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.

<u>1. Formation of Sulfur-Containing β -Lactam.</u> A 6-thiaisoheptanam derivative was prepared by treating a bisalkenyl- β -lactam with SCl₂ in a good yield. Oxidation and successive dehydrochlorination of the isoheptanam proceeded nearly quantitatively.

$$t-Bu \xrightarrow{N} t + SCl_2 \xrightarrow{CH_2Cl_2} t-Bu \xrightarrow{N} SCl_2 \xrightarrow{CH_2Cl_2} Teflux 4 h \xrightarrow{T} SCl_2 \xrightarrow{T}$$

2. Formation of 1,2,4-Thiadiazole. Nitriles activated by a Lewis acid such as AlCl₃ and FeCl₃ reacted with SCl₂ to give the thiadiazoles.

$$R-C \equiv N + SCl_2 - \frac{AlCl_3}{80-120^{\circ}C, 12-45 h}$$
 $R = Ar, t-Bu$
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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.



Application of the adducts to synthesis of a benzothiazinone, thiazolinones, and iminothiazolines was studied.