

Title	Pyrolytic S→N methyl migration of N, N-dimethyl-N'-(4-methyl-2-thiazolyl)-S-methylisothiourea
Sub Title	
Author	与田, 玲子(Yoda, Reiko) 山本, 有一(Yamamoto, Yuichi) 松島, 美一(Matsushima, Yoshikazu)
Publisher	共立薬科大学
Publication year	1984
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.29 (1984.) ,p.43- 44
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000029-0043

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Pyrolytic S→N Methyl Migration of N, N-Dimethyl-N'-(4-methyl-2-thiazolyl)-S-methylisothiurea*

Reiko YODA, Yuichi YAMAMOTO and Yoshikazu MATSUSHIMA

与田玲子, (故)山本有一, 松島美一

In an effort to establish N-(2-thiazolyl)thioureas as a new series of chelating ligands, we prepared a number of derivatives methylated at the thiourea and the thiazole nitrogen atoms and at the thiourea sulfur atom. In the course of the investigation, we found a new pyrolytic methyl transfer reaction proceeded smoothly without any solvent.

N,N-dimethyl-N'-(4-methyl-2-thiazolyl)-S-methylisothiurea (**1a**) was heated at 155°, for 14 h. Chromatography of the pyrolytic products gave a yellow crystalline compound, which was identified as N,N-dimethyl-N'-(3,4-dimethyl-4-thiazolin-2-ylidene)thiourea (**2a**) by comparing its physicochemical properties with those of an authentic sample synthesized from 2-imino-3,4-dimethyl-4-thiazoline and N,N-dimethylthiocarbonyl chloride. Similarly, pyrolysis of N,N-dimethyl-N'-(4,5-dimethyl-2-thiazolyl)-S-methylisothiurea (**1b**) and N,N-diethyl analogs of **1a** and **1b** (**1c**, and **1d**) gave the corresponding (3-methyl-4-thiazolin-2-ylidene)thioureas (**2b**, **2c**, and **2d**, respectively). (Chart 1) The results indicate

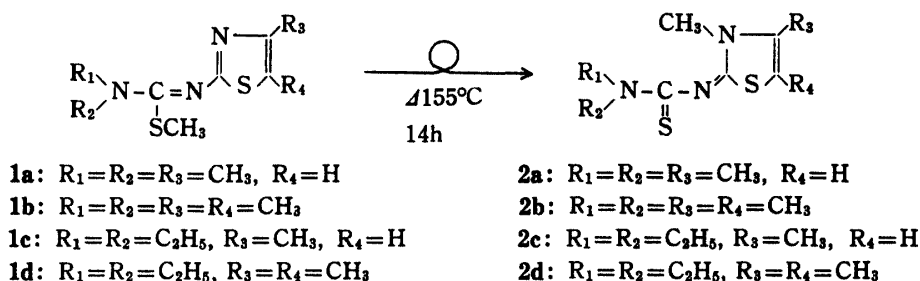


Chart 1

that the reactions include pyrolytic S→N migration of methyl group. The studies of mechanism using S-deuteromethyl derivatives showed that the reaction involves intermolecular transfer of the methyl group.

A similar S→N migration of ethyl group was demonstrated in S-ethyl analog of **1a**. N,N-Dimethyl-N'-(4-methyl-2-thiazolyl)-S-ethylisothiurea was pyrolyzed to form N,N-dimethyl-N'-(3-ethyl-4-methyl-4-thiazolin-2-ylidene)thiourea.

N-methyl-(2-thiazolyl)-S-methylisothiureas were pyrolyzed under conditions similar to those used for N,N-dimethylisothiurea analogs and the products were analyzed by means of thin layer chromatography. The spots of the methyl migrated compounds

* 本報告は *Chem. Pharm. Bull.*, **32**, 2224—2229 (1984) に発表

were not found in the chromatograms.

The results clearly indicate that the pyrolytic S→N methyl migration takes place in N,N-dimethyl-N'-thiazolyl-S-methylisothiureas but not in N-monomethyl analogs. The results were interpreted in terms of predominant species in an equilibrium between *E* and *Z* forms.