N-(α-Aminoalkyl)benzotriazoles: Novel "Nonstabilized" α-Aminocarbanion Synthons

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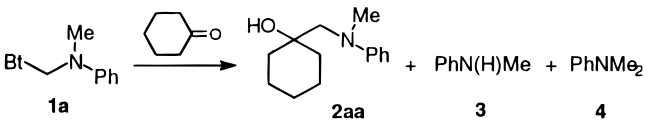
C−Benzotriazole bonds were selectively transformed to give the corresponding α-aminocarbanions when *N*-(α-aminoalkyl)benzotriazoles were reacted with either Li/LiBr or SmI_2 in the presence of representative electrophiles. The ranges of applicability of the two reagents complement each other, and together the two protocols provide a general route from readily available crystalline starting materials to a variety of "nonstabilized" α-aminocarbanions that can be trapped in moderate to good yields.

Introduction

α-Aminocarbanions comprise a most important class of functionalized organolithium compounds of great interest as synthetic intermediates.[1] "Stabilized" α-aminocarbanions, in which a temporary activating group is attached to the nitrogen atom, are well known and extensively exploited in synthetic organic chemistry.[1−3] Although "nonstabilized" α-aminocarbanions were observed as early as 1965,[4] they have received much less attention than the "stabilized" type, mainly due to the lack of appropriate methods for their generation. Most synthetic routes to "nonstabilized" α-aminocarbanions are based on the following methods: (i) direct lithiation by a powerful base, which succeeds only for a few specific examples;[5] (ii) direct lithiation of an amine−Lewis acid complex;[6] (iii) transmetalation of α-aminoorganotin compounds[7] that, although undergoing facile lithiation and subsequent reactions, suffer difficulties of starting material synthesis (see, however, ref 7d,e) and byproduct separation (*e.g.*, Bu_4Sn); (iv) reductive lithiation of α-thio,[8] α-cyano,[9] and α-alkoxy amines[10] or -imines[11] by lithium or potassium metals; (v) SmI_2-mediated amine metalation for the special case of *N*-(*o*-iodobenzyl)amines.[12] Notably, none of the aforementioned literature methods involves a C−N bond transformation for the preparation of α-aminocarbanions.

Scheme 1



Reaction conditions	2aa	3	4
Li, -78 °C, 2h; H_2O, -78 °C	47%	24%	23%
Li, -78 ~ 0 °C, 8h; H_2O, 0 °C	very low	29%	42%
Li, LiBr, -78 °C, 4h; H_2O, -78 °C	70%	12%	16%
Li, LiBr, -78 ~ 0 °C, 8h; H_2O, 0 °C	62%	16%	22%

Recently, we found that C−benzotriazole bonds could be transformed into the corresponding carbanions[13] *via* reductive lithiation. This result encouraged us to investigate the possibility of converting *N*-(α-aminoalkyl)benzotriazoles into the corresponding α-aminocarbanions: this has resulted in the present paper, which outlines new methodology providing a facile and novel method to synthesize α-aminocarbanions as reactive intermediates. Reactions of these intermediates with electrophiles lead directly to polyfunctionalized molecules.

Results and Discussion

Li/LiBr Reactions. Reactions between *N*-[(*N*-phenyl-*N*-methylamino)methyl]benzotriazole (**1a**) and cyclohexanone were first attempted under various reaction conditions (Scheme 1, all yields in this scheme are GC/MS yields). These results showed that lithium alone worked to give a moderate yield of the desired 1,2-amino alcohol **2aa** at low temperature. However, when the reaction was quenched at 0 °C, the yield of compound **2aa** was reduced dramatically, to be barely detectable by GC/MS. Addition of 1 equiv of LiBr to the reaction mixture not only raised the yield (70% GC/MS, 58% isolated) but also stabilized the product before being quenched (62% GC/MS after quenching at 0 °C), whereas use of the Lewis acid $BF_3{\cdot}Et_2O$ as an additive resulted only in a very

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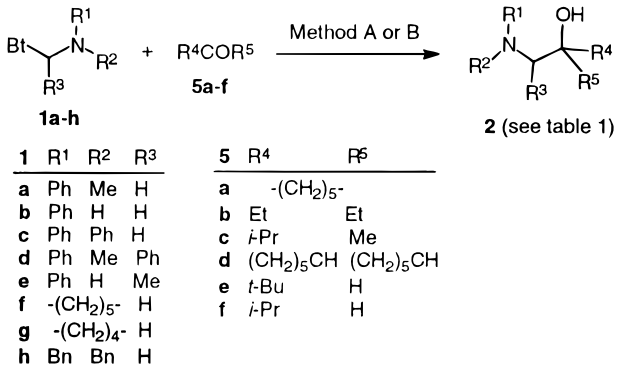
Scheme 2[a]



1	R1	R2	R3
a	Ph	Me	H
b	Ph	H	H
c	Ph	Ph	H
d	Ph	Me	Ph
e	Ph	H	Me
f	-(CH2)5-		H
g	-(CH2)4-		H
h	Bn	Bn	H

5	R4	R5
a	-(CH2)5-	
b	Et	Et
c	*i*-Pr	Me
d	(CH2)5CH	(CH2)5CH
e	*t*-Bu	H
f	*i*-Pr	H

[a] Method A: (i) Li, LiBr, THF, −78 °C, 4h; (ii) H_2O, −78 °C. Method: SmI_2, THF, 0 °C, 2−4 h.

