  Bull. Chem. Soc. Jpn., 60, 3291—3297 (1987)

Silicon Polonovski Reaction. Formation and Synthetic Application of α-Siloxy Amines

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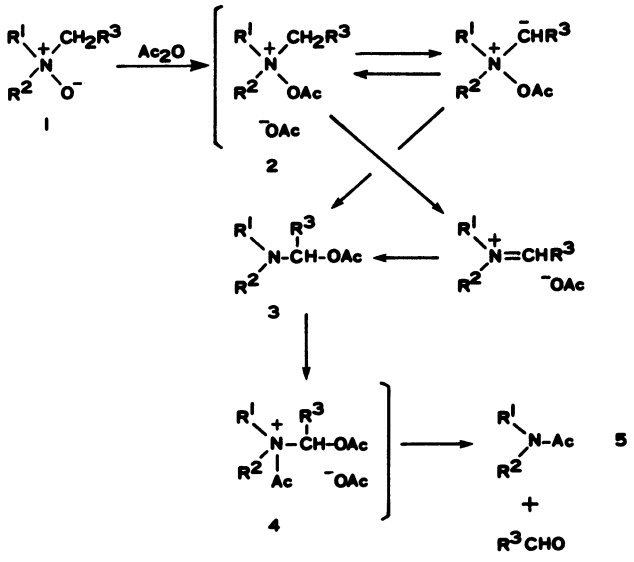
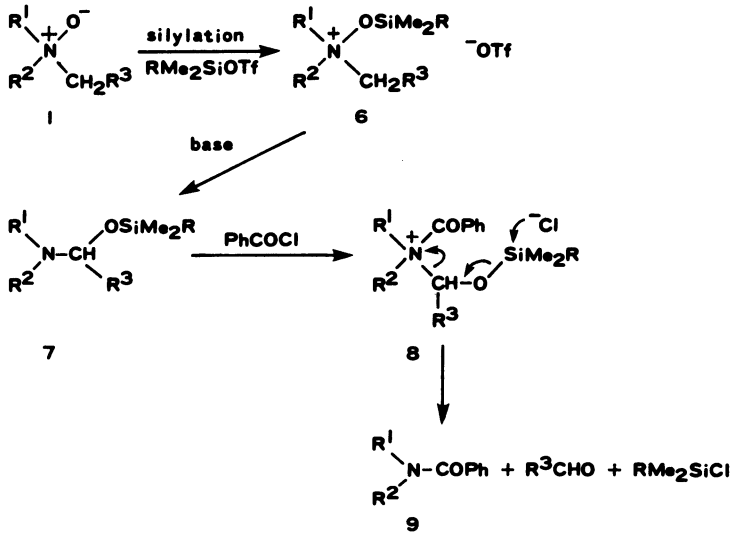
(Received March 20, 1987)

A new and versatile synthetic intermediate, α-siloxy amine was prepared in situ by the base-promoted rearrangement of a siloxyammonium salt obtained by treatment of a tertiary amine *N*-oxide with trialkylsilyl trifluoromethanesulfonate. The best combination of the base and silylating reagent was found to be methyllithium and *t*-butyldimethylsilyl trifluoromethanesulfonate. The reactions of α-siloxy amines with acyl halides and haloformates gave the corresponding amides and carbamates in moderate to good yields, respectively. Treatment of α-siloxy amines with acetic acid resulted in a direct dealkylation to free secondary amines. Fluoride induced alkylation of α-siloxy amines using alkyl halides as electrophiles leading to tertiary amines was also examined and demonstrated to be a new transalkylation method of amines.

Amine *N*-oxides are readily available compounds by oxidation of tertiary amines and the functionalization of the amines taking advantage of the oxidation state of the nitrogen atom seems potentially useful. Actually, the reaction of tertiary amine *N*-oxides with some acid anhydrides is well-known as the Polonovski reaction[1] and is used as a useful dealkylation method for tertiary amines to afford the corresponding amides. The Polonovski reaction is considered to proceed via α-acetoxyamine intermediate **3** which reacts again with the anhydride to give the dealkylated product **5** via ammonium salt **4** (Scheme 1). The use of acid anhydrides necessarily results in the formation of amide **5** as a final product although, in some limited cases, the formation of enamines or Mannich bases have been reported.[2] It occurred to us that the use of siloxyammonium ions **6** instead of acyloxyammonium ions **2** would lead to α-siloxy amine **7** by an appropriate base (Scheme 2). Since **7** can be expected



Scheme 1.



