

Reactions of Hydrazinium Thiocyanate with Alcohols

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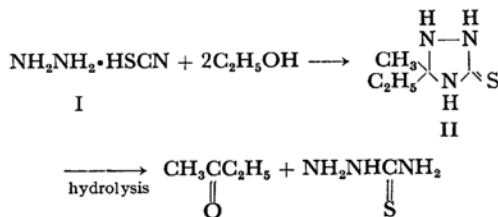
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During the course of an investigation of the reactions of thiocyanogen with acylhydrazines, it was found that hydrazinium thiocyanate (I) reacted with ethanol or 2-butanol, and in both cases an interesting heterocyclic compound, 3-ethyl-3-methyl-1,2,4-triazolidine-5-thione (II), was formed.

When a mixture of the aqueous solution of I and ethanol was allowed to stand at room temperature, white needles, II mp 116°C were obtained. The elemental analysis and MS spectral data of II gave a molecular formula $C_5H_{11}N_3S$. The IR spectrum (KBr) showed absorption bands at 3130, 2960, 2920, 2850, 1520, 1400, 1225, 1180, 960, and 830 cm^{-1} . The NMR spectrum (CD_3OD) exhibited peaks at τ 9.30 (3H, methyl-protons, triplet, $J=7.0$ cps), 8.63 (3H, methyl-protons, singlet), and 8.43 (2H, methylene-protons, quartet, $J=7.0$ cps), indicating that the methyl and the ethyl groups were both attached to the same carbon atom.

From these data and the results of the hydrolysis of II, the following structure was deduced.



The MS spectrum also supported the structure, viz., it showed the molecular peak at m/e 145 and peaks at m/e 130 (M-15) and m/e 116 (M-29). The m/e 86 peak derived from the loss of HNCS showed the presence of an $-\text{NH}\cdot\text{CS}-$ group in the molecule. Peaks at m/e 100, 96, and 82 indicated the formation of a stable triazole skeleton.

When the reaction of I with ethanol was carried out in the absence of water, another product $C_{10}H_{18}N_4S_2$ (III), mp 180°C (dec.) was isolated in a significant quantity in addition to II. Sunner¹⁾ reported this compound (III) to be the product in the reaction of methyl ethyl ketone with I. However, when we carried out the same reaction, II was obtained in a fairly large quantity together with III.

2-Butanol reacted also with I and gave only II, both in the presence and absence of water.

This type of cyclization does not occur with the lower *n*-alcohols, except ethanol.

The triazolidine formations from ethanol, 2-butanol, and methyl ethyl ketone seem to be related to each other, and the reaction mechanisms are now being studied.

1) S. Sunner, *Svensk Kem. Tidsskr.*, **67**, 361 (1955).