Tandem Brook Rearrangement/Silicon Polonovski Reaction via Oxidative Generation of Ammonium Ylides

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Abstract: A tandem Brook rearrangement/silicon Polonovski reaction has been achieved by in situ generation of ammonium ylides via the oxidation of α-silyl-tertiary amines. Furthermore, we found that the oxidation of N-(1-cyano-1-silyl)methyl-tertiary amines with peracids induced the tandem Brook rearrangement/silicon Polonovski reaction/fragmentation to give formamide derivatives in moderate yields.

Key words: tertiary amine N-oxides, Polonovski reaction, Brook rearrangement, tandem reaction, dealkylation

1 INTRODUCTION

N-dealkylations of tertiary amines using different reagents, such as cyanogen bromide, alkyl chloroformates, azocarboxylic esters, and nitrous acid, are well-established reactions, but they generally require severe experimental conditions, often inducing undesirable side reactions. Among the possible routes, the Polonovski reaction is particularly useful for the N-dealkylation of tertiary amines in mild conditions.

The Polonovski reaction generally proceeds by the treatment of tertiary amine N-oxides with acetic anhydride to give N-acetyl derivatives (Scheme 1). Tertiary amine N-oxides 1 are easily prepared by the oxidation of tertiary amines. After treating 1 with acetic anhydride, the counter-ion (OAc) attacks the N-acetoxy ammonium 2 to give ammonium ylides 3. Subsequently, 3 rearranges to tertiary amines 5, which then reacts with acetic anhydride to give N-acetyl derivatives 7. Depending on the structure of the tertiary amines and the experimental conditions, the reaction is able to stop at the iminium salt 4, which can be used for further reactions such as Mannich reaction.

Following the original work by Polonovski et al., several modifications have suggested in the literature. Okazaki and Tokitoh reported that the activation of amine N-oxides 1 with silyl activators such as tert-butyldimethylsilyl triflate (TBDMSOTf) could give α-siloxy tertiary amines 11, which could then be treated with acetic anhydride to give N-acetyl derivatives 7. This reaction is known as the silicon Polonovski reaction (Scheme 2).

Although the silicon Polonovski reaction is useful for preparing functionalized amines by using α-siloxy tertiary amines 11, relatively strong bases, such as alkyllithium, are...
required to generate ammonium ylides. Undesirable side reactions, most likely associated with the presence of these strong bases, have been reported, including the Hofmann elimination and [1,2]rearrangement\(^{23, 24}\). Therefore, weaker bases or milder reaction conditions compatible with a large variety of functional groups are still desired.

In this regard, the generation of ammonium ylides under mild conditions, in which fluoride ions attack the silyl groups introduced in the alpha position of the quaternary ammonium ions, represents an interesting alternative\(^{25}\). This motivated us to test a modification of the silicon Polonovski reaction, under mild conditions by using functionalized tertiary amines\(^{26}\).

Herein, we report on a modification of the silicon Polonovski reaction for the generation of ammonium ylides under mild conditions without using any strong bases. Ammonium ylides 15 were generated in situ by the cleavage of carbon–silicon bonds with the Brook rearrangement\(^{27}\) of silyl-substituted tertiary amine\(^{28, 29}\) N-oxides 14, then underwent the silicon Polonovski reaction to afford amine derivatives 18 via \(\alpha\)-siloxy tertiary amines 17 (Scheme 3).

Notably, formamides 19 were obtained by the tandem Brook rearrangement/silicon Polonovski reaction/fragmentation in a one-pot manner using tertiary amines with the silyl group in the alpha position relative to the \(N\)-cyanoacetyl group.

To the best of our knowledge, studies on consecutive reactions including the Polonovski reaction have been mainly limited to the synthesis of indole alkaloids. Few reactions involving acyclic amines have been reported\(^{30}\). We therefore chose to use acyclic amine \(N\)-oxides as substrates.

