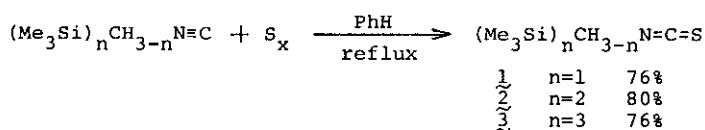


SYNTHESIS OF HETEROCYCLES USING ISOTHIOCYANATOMETHANIDE

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Functionalized isothiocyanates are useful reagents for heterocycle synthesis particularly when a carbanion center can be generated in the α -position relative to nitrogen. The well-known fluoride ion-induced liberation of carbanions from silyl compounds would indicate that silylated methyl isothiocyanate is a suitable precursor for isothiocyanatomethanide.

Trimethylsilylmethyl isothiocyanate (1), bis(trimethylsilyl)methyl isothiocyanate (2), and tris(trimethylsilyl)methyl isothiocyanate (3) were prepared by the addition of sulfur to corresponding silylated methyl isocyanides.



The isothiocyanate 1 was allowed to react with carbonyl compounds in the presence of a catalytic amount of $n\text{-Bu}_4\text{NF}$ to produce the oxazolidine-2-thione derivatives 4. Similarly the isothiocyanate 2 reacted with aldehydes, but the oxazolidine-2-thione derivatives 6 were produced in lower than 6% yield. The styryl isothiocyanate 5 was obtained as a main product in this case. The reaction of the isothiocyanate 3 with benzaldehyde in the presence of a catalytic amount of $n\text{-Bu}_4\text{NF}$ afforded α -(trimethylsilyl)styryl isothiocyanate (7) and 4-benzyl-5-phenyl-4-oxazoline-2-thione (8) in 26% and 7% yields, respectively. The methodology mentioned above was able to be applied to the reaction of 1 and 2 with imines to produce the imidazolidine-2-thione derivatives 9 and 10, respectively. The isothiocyanate 1 also reacted with the azadiene 12 to afford 3-phenyl-4-styryl-imidazolidine-2-thione (11) in 32% yield.

