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Title	Proton-induced ring transformation of 2-imino-3-thiocarbamoyl-4-thiazoline
Sub Title	
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Publisher	共立薬科大学
Publication year	1985
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.30 (1985.) ,p.89- 89
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000030-0089

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Proton-Induced Ring Transformation of 2-Imino-3-thiocarbamoyl-4-thiazoline*

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We previously found that 2-thiazolylthioureas are potentially useful chelating agents, which can be used for spectrophotometric determination of metal ions. For the preparation of this series of compounds, we have reported several synthetic methods. One of the methods involves the reaction of 2-aminothiazole and thiocarbamoyl chloride.

In an attempt to prepare 1,1,3-trimethyl-3-(4-methyl-2-thiazolyl)thiourea (**4a**) from 4-methyl-2-methylaminothiazole (**1a**) and N,N-dimethylthiocarbamoyl chloride (**2a**), we found a unique proton-induced ring transformation of 2-imino-3-thiocarbamoyl-4-thiazolines.

The reaction of **1a** and **2a** in a nonpolar solvent gave the following four products including the expected one ; 4-methyl-2-methylimino-3-(N,N-dimethylthiocarbamoyl)-4-thiazoline (**3a**), **4a**, 4-methyl-2-methylamino-5-(N,N-dimethylthiocarbamoyl)thiazole (**5a**), and 1,1-dimethyl-(3,4-dimethyl-2(3H)thiazolylidene)thiourea (**6a**). The 2-phenylamino analog of **1a** (**1b**) gave the corresponding phenyl compounds (**3b**—**6b**) on reaction with **2a**. Compounds **3a** and **3b** were isomerized to **6a** and **6b**, respectively, in dioxane with a drop of hydrochloric acid. From studies with ^{15}N-labeled compounds, a mechanism is proposed involving a proton-induced ring transformation of **3**, *via* protonation of **3**, cleavage of the 3,4-bond, and bond formation between the imino nitrogen and 4-carbon atoms. A similar ring transformation took place with 3-N,N-dimethylcarbamoyl analogs of **3a** and **3b**, but not with a thiazolidine analog of **3b**.

* 本報告は *Chem. Pharm. Bull.*, 32, 4292—4299 (1984) に発表