Scheme 2.

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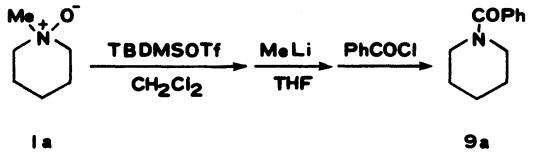
to react with various electrophiles, it would become a useful intermediate in functionalization of tertiary amines. In this article we report that this expectation was indeed fulfilled and tertiary amines could be converted into various types of secondary amine derivatives by this methodology.[3]

Results and Discussion

Rearrangement of Siloxyammonium Salts; Formation of α-Siloxy Amines. Siloxyammonium salts were prepared from the tertiary amine *N*-oxides and trialkylsilyl trifluoromethanesulfonate and subjected to a base-promoted rearrangement leading to α-siloxy amines (Scheme 2). The formation of the siloxy amines was confirmed by trapping with acyl halides to give the corresponding amides. For example, *N*-methylpiperidine *N*-oxide (**1a**) was allowed to react with *t*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) in dichloromethane at 0 °C to give the corresponding siloxyammonium salt **6a**, the quantitative formation of which was confirmed by NMR spectroscopy.[4] After replacement of the solvent by tetrahydrofuran (THF), **6a** was treated with methyllithium at 0 °C and then with benzoyl chloride at room temperature to afford the expected amide **9a** in 76% yield (Eq. 1). The effects of silylating agents and



(1)

1a **9a**

bases on the yields were studied by using the reaction of Eq. 1 and the results are shown in Table 1.[5]

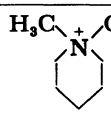
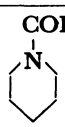
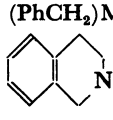
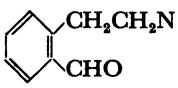
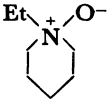
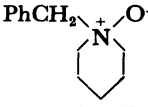
Although alkyllithiums, lithium amides, lithium phenoxide, and potassium *t*-butoxide were effective as a base, methyllithium gave the best result. Tertiary amines such as triethylamine, *N,N*-diisopropylethylamine (Hünig base), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which were often used as a base in the Polonovski reaction, were of no use in the present case probably because their basicity is not high enough to cause rearrangement because of low leaving ability of the siloxyl group. As for a silylating reagent, TBDMSOTf was more effective than TMSOTf.[6] This is most likely due to the steric protection of the silicon atom by the *t*-butyl group which makes the expected deprotonation preferable to the undesirable nucleophilic attack to the silicon atom by the base. Since the best combination of the reagents was found to be TBDMSOTf and methyllithium, this combination is used in the following reactions.

Table 1. Yields of *N*-Benzoylpiperidine (**9a**)

Base	Me_3SiOTf	*t*-$BuMe_2SiOTf$
n-BuLi	50	70
s-BuLi	c)	66
t-BuLi	65	73
MeLi	66	76
$(Me_2CH)_2NLi$[a]	48	c)
$(Me_3Si)_2NLi$[a]	49	45
ArOLi[a,b]	c)	36
t-BuOK[a]	c)	12

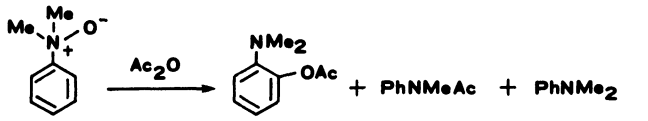
a) These bases were prepared and used as a THF solution. b) Ar=2,6-di-*t*-butyl-4-methylphenyl. c) These combinations were not examined.

Table 2. Amide Formation from Tertiary Amine *N*-Oxides[a]

Entry	*N*-Oxide **1**		Amide **9**		Yield/%[b]
a		**1a**		**9a**	76
b	$(PhCH_2)_3N^+-O^-$	**1b**	$(PhCH_2)_2PCOPh$	**9b**	88[c]
c	$PhMe_2N^+-O^-$	**1c**	PhMeNCOPh	**9c**	51
d	$Et_3N^+O^-$	**1d**	Et_2NCOPh	**9d**	57
e	$(PhCH_2)Me_2N^+-O^-$	**1e**	R^1R^2NCOPh	**9e**, **9e′**	81[d]
f		**1f**		**9f**	67
g		**1g**		**9a**	33
h		**1h**		**9a**	45

a) Used reagents were TBDMSOTf, methyllithium, and benzoyl chloride. b) Isolated yield. c) Benzaldehyde (56%) was also obtained. d) $R^1=R^2=Me$ **9e** 52%; $R^1=Me$, $R^2=PhCH_2$ **9e′** 29%.

