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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 <sup>15</sup>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**.

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