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

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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-methylisothiourea (**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-dimethylthiocarbamoyl chloride. Similarly, pyrolysis of N,N-dimethyl-N'-(4,5-dimethyl-2-thiazolyl)-S-methylisothiourea (**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

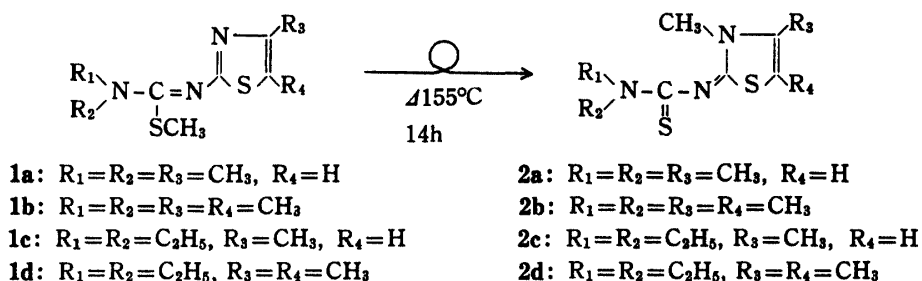


Chart 1

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-ethylisothiourea was pyrolyzed to form N,N-dimethyl-N'-(3-ethyl-4-methyl-4-thiazolin-2-ylidene)thiourea.

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

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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.