Trimethylsilyldiazomethane

Compiled by Neil S. Hodnett

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Introduction

The commercially available reagent trimethylsilyldiazomethane1 can be used as a stable and safe alternative to diazomethane in one-carbon homologations, as in the Arndt–Eistert reaction,2 the homologation of carbonyl compounds3,4 and O-methylation of carboxylic acids, phenols and alcohols. Additionally, the reagent can serve as a C–N–N synthon for the preparation of azoles.

Abstracts

(A) Trimethylsilyldiazomethane (TMSCHN₂) reacts rapidly with carboxylic acids in benzene or toluene in the presence of methanol, at room temperature, to afford the methyl esters in very high yields.6 This method is particularly useful in quantitative analysis of fatty acids by gas chromatography.

(B) Both cyclic and acyclic ketones react with TMSCHN₂ in the presence of boron trifluoride etherate to give the ring or chain homologated ketones. The steric bulk of the trimethylsilyl group promotes regioselective methylene insertion.

(C) While TMSCHN₂ will only react with activated nitriles, its lithium salt, TMSC(Li)N₂ reacts smoothly with aromatic, heteroaromatic and aliphatic nitriles to give the corresponding 4-substituted 5-trimethylsilyl-1,2,3-triazoles.7 Reaction of TMSC(Li)N₂ with α,β-unsaturated nitriles can also afford pyrazoles in some cases.

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(D) TMSCHN$_2$ has been employed in asymmetric dipolar cycloadditions with chiral acrylates, to afford optically active $\Delta^2$-pyrazolines. The cycloadditions proceed in high yield with a high degree of diastereoselectivity. This methodology has also been applied to the synthesis of the indolizidine metabolite stellettamide A.$^{12,13}$

(E) TMSCHN$_2$ reacts directly with N-sulfonyl imines to furnish C-silylaziridines in good yields and high cis-stereoselectivities.$^{14,15}$ The resulting products undergo substitution of the silyl group with high diastereoselectivity and ring opening by nucleophiles with complete regioselectivity.

References