Dealkylation of Tertiary Amines. a) Amide Formation. The conversion of several amine *N*-oxides into the corresponding benzamide with TBDMSOTf and methyllithium was carried out, and the results are summarized in Table 2. Since tertiary amines can be oxidized to the corresponding *N*-oxides almost quantitatively, this reaction provides a new general method for the dealkylation of tertiary amines to secondary amine derivatives. Although, as mentioned above, a similar conversion of tertiary amine *N*-oxides into amides of secondary amines can be achieved by the Polonovski reaction using acid anhydrides, the present method has the advantage of affording a dealkylated product selectively in some cases, since the Polonovski reaction of aromatic amine *N*-oxides such as *N*,*N*-dimethylaniline oxide (**1c**) is reported to give a rearranged product, *o*-acetoxy-*N*,*N*-dimethylaniline (**10**), as a main product (Eq. 2).[8] In the case of

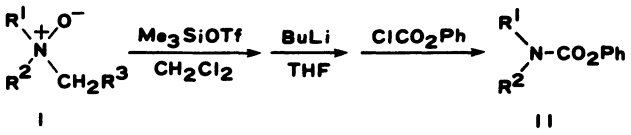


1c 10 (2)

tribenzylamine oxide (**1b**), benzaldehyde, an expected product, was isolated in 56% yield in addition to amide **9b**. The formation of the aldehyde was also confirmed by the isolation of its 2,4-dinitrophenylhydrazone in 56% yield. Furthermore, it is also noteworthy that the product was a benzaldehyde derivative **9f** in the case of 2-methyl-1,2,3,4-tetrahydroisoquinoline *N*-oxide (**1f**), since it suggests that the rearrangement took place regioselectively at the benzyl position.

The results listed in Table 2 suggest that the regioselectivity of this dealkylation is controlled by the acidity of α-hydrogen in the siloxyammonium salts **6** to be deprotonated by the base, and in the cases of **1a** and **1f** the dealkylation proceeded regioselectively to give the amides **9a** and **9f**, respectively.

b) Carbamate Formation. When phenyl chloroformate was used as an electrophile in the reaction with α-siloxy amines, the final product was the corresponding carbamate **11**. The results obtained for the reactions of several tertiary amine *N*-oxides are given in Table 3.



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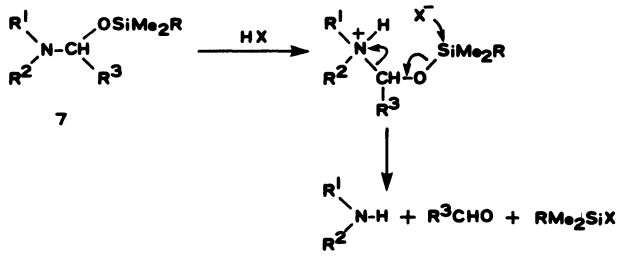
Since the combination of TBDMSOTf and methyllithium was not used in these reactions, the yields of the carbamates have not been optimized.

c) Direct Dealkylation into Secondary Amines. We next examined the direct dealkylation of tertiary amines via α-siloxy amines. If an appropriate protic acid is used as an electrophile, α-siloxy amine **7** is expected to be converted into the corresponding secondary amine (Scheme 3).

As expected, sequential treatment of tribenzylamine oxide (**1b**) with TBDMSOTf, methyllithium, and acetic acid afforded dibenzylamine in 67% yield.

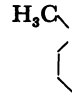
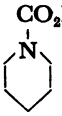
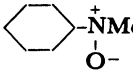
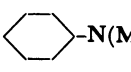
Furthermore, when treatment with acetic acid was carried out in the presence of isopentyl nitrite, *N*-nitrosodibenzylamine was obtained in 85% yield. A similar result was obtained in the case of *N*-methylpiperidine *N*-oxide (**1a**) to give *N*-nitrosopiperidine in 41% yield.

Transalkylation of Tertiary Amines. Although transalkylation reactions (i.e., the replacement of a substituent on the nitrogen atom by other groups) are useful for the introduction of a new functional group



Scheme 3.

