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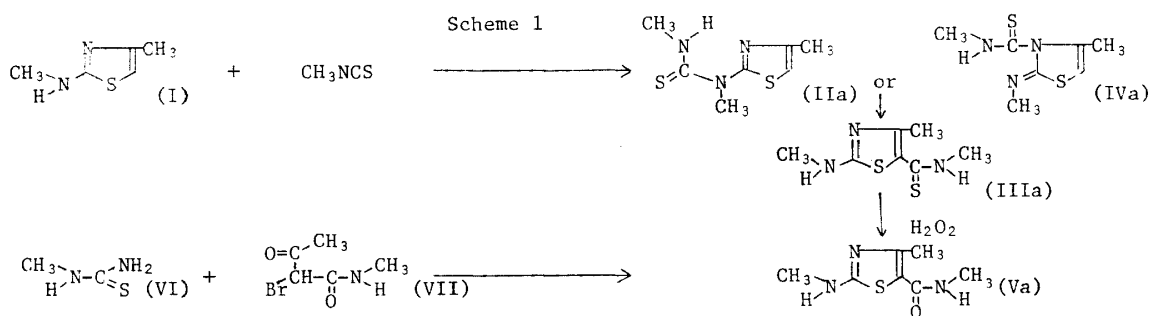
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NEW SYNTHESIS OF 4-METHYL-2-METHYLAMINO-5-(N-METHYLTHIOCARBAMOYL) THIAZOLE BY THERMAL ISOMERIZATION

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The reaction of 4-methyl-2-methylamionthiazole (I) with methyl isothiocyanate in toluene in the presence of pyridine gave the crystals of mp 56-57°C (IIa) having R_f value of 0.75 (2-propanol: ether, 1: 1), λ_{\max} (2-propanol) 260 (sh.), 291 nm ($\epsilon=19500$) and yellow crystals of mp 249-250°C (IIIa) having R_f value of 0.53, λ_{\max} (2-propanol) 294 ($\epsilon=6310$), 340 nm ($\epsilon=11500$).



The elemental analysis and mass spectral data (MW 201) gave a molecular formula of C₇H₁₁N₃S₂ for both (IIa) and (IIIa), isomeric to each other. The thermal isomerization of (IIa) in pyridine gave (IIIa). As the spectral interpretation could not differentiate 1, 3-dimethyl-1-(4-methylthiazol-2-yl) thiourea (IIa) and 4-methyl-2-methylimino-3-(N-methylthiocarbamoyl)-4-thiazoline (IVa), the structure of (IIa) was established by an X-ray analysis.

The NMR spectrum (d₆-DMSO) of (IIIa) showed signals at δ 2.29 (singlet, 3H, =C-CH₃), 3.10 (doublet, 3H, J=5.0 Hz, singlet after D₂O exchange, singlet after irradiation at 9.06, -NH), 2.28 (doublet, 3H, J=5.0 Hz, singlet after D₂O exchange, singlet after irradiation at 7.86, -NH), 9.06 (broad, 1H, disappeared after D₂O exchange, -CH₃-NH-), and 7.86 δ (broad, 1H, disappeared after D₂O exchange, CH₃NH-). The structure of (IIIa) was estimated from the appearance of two doublets for CH₃NH and the absence of a singlet due to H at position 5.

The product obtained by the alkaline H₂O₂ treatment of (IIIa) was identified with the product, 4-methyl-2-methylamino-5-(N-methylcarbamoyl)thiazole (Va) from the reaction of (VI) and (VII), by the mixed mp, and from UV, Mass and NMR spectral comparison.

* 本報告は Chemistry Letters, 1147-1148 (1975) に発表。

Table I shows the result of monitoring of the thermal rearrangement of (IIa) to (IIIa), by measuring the absorption at 340 nm due to (IIIa) every 2.5 hr in a different solvent. This result suggests that an essential factor in the rearrangement is the presence of pyridine.

Table I				
Solvent	Absorption at 340 nm ^{b)}	Reflux time (hr)	IIIa Yield (%)	
Cyclohexane	—	30	0	a) Ratio 2 : 1
Toluene	—	30	0	b) Time required for
Toluene-pyridine ^{a)}	> 5 hr	10	80	the appearance of
Pyridine	> > 5 hr	30	90	the absorption at
				340 nm