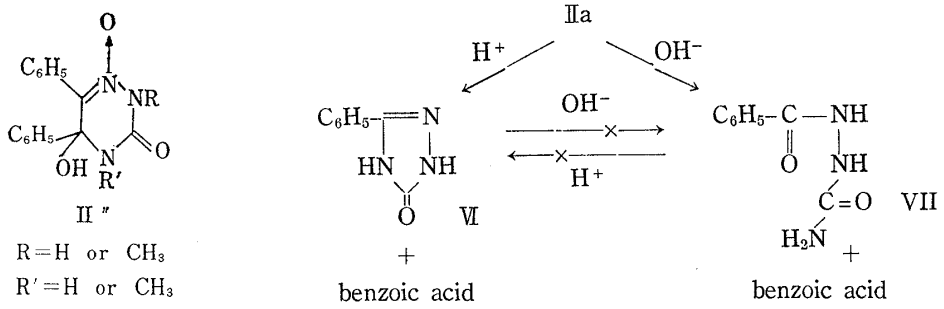
IIa was hydrolized to 3-hydroxy-5-phenyl-1,2,4-triazole (VI)[6] and benzoic acid in acidic medium, while basic hydrolysis gave 1-benzoyl semicarbazide[7] (VII) and benzoic acid.



It can be stated that VI and VII formed, respectively, *via* independent route, because the conditions where VII was formed could effect no change on VI and on the contrary, VII was not cyclized to VI by the reaction conditions simillar to those where VI resulted from IIa. Analogous degradating reactions were carried out on IIb. Careful considerations on the mechanism of these hydrolysis reactions also suggest the oxazirino-structure of IIa and IIb, on which we will discuss in near future.

It is noteworthy that IIa and IIb are unexpectedly stable and show hardly any chemical properties specific for non-cyclic oxaziranes.[5] Furthermore, the covalent hydrations are extraordinarily rigid; all attempts at dehydration by chemical methods were unsuccessful.

As a conclusion, the "covalently hydrated oxazirino-*as*-triazines" as a whole may be stated as new heterocyclic compounds.

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The Synthesis of 2-Methyl-4-amino-5-β-ethoxyvinylpyrimidine

We have previously reported[1,2] that 2-substituted-4-amino-5-alkoxymethylpyrimidine (I) was readily synthesized by the reaction of amidine and 2-methoxymethylene-3-alkoxy-propionitrile (II).[3] The condensation reactions of II as the three carbon source were also reported.[4]

1) A. Takamizawa, K. Ikawa, K. Tori: Yakugaku Zasshi, **78**, 647 (1958).
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3) A. Takamizawa, K. Hirai, S. Sumimoto: *Ibid.*, **14**, 238 (1966).
4) A. Takamizawa, K. Hirai, Y. Sato, K. Tori: J. Org. Chem., **29**, 1740 (1964).

Recently, several reactions of 3-cyanopropionaldehyde (III) have been reported.[5)]

The present communication describes the reaction of enol ether (IV) with acetamidine to give 2-methyl-4-amino-5-β-ethoxyvinylpyrimidine (V). 2-Sodioformyl compound (VI) was derived from III by the reaction with sodium ethoxide and ethyl formate, and VI was methylated by dimethylsulfate as cited before[6)] in the synthesis of II to give enol ether (IV), b.p.$_{3.5}$ 98~104°, as an unstable oil. The reaction of IV with acetamidine was carried out in ethanol solution to give colorless prisms (from benzene-petr. benzine) of m.p. 110~112°, $C_9H_{13}ON_3$ (V). UV spectrum of this compound showed the maxima at 267 and 307.5 mμ indicating the presence of conjugation with pyrimidine ring. NMR*[1] spectrum exhibited that this compound was a single product and the signal peaks were shown as follows: 8.68^t (J=7, $OCH_2C\underline{H}_3$), 7.52^s (pyrimidine C-2-Me), 6.03^q (J=7, $OC\underline{H}_2CH_3$), 5.02^d (J=7, =CHO-), 4.48^b (NH_2), 3.77^d (J=7, $\Vert$-CH=), 1.66^s (pyrimidine C-6-H). Ozonolysis of this compound gave 2-methyl-4-amino-5-formylpyrimidine (VII).[7)] Therefore, the structure of V was confirmed to be 2-methyl-4-amino-5-β-ethoxyvinylpyrimidine. The crystals obtained from the recrystallization filtrate of V was revealed to be a mixture of V and its isomer by NMR spectrum. This spectrum showed the peaks in addition to those of V as follows: 8.65^t (J=7, $OCH_2C\underline{H}_3$), 7.52^s (pyrimidine C-2-Me), 6.08^q (J=7, $OC\underline{H}_2CH_3$), 4.52^d (J=13, =CHO-), 3.25^d (J=13, $\Vert$-CH=), 1.97^s (pyrimidine C-6-H). The spin-spin coupling constant for *trans* protons on olefinic double bond is larger than that for *cis* compound.[8)] Therefore, it was concluded that the crystals of m.p. 110~112° (V), showing the signals of protons on olefinic double bond at a higher field than those of its isomer with J=7 c.p.s., was *cis* compound. The formation of V from IV was assumed to take the course A or B giving a mixture of *cis* and *trans* isomers (Chart 1).

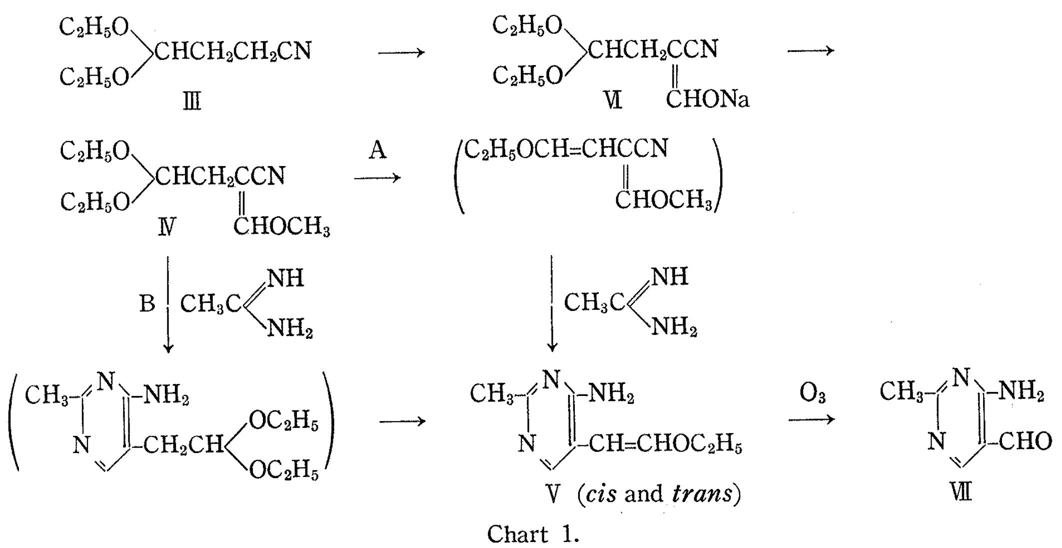

Chart 1.

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*1 NMR specutra were recorded on a Varian A-60 spectrometer by using solution in $CDCl_3$ containing $(CH_3)_4Si$ as an internal reference; chemical shifts (τ), coupling constants (J, c.p.s.). Peak multiplicities are presented by s (singlet), d (doublet), t (triplet), and b (broad).

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