2 Experimental

2.1 General.

Fourier-transform infrared (FT-IR) spectra were acquired on a Jasco FT/IR-4100 FT-IR spectrometer. \(^1\)H and \(^13\)C nuclear magnetic resonance (NMR) spectra were acquired on a 400-MHz JEOL JNM-ALS 400 spectrometer and a 270-MHz JNM-EX270 spectrometer, respectively. Unless mentioned otherwise, deuterated chloroform was used as the solvent, and tetramethylsilane was used as the internal standard. The chemical shifts in the \(^1\)H NMR spectra are reported in parts per million downfield from tetramethylsilane, and those in the \(^13\)C NMR spectra are referenced to the internal solvent standard. Coupling constants \(J\) are given in hertz. Elemental analyses (C, H, N) were conducted using a PerkinElmer 2400 Series II CHNS/O elemental analyzer (2400 Series II). High-resolution mass spectrometry (HRMS) was performed using a Hitachi High-Technologies NanoFrontier LD mass spectrometer. Thin-layer chromatography (TLC) was conducted on precoated Merck TLC plates with silica gel 60 F-254. Column chromatography
was performed using Cica-Merck silica gel 60 (Kanto Chemical Industries). All reagents were obtained from commercial suppliers and used as received. Amine 20 was synthesized by the general N-alkylation of secondary amine 21a. Amines 21a and 35 were synthesized by previously reported methods\textsuperscript{31,32}.

2.2 General procedure for the reaction of tertiary amine 20 with peracid (Table 1).

Unless otherwise mentioned, the reaction was performed with 20a-b and peracid in a 20 mL solution under argon atmosphere.

In the case of entry 1, 1.5 molar equivalents of peracid was added to stirred amine solution 20a (0.5 g, 1.7 mmol) at \(-78^\circ\text{C}\). The reaction mixture was slowly heated up to \(-40^\circ\text{C}\), and then stirred at constant temperature for 5-16 h. The reaction mixture was then slowly heated up to 0°C under stirring for 4 h (the total time for these steps was thus 9-20 h). After quenching with 20 mL of half-saturated aqueous Na\textsubscript{2}SO\textsubscript{4}, the reaction mixture was stirred for 3 h at ambient temperature. The organic layer was removed, and the aqueous layer was extracted with EtOAc (20 mL) for 3 times. The combined organic layer was washed with brine, dried with Na\textsubscript{2}CO\textsubscript{3}, filtered, and evaporated. The residue was purified by column chromatography on silica gel with hexane/EtOAc (3/1) to give the corresponding amine 21a (0.2 g, 46%) as an oil and a trace amount of amine 28 (5.8 mg, 1%).

In the cases of entries 2-5, the quenching method was changed. Instead of 20 mL of half-saturated aqueous Na\textsubscript{2}SO\textsubscript{4}, acetic anhydride (4.8 mL, 51.6 mmol) and pyridine (4.2 mL, 51.6 mmol) were employed. The combined organic layer was washed with sat. aq. CuSO\textsubscript{4} (50 mL), half-saturated Na\textsubscript{2}SO\textsubscript{4} (20 mL), and 1 M aq. NaOH (20 mL) sequentially.

2. (N-methyl)-(N-trimethylsilylmethyl)amino-1-benzoxo-3-methyl-but-3-ene (20a): IR (neat): 2954, 2898, 2857, 2777, 1453, 1248, 1111, 894, 856, 736, 697 cm\(^{-1}\).\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 0.03 (s, 9H), 1.71 (s, 3H), 1.92 (dd, J = 14.4, 29.5 Hz, 2H), 2.21 (s, 3H), 2.92 (t, J = 5.9 Hz, 1H), 3.51 (d, J = 9.8 Hz, 1H), 3.53 (d, J = 9.5 Hz, 1H), 3.65 (d, J = 9.5 Hz, 1H), 3.67 (d, J = 9.8 Hz, 1H), 4.51 (dd, J = 12.1, 14.1 Hz, 2H), 4.85 (s, 1H), 4.91 (s, 1H), 7.25-7.35 (m 5H).\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 12.0, 20.4, 24.7, 46.1, 69.7, 71.9, 73.2, 112.9, 127.4, 127.6, 128.2, 138.3, 144.9.\) Anal. Calcld for C\textsubscript{12}H\textsubscript{11}NOS: C, 70.04; H, 10.03; N, 4.80%. Found: C, 69.77; H, 9.94; N, 4.80%.

