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## Synthesis and Reactions of New Vinyl Isothiocyanates

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## SYNTHESIS AND REACTIONS OF NEW VINYL ISOTHIOCYANATES<sup>1</sup>

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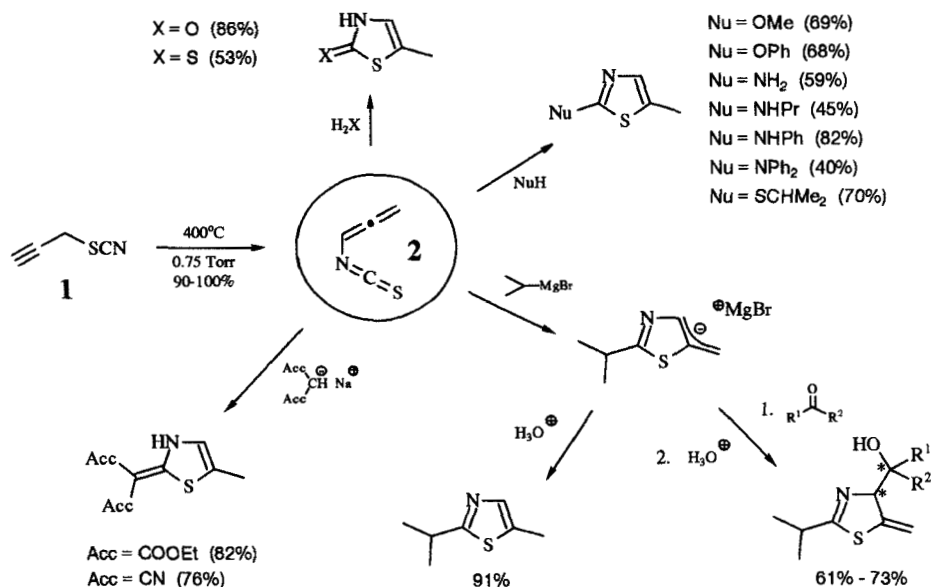
**Abstract** New vinyl isothiocyanates, which can be prepared from easily accessible thiocyanates by [3,3] sigmatropic shifts, show unusually high reactivity used for the synthesis of heterocyclic sulfur compounds.

### INTRODUCTION

The isomerization of allyl thiocyanate to allyl isothiocyanate (mustard oil) has been thoroughly investigated and is interpreted as a [3,3] sigmatropic rearrangement. We recently reported the preparation of the highly reactive allenyl isothiocyanates, which can be easily obtained from propargyl thiocyanates by gas-phase thermolysis (e.g., **1** → **2**, see Scheme 1).<sup>2</sup> In this communication, we show that cumulenes of type **2** are suitable for the synthesis of a variety of heterocyclic sulfur compounds.

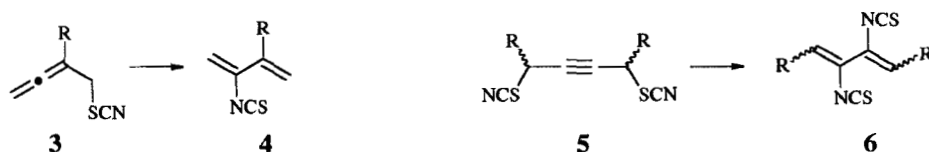
### RING CLOSURE OF ALLENYL ISOTHIOCYANATES

In spite of its pronounced tendency to polymerize, the mustard oil **2** reacts with oxygen-, nitrogen-, sulfur-, or carbon-containing nucleophiles to afford good yields of thiazoles (see Scheme 1). However, cumulenes of type **2** can also be used to prepare other 5-membered or 6-membered heterocyclic sulfur compounds.

SCHEME 1 Reactions of allenyl isothiocyanate **2** with nucleophiles.

### SYNTHESIS OF ISOTHIOCYANATE-SUBSTITUTED 1,3-BUTADIENES

Similar [3,3] sigmatropic rearrangement reactions also allow the preparation of isothiocyanate-substituted 1,3-butadienes (e.g., **3**  $\rightarrow$  **4** and **5**  $\rightarrow$  **6**, see Scheme 2), which are suitable for cycloaddition reactions.

SCHEME 2 Synthesis of isothiocyanate-substituted 1,3-butadienes ( $\text{R} = \text{H}, \text{Me}$ ).

### REFERENCES

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2. K. Banert, H. Hückstädt, and K. Vrobel, *Angew. Chem.*, **104**, 72 (1992); *Angew. Chem. Int. Ed. Engl.*, **31**, 90 (1992).