Table 3. Carbamate Formation via α-Siloxy Amine[a]

Entry	*N*-Oxide **1**		Carbamate **11**		Yield/%
1		**1a**		**11a**	65
2	$PhMe_2N^+-O^-$	**1c**	$PhMeNCO_2Ph$	**11c**	40
3	$Et_3N^+-O^-$	**1d**	Et_2NCO_2Ph	**11d**	41
4		**1i**		**11i**	23

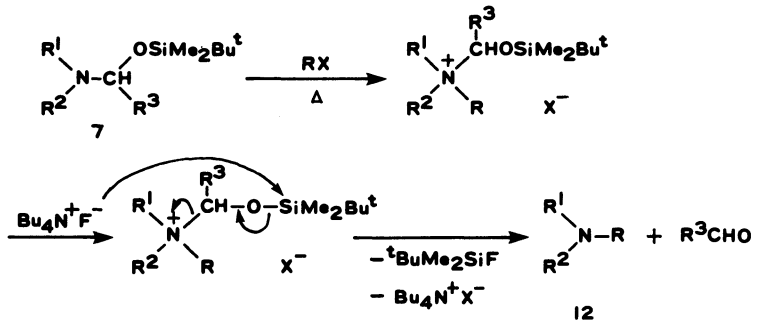
a) TMSOTf, butyllithium, and phenyl chloroformate were used.

into amines, there have been very few reports on direct transalkylation[9] and the conventional methods involve some steps, i.e., dealkylation to free secondary amines and their realkylation.[10] We have found that the use of alkyl halides as an electrophile in the reaction of α-siloxy amines in the presence of fluoride ion results in transalkylation of tertiary amines (Scheme 4). Thus, treatment of α-siloxy amines **7** (obtained in situ from amine *N*-oxides **1**) with alkyl halides followed by desilylation with fluoride ion (n-$Bu_4N^+F^-$/THF) in a sealed tube at 110 °C afforded the corresponding transalkylation products **12** in moderate yields.[11] Results obtained from the reactions of *N*-methylpiperidine *N*-oxide (**1a**) and triethylamine oxide (**1d**) with several alkyl halides are summarized in Table 4. In contrast to the dealkylation reaction by acyl halide or haloformate, this transalkylation proceeds only in the presence of fluoride ion and with heating perhaps due to poor reactivity of alkyl halides in quaternization and to low activating facility of the alkyl group in desilylation step. Of particular note among these results is the introduction of carbonyl functionality into new alkyl groups (entries 4, 5, and 8), which provides a route not only for the prolongation of alkyl chains but for the modification of *N*-alkyl groups, i.e., the formal functionalization of α-position of tertiary amines.

In summary, we have established a new method for a facile formation of α-siloxy amines by "silicon Polonovski reaction," and some successful applications of this versatile synthetic intermediate to the functionalization of amines by the reactions with electrophiles. Although dealkylation of tertiary amines to secondary amine derivatives can be achieved by several methods such as the Polonovski reaction[2] and the von Braun reaction,[12] the present method has the following advantages. (1) Various derivatives of secondary amines including free amines can be obtained directly using appropriate electrophiles. (2) Facile transalkylation reactions of tertiary amines are feasible using fluoride induced desilylation of α-siloxy amines. In view of ready availability of tertiary amine *N*-oxides and a variety of electrophiles and of the achievement of the direct dealkylation and transalkylation of tertiary amines, we believe that the "silicon Polonovski reaction" described here will provide a new convenient synthetic method for nitrogen containing compounds including natural products.

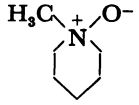
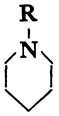
Experimental

All the melting points and boiling points were not corrected. ^1H NMR spectra were measured with Hitachi R-



Scheme 4

Table 4. Transalkylation of Tertiary Amines via Their *N*-Oxides

Entry	*N*-Oxide **1**		RX	Time/h	Product **12**	Yield/%
1		**1a**	$PhCH_2Cl$	10	 **12a**; R=CH_2Ph	58
2		**1a**	n-AmBr[a]	10	**12a**; R=n-Am	45
3		**1a**	n-OcBr[b]	6	**12a**; R=n-Oc	47
4		**1a**	$BrCH_2CO_2Et$	5	**12a**; R=CH_2CO_2Et	38
5		**1a**	$BrCH_2COPh$	10	**12a**; R=CH_2COPh	33
6	$Et_3N^+-O^-$	**1d**	$PhCH_2Cl$	10	Et_2N-CH_2Ph (**12d**)	65
7		**1d**	n-OcBr	10	Et_2N-n-Oc (**12d**)	51
8		**1d**	$BrCH_2CO_2Et$	10	Et_2N-CH_2CO_2Et (**12d**)	31

a) n-Am=$(CH_2)_4CH_3$. b) n-Oc=$(CH_2)_7CH_3$.

