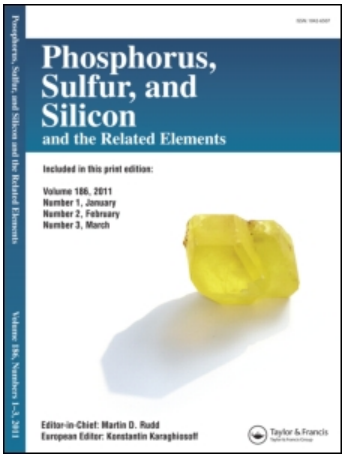

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Synthesis and Reactions of New Vinyl Isothiocyanates

Klaus Bankert[a]; Stefan Groth[a]; Holger Hückstädt[a]; Kai Vrobel[a]
[a] Technische Universität Chemnitz-Zwickau, Institut für Chemie, Chemnitz, Germany

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SYNTHESIS AND REACTIONS OF NEW VINYL ISOTHIOCYANATES[1]

KLAUS BANERT,* STEFAN GROTH, HOLGER HÜCKSTÄDT, AND KAI VROBEL

Technische Universität Chemnitz-Zwickau, Institut für Chemie, Straße der Nationen 62, D-09111 Chemnitz, Germany

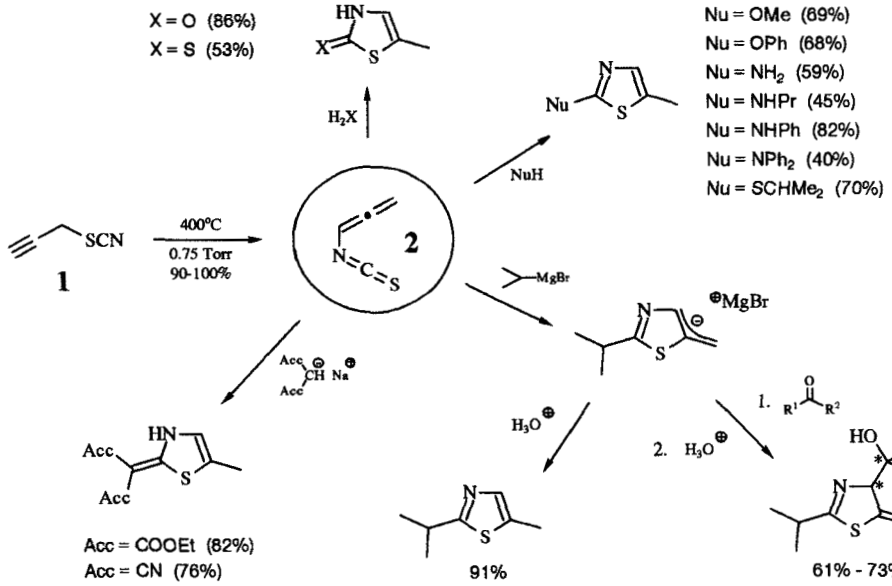
Abstract New vinyl isothiocyanates, which can be prepared from easily accessible thiocyanates by [3,3] sigmatropic shifts, show unusually high reactivity used for the synthesis of heterocyclic sulfur compounds.

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).[2] 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

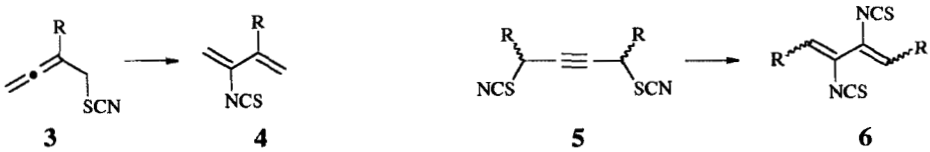
In spite of its pronounced tendency to polymerize, the mustard oil **2** reacts with oxygen-, nitrogen-, sulfur-, or carbon-containing nucleophiles to afford good yields of thiazoles (see Scheme 1). However, cumulenes of type **2** can also be used to prepare other 5-membered or 6-membered heterocyclic 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** → **4** and **5** → **6**, see Scheme 2), which are suitable for cycloaddition reactions.



SCHEME 2 Synthesis of isothiocyanate-substituted 1,3-butadienes (R = H, Me).

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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).