

Base-promoted Rearrangement of Siloxyammonium Salts: a New Method of Dealkylation of Tertiary Amines *via* Their *N*-Oxides

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Siloxammonium salts prepared from tertiary amine *N*-oxides and trialkylsilyl trifluoromethanesulphonate undergo rearrangement in the presence of strong bases to give α -siloxamines, which can be converted into secondary amine derivatives.

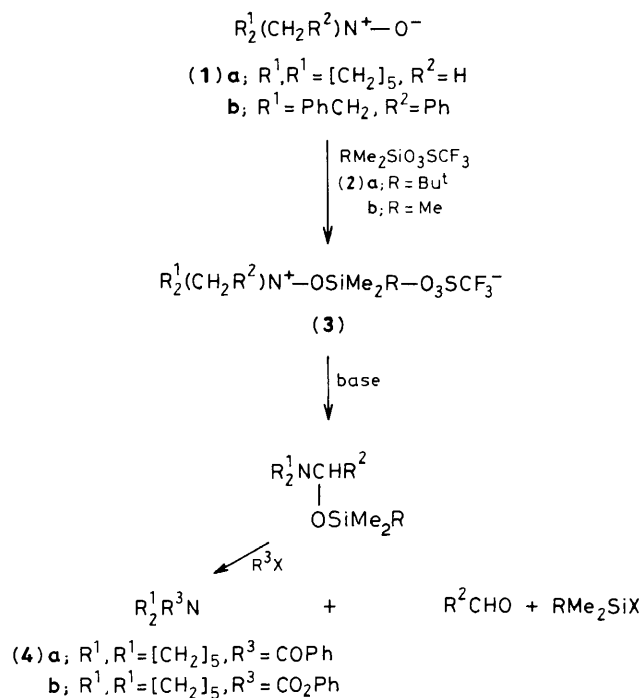
Although base-promoted rearrangements of quarternary ammonium salts (*i.e.* Stevens rearrangement and Sommelet-Hauser rearrangement) have been studied extensively and have become very important reactions from a synthetic point of view, the reactions have so far been limited to those of alkyl- or alkylaryl-substituted ammonium salts.¹

We report here the first example of the base-promoted rearrangement of siloxammonium salts leading to α -siloxamines which eventually give derivatives of secondary amines (Scheme 1).[†]

The siloxammonium salts are easily prepared by the reaction of tertiary amine *N*-oxides with trialkylsilyl trifluoromethanesulphonates.

A typical example is as follows. *N*-Methylpiperidine *N*-oxide (**1a**) (2 mmol) was allowed to react with *t*-butyldimethylsilyl trifluoromethanesulphonate (**2a**) (2.2 mmol) in dichloromethane at 0°C to give (**3**), the quantitative formation of which was confirmed by n.m.r. spectroscopy. After replacement of the solvent by tetrahydrofuran, (**3**) was treated with methyl-lithium (2.6 mmol) at 0°C and then with benzoyl chloride (3 mmol) at room temperature to afford the amide (**4a**) in 76% yield. Similar results were obtained when *n*-butyl-lithium (70%) or *t*-butyl-lithium (73%) was used in place of methyl-lithium. Lithium bis(trimethylsilyl)amide can also be used as the base although the yield is reduced (45%). When trimethylsilyl trifluoromethanesulphonate was used in place of *t*-butyldimethylsilyl trifluoromethanesulphonate, the yields were somewhat decreased [yields of (**4a**): BuLi 50%; Bu^tLi 65%; MeLi 66%; Pr₂NLi 48%; (Me₃Si)₂NLi 49%]. Results using other *N*-oxides are given in Table 1.

Since tertiary amines can be oxidized to the corresponding *N*-oxides almost quantitatively,² this rearrangement provides a new general method for the dealkylation of tertiary amines to secondary amine derivatives. When chloroformate is used instead of acyl chloride, the final product is the corresponding carbamate. For example, (**1a**) was converted into carbamate (**4b**) in 65% yield using (**2b**), *n*-butyl-lithium, and phenyl



Scheme 1

[†] Recently the reaction of tribenzylamine *N*-oxide with *n*-butyl-lithium has been reported to give 1-benzyl-2,3-diphenylaziridine, dibenzylamine, and benzaldehyde: H. Takayama and T. Nomoto, *J. Chem. Soc., Chem. Commun.*, 1982, 408.

Table 1. Formation of amides from tertiary amine *N*-oxides using *t*-butyldimethylsilyl trifluoromethanesulphonate, methyl-lithium, and benzoyl chloride

<i>N</i> - Oxide (1)	Amide (4)	Yield (%) ^a
		76
$(\text{PhCH}_2)_3\text{N}^+\text{O}^-$	$(\text{PhCH}_2)_2\text{NCOPh}$	88 ^b
$\text{PhMe}_2\text{N}^+\text{O}^-$	PhMeNCOPh	51
$\text{Et}_3\text{N}^+\text{O}^-$	Et_2NCOPh	57
$(\text{PhCH}_2)\text{Me}_2\text{N}^+\text{O}^-$	$\text{R}^1\text{R}^2\text{NCOPh}$	81 ^c
		67

^a Isolated yield. ^b Benzaldehyde (56%) was also obtained.^c $\text{R}^1 = \text{R}^2 = \text{Me}$ 52%; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{PhCH}_2$ 29%.

chloroformate. Free amines can be obtained when the reaction mixture is heated with acetic acid (5–10 equiv.); dibenzylamine was obtained in 67% from (1b) using (2a) and

methyl-lithium. When isopentyl nitrite was added to the reaction mixture containing acetic acid (5–10 equiv.), *N*-nitrosodibenzylamine was isolated in 85% yield.

Although a similar conversion of tertiary amine *N*-oxides into amides of secondary amines can be achieved using acid anhydrides (Polonovski reaction),³ the present method has the following advantages. (1) Various derivatives of secondary amines including free amines can be obtained directly using appropriate electrophiles (*i.e.* R^3X in Scheme 1). (2) The Polonovski reaction of aromatic amine *N*-oxides such as *N,N*-dimethylaniline *N*-oxide gives a rearrangement product to the *o*-position of the ring,⁴ whereas the present method affords a dealkylation product (see Table 1).

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