6. (N-formyl-N-trimethylsilylmethyl)amino-1-benzoxo-3,7-dimethyl-octa-2,7-diene (21c): IR (neat): 2935, 2857, 1649, 1452, 1398, 1363, 1319, 1089, 1069, 1010, 903, 740, 699 cm\(^{-1}\).\textsuperscript{1}H NMR (270 MHz, CDCl\textsubscript{3}) of a major rotamer: \(\delta 1.64 (s, 3H), 1.65 (s, 3H), 1.76-2.06 (m, 4H), 2.12 (s, 3H), 2.69 (s, 3H), 4.03 (d, J = 6.8 Hz, 1H), 4.51 (s, 2H), 4.87 (s, 1H), 5.00 (s, 1H), 5.11 (dd, J = 4.3, 9.8 Hz, 1H), 5.40 (t, J = 6.7 Hz, 1H), 7.28-7.35 (m, 5H).\textsuperscript{13}C NMR (270 MHz, CDCl\textsubscript{3}) of a minor rotamer: \(\delta 1.66 (s, 3H), 1.70 (s, 3H), 1.76-2.06 (m, 4H), 2.13 (s, 3H), 2.68 (s, 3H), 4.04 (m, 1H), 4.51 (s, 2H), 4.89 (s, 1H), 5.01 (s, 1H), 5.43 (t, J = 6.7 Hz, 1H), 7.28-7.35 (m, 5H).\) The rotamer ratio was 69: 31 on the determination by \textsuperscript{1}H NMR. \textsuperscript{13}C NMR (68 MHz, CDCl\textsubscript{3}) of rotamers: \(\delta 16.7, 16.8, 21.2, 21.3, 21.8, 22.2, 22.9, 27.2, 27.8, 29.4, 35.9, 36.0, 55.7, 61.3, 66.5, 66.6, 72.2, 72.3, 112.6, 113.1, 120.8, 121.6, 127.5, 127.6, 127.7, 127.8, 128.3, 138.4, 139.0, 139.9, 142.9, 143.7, 171.2.\) Anal. Calcld for C\textsubscript{12}H\textsubscript{16}N=O\textsubscript{2}: C, 76.15; H, 9.27; N, 4.44%. Found: C, 75.84; H,
9.28; N, 4.34%.

N-(1-benzoyloxymethyl-2-methyl)-2,3-epoxypropyl-N-methyl-aminomethyl-3-chlorobenoate (28): IR (neat): 2966, 2919, 2861, 1732, 1575, 1453, 1287, 1253, 1051, 994, 749, 698 cm\(^{-1}\). \(^1\)H NMR (270 MHz, CDCl\(_3\)): \(\delta\) 1.73 (s, 3H), 2.67 (s, 3H), 3.35 (t, \(J = 5.4\) Hz, 1H), 3.57 (dd, \(J = 5.4, 8.1\) Hz, 1H), 3.75 (dd, \(J = 5.4, 8.1\) Hz, 1H), 4.48 (dd, \(J = 13.5, 21.6\) Hz, 2H), 4.97 (s, 2H), 5.60 (dd, \(J = 8.1, 10.8\) Hz, 2H), 7.26-7.42 (m, 5H). 7.56 (d, \(J = 12.0\) Hz, 1H), 8.06 (s, 1H). \(^1^3\)C NMR (68 MHz, CDCl\(_3\)): \(\delta\) 44.8, 69.3, 73.2, 73.5, 91.6, 116.2, 127.6, 127.9, 128.3, 129.8, 129.8, 131.7, 133.2, 134.6, 138.0, 142.1, 164.7. Anal. Calcd for C\(_{21}\)H\(_{24}\)ClNO\(_4\): C, 64.69; H, 6.20; N, 3.59%. Found: C, 73.3, 115.0, 115.3, 127.6, 128.3, 137.6, 143.2. H. Shibuya, T. Nakago and S. Inoue et al. J. Oleo Sci. 66, (8) 833-842 (2017).

