 (4.23), 268 (4.43), 350 (4.05), 375 (4.06), 388 (4.05), 428 (2.99). NMR (DMSO-d_6) δ: 6.94 (1H, triplet), 6.70 (1H, triplet), 6.26 (2H, doublet), 6.17 (1H, doublet), 5.50 (1H, doublet), 4.64 (1H, singlet), 1.40 (3H, singlet), all coupling constants being *ca.* 8 Hz.

The free base, 2-methyl-1-azacycl[3,3,3]azine (V) was obtained as yellowish brown precipitate (λ_{max}^{EtOH} mμ: 270, 283 (shoulder), 387, 405, 417, 428) by treatment of IV with potassium carbonate solution but the product was unstable and could not be purified by recrystallization. Then the NMR spectrum of the crude free base (V) in $CDCl_3$ was recorded: δ 5.64 (1H, triplet),

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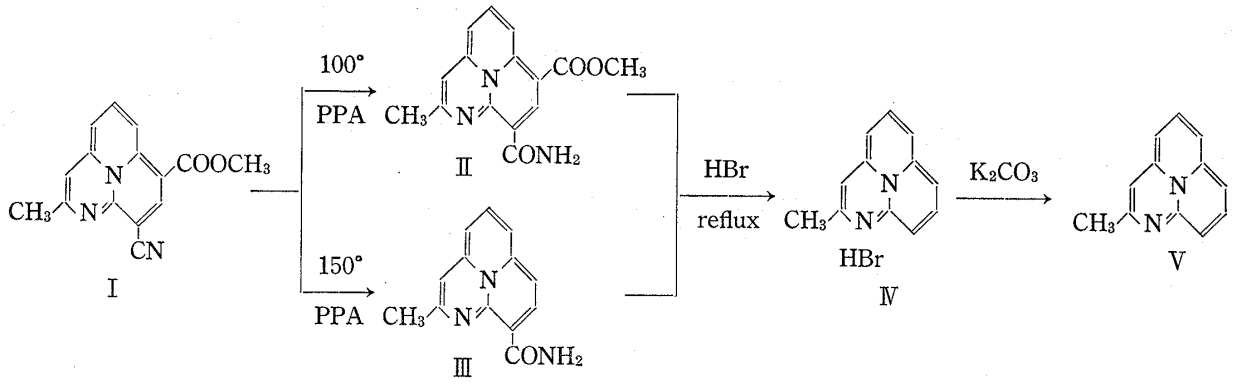

Chart 1

5.40 (1H, triplet), 4.54 (1H, doublet), 4.28 (1H, doublet), 4.24 (1H, doublet), 3.84 (1H, doublet), 3.71 (1H, singlet), 1.02 (3H, singlet), all coupling constants being *ca.* 8 Hz.

Recently, Ceder and co-worker[3] reported the synthesis of 2-methyl-1,3,6-triazacycl-[3,3,3]azine which possessed aromatic properties but we do not regard this low degree of deshielding as evidence of an aromatic property in a new [12] annulene heterocyclic ring system, azacyclazine (V).

The structures of the products (I, II, III, IV) are confirmed by satistactory elemental analyses, infrared and ultraviolet spectra. Further works on the purification of the free base (V) by sublimation and the synthesis of the parent compound are in progress.

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Synthesis and Reactions of Thiamine Disulfide Sulfur Analogues

We have previously reported[1,2] the synthesis of thiamine sulfur analogues and methylsulfinylethylthiamine (MSIT, I) was found to be very effective against avian coccidiosis.[3] Here, we wish to report a ready transformation of MSIT into disulfides through intramolecular thiol-sulfoxide interaction.

An aqueous solution of MSIT was adjusted to pH 7—8 by the addition of sodium bicarbonate. A crystalline product separated which showed three spots on thin-layer chromato-

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