TRIMETHYLSILYLDIAZOMETHANE: A NEW SYNTHON FOR THE PREPARATION OF PYRAZOLES

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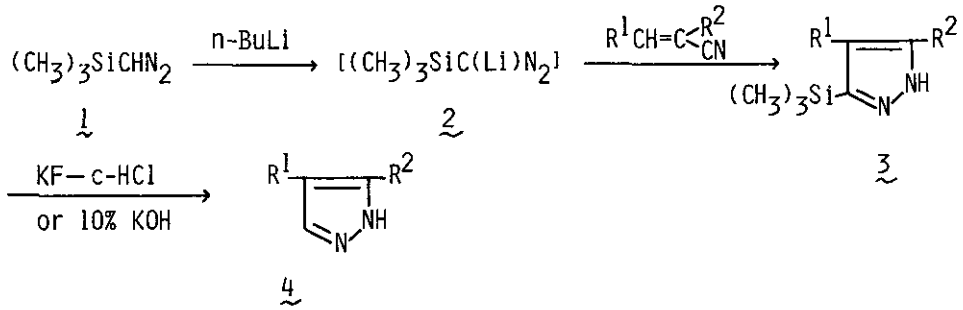
Recently we have reported that trimethylsilyldiazomethane($TMSCHN_2$, $(CH_3)_3SiCHN_2$, 1), as a stable and safe substitute for very hazardous diazomethane, can be effectively used as a [C-N-N] synthon for the preparation of tetrazoles[1] and 1,2,3-triazoles[2]. As an extension of these works[3], a new preparation of pyrazoles using 1 was investigated.

We have found that lithium trimethylsilyldiazomethane (2), easily prepared from 1 and n-butyl lithium, reacts smoothly with α,β-unsaturated nitriles under mild reaction conditions in diethyl ether to give 4-substituted or 3,4-disubstituted 5-trimethylsilylpyrazoles (3) in good yields. Removal of the trimethylsilyl group of 3 has been easily achieved with potassium fluoride-hydrochloric acid or 10% potassium hydroxide in ethanol to afford the corresponding pyrazoles (4). The overall process provides a new method for the preparation of pyrazoles.



1 2 3 4

1) T. Aoyama and T. Shioiri, Chem. Pharm. Bull., 30, 3450 (1982).
2) T. Aoyama, K. Sudo, and T. Shioiri, Chem. Pharm. Bull., 30, 3849 (1982).
3) T. Aoyama, A. Fukushima, and T. Shioiri, to be presented in this Congress.