24B, Hitachi R-20B (60 MHz), and JEOL JNM-FX90Q (90 MHz) spectrometers using tetramethylsilane as an internal standard. ^{13}C NMR spectra were measured with JEOL JNM-FX90Q. The NMR spectra were measured in deuteriochloroform at room temperature unless otherwise noted. MS spectra were measured with JEOL JMS-D300 mass spectrometer. All the experiments were carried out in argon or nitrogen atmosphere.

Materials. Amine *N*-oxides were prepared by oxidation of the corresponding amines by either 30% hydrogen peroxide or *m*-chloroperbenzoic acid. 2-Methyl-1,2,3,4-tetrahydroisoquinoline[13] and *N*-benzylpiperidine[14] were prepared by the reported method. The other amines used were commercial products.

Formation of Amides. The procedure with *N*-methylpiperidine *N*-oxide (**1a**) is typical.

General Procedure. Transformation of *N*-Methylpiperidine *N*-Oxide (1a) into *N*-Benzoylpiperidine (9a). To a solution of *N*-methylpiperidine *N*-oxide (**1a**) (140.4 mg, 1.22 mmol) in 10 ml of dichloromethane was added *t*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) (355 mg, 1.1 equiv) at 0 °C and the mixture was stirred for 30 min at this temperature. After the replacement of the solvent into 10 ml of THF, to this solution was added methyllithium (1.59 mmol, 1.3 equiv) at 0 °C, during which time an evolution of gas was observed. After stirring for 1 h, to this solution was added 0.21 ml (1.81 mmol, 1.5 equiv) of benzoyl chloride at 0 °C, and the mixture was stirred overnight at room temperature. The solvent was evaporated and the resulting oil was submitted to chromatography (Al_2O_3, hexane–ether 3:1) to afford *N*-benzoylpiperidine (**9a**) (175.3 mg, 76%, oil). The structure of the product was confirmed by the following spectral data and by comparison with an authentic sample. **9a**: ^1H NMR δ=1.6 (brs, 6H), 3.5 (brs, 4H), and 7.35 (s, 5H); MS *m/z* (rel, intensity) 189 (M^+, 16%), 188 (34), 122 (29), 105 (100), and 77 (86).

The amide formation from other *N*-oxides listed in Table 2 were carried out in a similar way. The spectral data of the products were as follows. **9b—e** were identified by comparison of these spectral data with those of anthentic samples prepared by benzoylation of the amines. **9b**: White solid; ^1H NMR δ=4.5 (brs, 4H) and 6.7—7.6 (m, 15H); MS *m/z* 301 (M^+, 3%), 211 (18), 210 (34), 149 (12), 105 (100), 98 (8), 91 (19), 84 (30), and 77 (36). **9c**: Pale yellow oil; ^1H NMR δ=3.48 (s, 3H) and 6.7—7.6 (m, 10H); MS *m/z* 211 (M^+, 21%), 122 (22), 105 (100), and 77 (92). **9d**: Colorless oil; ^1H NMR δ=1.1 (brt, *J*=7 Hz, 6H), 3.0—3.7 (m, 4H), and 7.3 (s, 5H); MS *m/z* 177 (M^+, 18), 176 (25), 105 (100), and 77 (42). **9e**: Colorless oil; ^1H NMR δ=2.93 (s, 6H) and 7.25 (s, 5H). **9e'**: Pale yellow oil; ^1H NMR δ=2.87 (s, 3H), 4.53 (brs, 2H), and 7.27 (s, 5H). **9f**: White paste; ^1H NMR δ=1.9—4.1 (m, 7H), 6.9—7.6 (m, 9H), and 9.81, 10.24 (brd, 1H); ^{13}C NMR (−50 °C) δ=193.75, 193.40, 172.03, 171.13, 140.80, 139.33, 135.84, 135.73, 135.49, 134.49, 133.86, 133.37, 133.21, 131.94, 129.50, 129.01, 128.23, 128.07, 127.36, 126.77, 126.01, 51.46, 48.67, 38.17, 33.15, 31.96, and 30.45; MS *m/z* 267 (M^+, 1%), 161 (22), 149 (11), 148 (29), 136 (12), 132 (5), 119 (5), 118 (39), 106 (9), 105 (100), 91 (6), 90 (16), 77 (31), and 57 (10); High-MS, Found: *m/z* 267.1258. Calcd for $C_{17}H_{17}NO_2$: M, 267.1258.