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2-\((\text{-trimethylsilyl})\) cyanomethyl-N-methyl/aminol-1-5

2.3 General procedure for the synthesis of 4-cyano-4-silylallic amines 29a-e.

Unless otherwise noted, the reaction was performed with tertiary amine 35, silyl reagent, and lithiu diisopropylamide (LDA) in tetrahydrofuran (THF) under argon atmosphere.

To a stirred solution of amine 35 (0.5 g, 2.1 mmol) in 10 mL THF, 2.0-4.0 molar equivalents of silyl reagent was added at \(-78^\circ\)C. After 0.5 h, 2.5-5.0 molar equivalents of LDA solution in THF (1.5 mol L\(^{-1}\), 3.4-6.9 mL) was added, and the reaction solution was stirred at the same temperature for one more hour. After the reaction mixture was slowly heated up to ambient temperature, the volatile compounds in the reaction mixture were evaporated, and the remaining solution was diluted with 15 mL of ether and filtered. The organic layer was washed with sat. aq. NaHCO\(_3\) (5 mL) and separated. The water layer was extracted with EtOAc (10 mL) for three times. The combined organic layer was washed with brine, dried with Na\(_2\)SO\(_4\), and evaporated. The residue was carefully purified by column chromatography on silica gel with hexane/ether (15/1) to give an oil containing the corresponding amines 29a-d in the following amounts: 29a, 0.3 g (Y. 39%); 29b, 0.3 g (Y. 46%); 29c, 0.4 g (Y. 53%); 29d, 0.4 g (Y. 49%). Meanwhile, 0.4 g of amine 29e was obtained (Y. 44%) by replacing amine 35 with the corresponding geranyl amine.

2-(N-cyanomethyl-N-methyl) amino-1-benzoylozy-3-methylbut-1-ene (29e): IR (neat): 2946, 2917, 2863, 2798, 1454, 1112, 907, 741, 699 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.70 (s, 3H), 2.37 (s, 3H), 3.11 (dd, \(J = 4.0, 6.0\) Hz, 1H), 3.52-3.68 (m, 4H), 4.52 (dd, \(J = 11.6, 21.6\) Hz, 2H), 4.95 (dd, \(J = 1.6, 11.6\) Hz, 1H), 5.02 (s, 1H), 5.03 (s, 1H), 7.25-7.34 (m, 5H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 18.9, 40.4, 43.9, 68.1, 71.3, 73.3, 115.0, 115.3, 127.6, 128.3, 137.6, 143.2. Anal. Calcd for C\(_{15}\)H\(_{20}\)N\(_2\): C, 73.74; H, 8.25; N, 11.47%. Found: C, 73.51; H, 8.23; N, 11.44%.

6-(N-cyanomethyl-N-methyl) amino-1-benzoylozy-3,7-di-tetramethyleth-2,7-diene as a starting material of 29e: IR (neat): 3066, 3029, 2946, 2860, 2795, 1649, 1496, 1452, 1372, 1330, 1204, 1121, 1070, 1028, 906, 861, 739, 699 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.40-1.89 (m, 4H), 1.61 (s,
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α

400 MHz, CDCl3 δ 6.6, 1H δz 2.76

Amine 1453, 1366, 1255, 1070, 841, 823, 807, 737 cm −1.

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washed with 1 N aq. NaOH

extracted with EtOAc

2.4 General procedure for the reaction of α-cyano-α-silylalloy amino-1-benzamidoxo-3,7-dimethylocta-2,7-diene (29e) as a mixture of reactants: IR (neat): 2953, 2931, 2858, 1466, 1453, 1366, 1255, 1070, 841, 823, 807, 737 cm −1. 1H NMR (400 MHz, CDCl3) δ 0.20 (s, 3H), 0.97 (s, 3H), 1.41-1.92 (m, 4H), 1.63 (s, 3H), 1.65 (s, 3H), 2.24 (s, 3H), 2.76 (dd, J = 3.9, 10.5 Hz, 1H), 3.54 (s, 1H), 4.02 (d, J = 6.6 Hz, 2H), 4.51 (s, 1H), 4.89 (s, 1H), 4.94 (s, 1H), 5.39 (t, J = 6.6, 1H), 7.26-7.35 (m, 5H). 13C NMR (100 MHz, CDCl3) δ -65.5, -5.7, 16.6, 17.5, 18.1, 26.4, 26.8, 36.7, 39.2, 40.6, 66.6, 71.4, 72.2, 115.0, 117.6, 121.1, 127.4, 127.7, 128.3, 138.4, 139.8, 143.7. HRMS (EI−TOF) m/z: [M + ] + Calcd for C28H34N2O5Si 426.3056; Found 426.3066.

