SULFUR DICHLORIDE AS A SULFUR TRANSFER REAGENT IN HETEROCYCLIC SYNTHESIS

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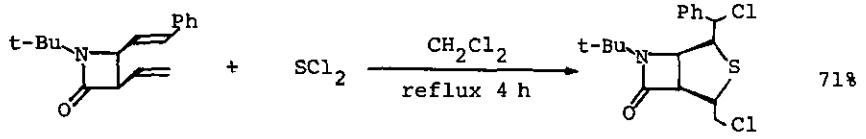
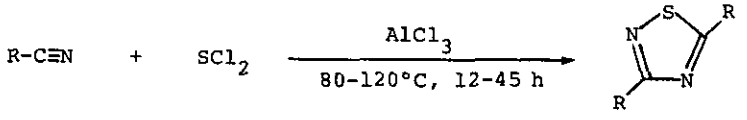
Sulfur dichloride is a highly potential enophilic reagent and easily forms bis(2-chloroalkyl) sulfides upon addition to olefins. However, utilization of sulfur dichloride in synthesis of sulfur-containing heterocycles has been considerably limited in spite of its ready availability and high reactivity.

Here we report several addition reactions of sulfur dichloride to unsaturated bonds such as a non-conjugated diene, a carbon nitrogen triple bond, conjugated azabutadienes, and cumulated double bonds, leading to various sulfur-containing heterocyclic compounds.

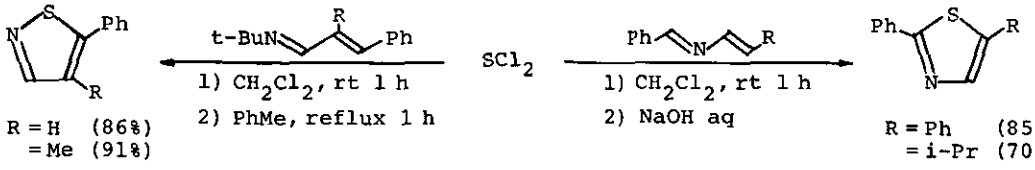
1. Formation of Sulfur-Containing β-Lactam. A 6-thiaisoheptanam derivative was prepared by treating a bisalkenyl-β-lactam with SCl_2 in a good yield. Oxidation and successive dehydrochlorination of the isoheptanam proceeded nearly quantitatively.



2. Formation of 1,2,4-Thiadiazole. Nitriles activated by a Lewis acid such as $AlCl_3$ and $FeCl_3$ reacted with SCl_2 to give the thiadiazoles.



3. Formation of Thiazole and Isothiazole. Sulfur dichloride easily reacted with 1-t-butyl-1-azabutadienes to give isothiazoles via isothiazolium chlorides. The dichloride also reacted with 2-azabutadienes to afford thiazole derivatives.



4. Formation of 1:1 Adduct with Heterocumulene. Addition of SCl_2 across the C=C bonds of ketene and ketenimines occurred to give 1:1 adducts quantitatively. Application of the adducts to synthesis of a benzothiazinone, thiazolinones, and iminothiazolines was studied.