Trapping of Benzaldehyde. To a solution of tribenzylamine oxide (147.5 mg, 0.49 mmol) in dichloromethane (10 ml) was added TBDMSOTf (142.3 mg, 1.1 equiv). After the solvent exchange into 5 ml of THF, MeLi (0.59 mmol, 1.2 equiv) was added at 0 °C and the mixture was stirred for 30 min. To this yellow solution was added an excess of acidic solution of 2,4-dinitrophenylhydrazine (0.25 g, 1.25 mmol/concd H_2SO_4 1.9 ml/EtOH 19 ml/H_2O 65 ml) and the mixture was stirred vigorously. The red brown precipitates were collected by filtration and dried to give benzaldehyde hydrazone (77.6 mg, 56%), mp 237 °C.[15]

Formation of Carbamates. As a typical example, the procedure with *N*-methylpiperidine *N*-oxide (**1a**) is described.

Transformation of 1a to 11a. To a solution of **1a** (226 mg, 1.97 mmol) in 12 ml of dichloromethane was added TMSOTf (656 mg, 1.5 equiv) and after the replacement of the solvent into THF (15 ml) was added *n*-BuLi (2.96 mmol, 1.5 equiv). To this solution was added 0.37 ml of phenyl chloroformate (462 mg, 1.5 equiv) at 0 °C and the mixture was stirred overnight at room temperature. After the removal of the solvent the residual oil was subjected to chromatography (Al_2O_3, hexane–ether 3:1) to afford the corresponding carbamate **11a** (264.3 mg, 65%) as a white solid.[16] **11a**: ^1H NMR δ=1.5—1.8 (m, 6H), 3.2—3.8 (m, 4H), and 6.8—7.5 (m, 5H); ^{13}C NMR δ=153.68, 151.67, 129.11, 124.97, 121.72, 45.30, 25.74, and 24.30; MS *m/z* 205 (M^+, 10%), 112 (100), 94 (45), 77 (16), and 72 (29).

Other *N*-oxides listed in Table 3 (**1c**, **1d**, and **1i**) were converted into the corresponding carbamates **11c**, **11d**, and **11i** in a similar way to **1a** in 40, 41, and 23% yields, respectively.[17] **11c**: Colorless oil; ^1H NMR δ=3.33 (s, 3H) and 6.5—7.4 (m, 10H); MS *m/z* 227 (M^+, 20%), 134 (100), 106 (34), 94 (42), and 77 (45). **11d**: Pale yellow oil; ^1H NMR δ=1.20 (t, *J*=7.5 Hz, 6H), 4.63 (q, *J*=7.5 Hz, 4H), and 6.8—7.5 (m, 5H); MS *m/z* 193 (M^+, 9%), 100 (100), 98 (15), 94 (12), 77 (7), and 72 (64). **11i**: Colorless oil; ^1H NMR δ=0.9—2.1 (m, 10H), 2.90 (s, 3H), 4.0 (brs, 1H), and 6.7—7.6 (m, 5H); MS *m/z* 233 (M^+, 7%), 140 (50), 94 (100), 83 (73), and 77 (10).

Dealkylation of Tribenzylamine via Its *N*-Oxide. To a solution of tribenzylamine oxide (**1b**) (172 mg, 0.57 mmol) in 10 ml of dichloromethane was added TBDMSOTf (180.6 mg, 1.2 equiv) and after the solvent exchange into THF (10 ml) was added MeLi (0.74 mmol, 1.3 equiv) at 0 °C. After stirring for 1 h at room temperature 0.32 ml (5.6 mmol, 9.8 equiv) of acetic acid was added to the reaction mixture at room temperature and then the mixture was refluxed for 2 h. After removal of the solvent the mixture was shaken with 30 ml of dichloromethane and 5% aq. NaOH solution. The aqueous layer was extracted with dichloromethane (20 ml×2) and the extracts were combined with the organic layer, dried over $MgSO_4$, and concentrated. The resulting oil was subjected to chromatography on alumina (hexane–ether) to give dibenzylamine (75.0 mg, 67%). The ^1H NMR spectrum of the product was consistent with that of an authentic sample.