2.4 General procedure for the reaction of α-cyano-α-silylalloy amino-1-benzamidoxo-3,7-dimethylocta-2,7-diene (29e) as a mixture of reactants: IR (neat): 2953, 2931, 2858, 1466, 1453, 1366, 1255, 1070, 841, 823, 807, 737 cm −1. 1H NMR (400 MHz, CDCl3) δ 0.20 (s, 3H), 0.97 (s, 3H), 1.41-1.92 (m, 4H), 1.63 (s, 3H), 1.65 (s, 3H), 2.24 (s, 3H), 2.76 (dd, J = 3.9, 10.5 Hz, 1H), 3.54 (s, 1H), 4.02 (d, J = 6.6 Hz, 2H), 4.51 (s, 1H), 4.89 (s, 1H), 4.94 (s, 1H), 5.39 (t, J = 6.6, 1H), 7.26-7.35 (m, 5H). 13C NMR (100 MHz, CDCl3) δ -65.5, -5.7, 16.6, 17.5, 18.1, 26.4, 26.8, 36.7, 39.2, 40.6, 66.6, 71.4, 72.2, 115.0, 117.6, 121.1, 127.4, 127.7, 128.3, 138.4, 139.8, 143.7. HRMS (EI−TOF) m/z: [M + ] + Calcd for C28H34N2O5Si 426.3056; Found 426.3066.

3 RESULTS

3.1 Tandem Brook rearrangement/silicon Polonovski reaction

First, we examined the silicon Polonovski reaction for the generation of ammonium ylides under mild conditions without any strong bases. Amines 20 were treated with peracid under different reaction conditions. The results are summarized in Table 1. Fortunately, the silicon Polonovski reaction smoothly proceeded to give the corresponding amine or amide depending on the work-up manners. Treatment of 20a with peracetic acid in THF gave the corresponding amine 21a (entry 1). It should be noted that the combination of peracetic acid and the relatively low-polarity solvent DCM gave the amide 21b in good yield (Entry 4).

The putative reaction mechanism when acetic anhydride is the quenching reagent is described in Scheme 4. Ammonium ylides 23 were generated by the cleavage of the carbon–silicon bond in the Brook rearrangement of tertiary amine N-oxides 22, which underwent subsequent silicon Polonovski reaction (from 23 to 25). The final fragmentation step (from 25 to 21) was induced by the addition of
acetic anhydride.

Interestingly, a small amount of tertiary amine 28 was obtained concomitantly. The iminium salt 24 reacted with mCPBA (a byproduct of mCPBA) to undergo exchange with the counter-anion (from 24 to 26). The attack by the counter-anion (chlorobenzoic anion) toward the iminium salt 26, followed by the oxidation, gave 28 (Scheme 5).

These synthetic routes, presented in Schemes 4 and 5, significantly contrast to that of the general silicon Polonovski reaction. Thus, the generation of ammonium ylides 23 followed by the formation of iminium salt 24 can be achieved without using a strong base.

### 3.2 Tandem Brook rearrangement/silicon Polonovski reaction/fragmentation

Although the tandem Brook rearrangement/silicon Polonovski reaction was achieved, a final fragmentation step (25 to 21), as described in Scheme 4, was necessary in the presence of an electrophilic reagent. We thus turned our attention to the tandem Brook rearrangement/silicon Polonovski reaction/fragmentation as a one-pot synthesis. To enable the successive reaction, the substituent, which serves as an eliminating group in the final step, was introduced to the amine 20. We thus synthesized α-cyano-α-silylallylic amines 29 and examined the reaction of amines 29 with peracetic acid in DCM. The results are summarized in Table 2.

