DEALKYLATION OF TERTIARY AMINES USING TMS REAGENTS

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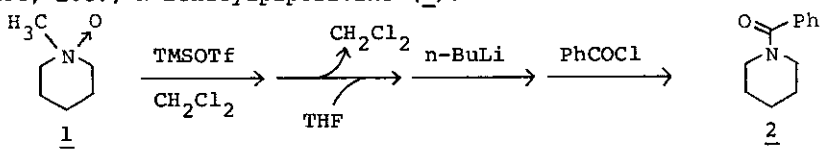
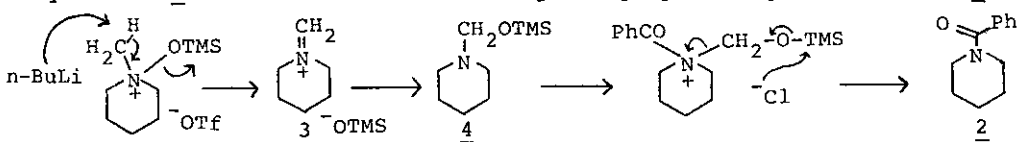
In the course of our studies on the syntheses of nitrogen containing heterocycles, we found a new dealkylation method of tertiary amines using TMS reagents. For example, after N-methylpiperidine was converted to its N-oxide (1) the N-oxide was treated with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dichloromethane, and then with butyllithium and benzoyl chloride in this order after exchange of the solvent into tetrahydrofuran to afford the corresponding dealkylation product, i.e., N-benzoylpiperidine (2).



1 2

The mechanism of the reaction is interpreted in terms of the intermediacy of the immonium salt (3) resulting from deprotonation by butyllithium and N-silyloxymethylamine (4) which reacts with the acylating agent to produce amide (2). This



3 4 2

dealkylation method was general; it occurred not only in the case of cyclic amine N-oxides such as 1 and 5 but also in the case of acyclic amine N-oxides such as 6, 7, and 8, and the amides were obtained in moderate to good yields.

5 6 7 8

Furthermore, this type of dealkylation was applied to carbamate formation; when phenyl chloroformate was used instead of benzoyl chloride in the last step of the reaction, the corresponding carbamates were obtained in all cases (1, 5, 6, 7, and 8).

Transalkylation based on this method will be described.