***N*-Nitrosation Reactions. a) Dibenzylamine.** To a solution of tribenzylamine oxide (**1b**) (213 mg, 0.7 mmol) in 7.5 ml of dichloromethane was added TBDMSOTf (240 mg, 1.3 equiv) and MeLi (0.91 mmol, 1.3 equiv) as described above and after the addition of acetic acid (0.4 ml, 10 equiv) the mixture was refluxed for 1 h. To this mixture was added isopentyl nitrite (0.47 ml, 5 equiv) at room temperature and

then the mixture was refluxed for 1 h. After evaporation of the solvent the residual oil was treated with 50 ml of 5% aq. NaOH solution and 50 ml of dichloromethane. The aqueous layer was extracted with dichloromethane (30 ml×3), and the extracts were combined with the organic layer, dried over $MgSO_4$, and concentrated. The residual oil was submitted to chromatography (Al_2O_3, hexane–CH_2Cl_2 6:1) to give *N*-nitrosodibenzylamine (135.3 mg, 85%) as a white solid; ^{1}H NMR δ=4.61 (s, 2H), 5.14 (s, 2H), and 6.7—7.8 (m, 10H); ^{13}C NMR δ=135.46, 134.81, 129.78, 129.56, 129.26, 129.11, 128.61, 55.76, and 45.85; MS *m/z* 226 (M^+, 11%), 181 (5), 149 (3), 118 (3), 105 (4), 92 (11), 91 (100), and 65 (13); white solid mp 57—8 °C (lit,[18] mp 58 °C).

b) Piperidine. To a solution of **1a** (192.7 mg, 1.68 mmol) in 10 ml of dichloromethane was added TBDMSOTf (532 mg, 1.2 equiv) at 0 °C, and after the solvent exchange into THF (15 ml) was added MeLi (2.1 mmol, 1.25 equiv). To this mixture was added 1 ml (10 equiv) of acetic acid and subsequently 15% ethanol solution of ethyl nitrite (2.5 ml, 3 equiv) and then the mixture was refluxed overnight. The solvent was evaporated and chromatography (Al_2O_3, hexane–ether 3:1) of the residual oil gave *N*-nitrosopiperidine (78.9 mg, 41%); colorless oil; ^{1}H NMR δ=1.2—1.9 (m, 6H), 3.6—3.9 (m, 2H), and 4.1—4.3 (m, 2H); ^{13}C NMR δ=50.84, 39.84, 26.49, 24.78, and 24.22. The properties of the product were identical with those of an authentic sample.[19]

Transalkylation. The procedure with **1a** and benzyl chloride is typical.

a) Transformation of 1a into *N*-Benzylpiperidine. To a solution of **1a** (115.0 mg, 1 mmol) in 10 ml of dichloromethane was added TBDMSOTf (290 mg, 1.1 equiv) and after the solvent exchange into THF (15 ml) was added MeLi (1.2 mmol, 1.2 equiv) at 0 °C. After stirring for 1 h at room temperature, to this solution was added benzyl chloride (0.17 ml, 189 mg, 1.5 equiv) and tetrabutylammonium fluoride (n-$Bu_4N^+F^-$) (THF solution, 1.1 mmol, 1.1 equiv) at room temperature. The mixture was then heated in a sealed tube at 110 °C for 10 h. After the evaporation of the solvent the resulting oil was subjected to chromatography (Al_2O_3, hexane–ether 3:1) to afford *N*-benzylpiperidine (**12a**; R=CH_2Ph) (101.7 mg, 58%). **12a** (R=CH_2Ph):[20] Colorless oil; ^{1}H NMR δ=1.1—1.8 (m, 6H), 2.1—2.5 (m, 4H), 3.5 (s, 2H), and 7.3 (s, 5H); MS *m/z* 175 (M^+, 46%), 174 (49), 98 (53), 92 (16), 91 (100), and 84 (56).