Fortunately, the silicon Polonovski reaction proceeded smoothly to give the corresponding formamides 30. When using 29a-b, which carry relatively small silyl groups, [2,3] sigmatropic rearrangement of the tertiary amine N-oxide was achieved.

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**Table 1** Reaction of amines 20 with peracid.

| Entry | Amine | Peracid | Solvent | Time/h | Product | Yield/% |
|-------|-------|---------|---------|--------|---------|--------|
| 1<sup>a</sup> | 20a | AcO₂H | THF | 20 | 21a | 46 |
| 2<sup>a</sup> | 20a | mCPBA | THF | 10 | 21b | 58 |
| 3<sup>a,b</sup> | 20a | mCPBA | DMF | 12 | 21b | 60 |
| 4<sup>a</sup> | 20a | AcO₂H | DCM | 8 | 21b | 99 |
| 5<sup>a</sup> | 20b | AcO₂H | THF | 9 | 21c | 64 |

<sup>a</sup> Isolated yield.  
<sup>b</sup> The reaction was quenched with half-saturated aqueous sodium sulfite.  
<sup>c</sup> The reaction was quenched with acetic anhydride.  
<sup>d</sup> The reaction was conducted at −50°C.

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Putative reaction mechanism for amine 20 with peroxide.

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occurred concomitantly with the sequence of reactions (entries 1 and 2). It should be noted that 29c-e, which possess bulky silyl groups, underwent the tandem reactions predominantly to give formamides 30 in moderate yields (entries 3 and 4). In addition, the present reaction was adapted to the relatively bulky amine 29e (Entry 5).

The synthesis of formamides 30 may include subsequent fragmentation steps (Scheme 6). These fragmentation steps may occur via the following pathways: (A) the cyano group is eliminated to form the iminium salt 34, and then the cyano anion attacks the silyl group \( R^7 \) and/or (B) the generated catalytic amount of the cyano anion attacks \( R^7 \), causing the elimination of the cyano group. This tandem Brook rearrangement/silicon Polonovski reaction/fragmentation reaction is advantageous over the conventional reaction \(^8, 9, 13-22\) because it can afford formamides directly using peracid only, without requiring an electrophilic reagent.

Meanwhile, the standard base-promoted silicon Polonovski reaction of tertiary amine \( N \)-oxide 35 gave a more complex mixture (Scheme 7). When using acyclic amine \( N \)-oxide, it is difficult to carry out the silicon Polonovski reaction because of competition from the [2,3] sigmatropic rearrangement of amine \( N \)-oxide in the basic condition.

Furthermore, we investigated the ammonium ylide 32 intermediate to determine whether the [2,3] sigmatropic rearrangement \(^{25, 33-35}\) would happen. The results revealed that [2,3] sigmatropic rearrangement did not occur due to the instability of the ylide, and the silicon Polonovski reaction predominated (Scheme 8).

### Table 2  Reaction of amines 29 with peracetic acid.

| Entry | Amine | \( R^7 \) | Product | Yield/%a |
|-------|-------|----------|---------|----------|
| 1     | 29a   | TMS      | 30a     | 25       |
| 2     | 29b   | TES      | 30a     | 37       |
| 3     | 29c   | TBDMS    | 30a     | 44       |
| 4     | 29d   | TIPS     | 30a     | 61       |
| 5     | 29e   | TBDMS    | 30b     | 50       |

a) Isolated yield.

**4 CONCLUSION**

We found that the oxidation of tertiary amine \( N \)-oxides
carrying silyl groups led to the generation of ammonium ylides by the Brook rearrangement, promoting a subsequent silicon Polonovski reaction to give amine derivatives. Furthermore, tertiary amines possessing silyl groups in the alpha position of N-cyanomethyl group underwent the tandem Brook rearrangement/silicon Polonovski reaction/fragmentation to give formamides. The present tandem sequence could be achieved using peracid only, without adding any strong bases. Moreover, N-dealkylation could occur at a silyl group of the alkyl chain. The present method has some advantages over the standard silicon Polonovski reaction, which requires very strong bases. We will report on its application to the synthesis of N-containing compounds in due course.
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