The other transalkylation reactions listed in Table 4 were carried out silimarly. In the case of benzoylmethylation, solid phenacyl bromide was added in one portion. **12a** (R=$(CH_2)_4CH_3$):[21] colorless oil; ^{1}H NMR δ=0.8—1.8 (m, 14H) and 1.9—2.5 (m, 6H); MS *m/z* 155 (M^+, 5%), 100 (8), 99 (9), 98 (100), 70 (6), and 57 (11). **12a**: (R=$(CH_2)_7CH_3$):[22] Colorless oil; ^{1}H NMR δ=0.6—1.8 (m, 21H), and 2.0—2.6 (m, 6H). **12a** (R=$CH_2CO_2CH_2CH_3$):[23] Pale yellow oil; ^{1}H NMR δ=1.27 (t, J=8 Hz, 3H), 1.2—2.0 (m, 6H), 2.4—2.7 (m, 4H), 3.21 (s, 2H), and 4.24 (q, J=8 Hz, 2H); MS *m/z* 171 (M^+, 5%), 157 (2), 127 (2), 114 (3), 99 (12), 98 (100), 86 (21), 84 (34), 71 (16), and 57 (21). **12a** (R=CH_2COPh):[24] Pale yellow oil; ^{1}H NMR δ=1.1—1.9 (m, 6H), 2.2—2.6 (m, 4H), 3.70 (s, 2H), 7.2—7.7 (m, 3H), and 7.9—8.3 (m, 2H). **12d** (R=CH_2Ph):[25] Pale yellow oil; ^{1}H NMR δ=1.00 (t, J=8 Hz, 6H), 2.53 (q, J=8 Hz, 4H), 3.64 (s, 2H), and 7.53 (s, 5H); MS *m/z* 163 (M^+, 5%), 162 (4), 148 (23), 142 (3), 105 (3), 92 (16), 91 (100), 86 (5), 77 (3), and 65 (8). **12d** (R=$(CH_2)_7CH_3$):[26] Colorless oil; ^{1}H NMR δ=0.7—1.9 (m, 15H), 0.89 (t, J=7.5 Hz, 6H), 2.0—2.5 (m, 2H), and 2.40 (q, J=7.5 Hz, 4H); MS *m/z* 185 (M^+, 15%), 170 (4), 142 (42), 100 (15), 91 (100), 58 (10), and 57 (15). **12d** (R=$CH_2CO_2CH_2CH_3$):[27] Pale yellow oil; ^{1}H NMR δ=1.00 (t, J=7.5 Hz, 3H), 1.16 (t, J=7.5 Hz, 6H), 2.57 (q, J=7.5 Hz, 4H), 3.54 (s, 2H), and 4.10 (q, J=7.5 Hz, 2H); MS *m/z* 159 (M^+, 5%), 145 (8), 144 (91), 130 (4), 116 (18), 88 (12), 86 (100), 72 (20), and 58 (25).

The authors are grateful to Shin-etsu Chemical Co. Ltd. for the generous gift of chlorosilanes.

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4) The quantitative formation of siloxyammonium salts **6** was confirmed by the following experiment. To a deuteriochloroform solution (0.5 ml) of **1a** (40 mg, 0.35 mmol) was added TMSOTf (93 mg, 1.2 equiv) under argon at 0 °C in an NMR sample tube. In the ^{1}H NMR spectrum of the mixture a singlet at δ 3.67 due to the *N*-methyl protons of siloxyammonium salts **6a** appeared at the expense of a singlet at δ 3.19 due to the *N*-methyl protons of **1a**. Furthermore, the *N*-α protons of the piperidine ring of **6a** appeared as a multiplet at about δ 3.6, while those of **1a** were observed as a multiplet at about δ 3.2, and the protons of trimethylsilyl group of **6a** were observed at δ 0.48 as a singlet peak. The low-field shift of the *N*-methyl and *N*-α protons suggested the formation of siloxyammonium salt **6a** and the absence of the *N*-methyl signal of **1a** at δ 3.19 showed the almost quantitative conversion into **6a**.

5) Any change in reaction time, temperature, stoichiometry of reactants, and additives did not improve the yield of the amide.

6) Trimethylsilyl chloride can also be used as a silylating agent, but much less effectively as expected from its low silylation ability.[7] The reaction using **1a**, trimethylsilyl chloride, butyllithium and phenyl chloroformate gave the corresponding carbamate in 24%, while the use of TMSOTf under otherwise identical conditions resulted in the yield of 65% (see Table 3).

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