Table 1. Preparations of β-Amino Alcohols 2

2	R1	R2	R3	R4	R5	reagent	yield, %
aa	Ph	Me	H	−(CH2)5−		Li/LiBr	58
aa	Ph	Me	H	−(CH2)5−		SmI_2	65
ab	Ph	Me	H	Et	Et	SmI_2	70
ae	Ph	Me	H	*t*-Bu	H	Li/LiBr	52
af	Ph	Me	H	*i*-Pr	H	SmI_2	70
be	Ph	H	H	*t*-Bu	H	Li/LiBr	50
cb	Ph	Ph	H	Et	Et	Li/LiBr	48
cc	Ph	Ph	H	*i*-Pr	Me	SmI_2	75
da	Ph	Me	Ph	−(CH2)5−		Li/LiBr	45
ea	Ph	H	Me	−(CH2)5−		Li/LiBr	40
gd	−(CH2)4−		H	(CH2)5CH	(CH2)5CH	SmI_2	54
hb	$PhCH_2$	$PhCH_2$	H	Et	Et	SmI_2	63

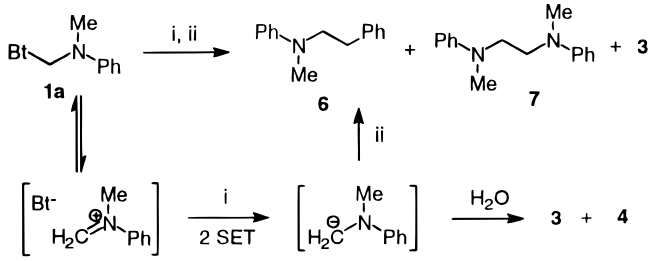
complex mixture. As seen from Scheme 1, *N*-methylaniline (**3**) was always formed as one of the byproducts in yields of 12−29%. This was obviously due to the breakage of the C−NPh(Me) bond rather than the C−Bt bond because of competition reactions of the two C−N bonds in the starting material. Another byproduct **4** was formed from the expected C−Bt bond scission.

A variety of other benzotriazole derivatives (**1b**−**e**) and carbonyl compounds (**5a**,**b**,**e**) have been employed in this reaction (Scheme 2, method A). The results are summarized in Table 1. It is noteworthy that various types of different benzotriazole adducts, from *N*-substituted anilines **1a**,**c**,**d** and *N*-unsubstituted anilines **1b**,**e**, with the α-carbon unsubstituted **1a**−**c** or substituted **1d**,**e**, all reacted with ketones **5a**,**b** or aldehydes **5e** to give preparatively useful yields of 1,2-amino alcohols **2**.

A complex mixture was obtained from the attempted reaction of *N*-(piperidinylmethyl)benzotriazole (**1f**, Scheme 2) with cyclohexanone, probably due to the low selectivity of the two C−N bonds present in compound **1f**. Upon comparison of the results from **1a**,**c**,**f**, it is clear that (α-aminoalkyl)benzotriazoles with a phenyl group connected to the nitrogen have higher C−Bt bond scission selectivities.

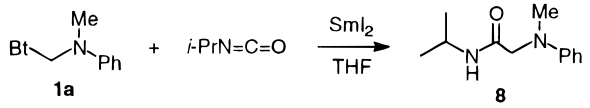
When *N*-[(*N*-phenyl-*N*-methylamino)methyl]benzotriazole (**1a**) was exposed to Li/LiBr in THF at −78 °C for 30 min, only *N*-methylaniline (**3**, 27%) and *N*,*N*-dimethylaniline (**4**, 73%) were found by GC/MS after the reaction mixture was quenched with water (Scheme 3). This indicates that compound **1a** can be reduced to the expected carbanion in the absence of an electrophile. No dimer of the (*N*-phenyl-*N*-methylamino)methyl radical was detected, which suggests that the immonium cation produced from *N*-[(*N*-phenyl-*N*-methylamino)methyl]benzotriazole (**1a**) could be reduced very quickly to the corresponding carbanion. However, when the preformed

Scheme 3[a]



[a] Key: (i) Li/LiBr, −78 °C, 30 min; (ii) $PhCH_2Br$.

Scheme 4



reactive intermediate reacted with benzyl bromide, *N*-methyl-*N*-phenethylaniline (**6**) was obtained together with some radical dimer *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-1,2-diethylamine (**7**).[14] Tsunoda *et al.*[8b] reported a similar observation of the formation of the amine dimer. This two-step reaction was not explored further in view of the successful reaction of *N*-(α-aminoalkyl)benzotriazoles and Grignard reagents to afford unsymmetrical tertiary amines of type **6**, as we reported previously.[15]

SmI_2 Reactions. In the previous paper,[13] we found that samarium diiodide could not convert *N*-(diphenylmethyl)benzotriazole into the correponding carbanion. However, it was found that *N*-[(*N*-phenyl-*N*-methylamino)methyl]benzotriazole (**1a**) did react with ketones in the presence of SmI_2 at 0 °C (Scheme 2, Method B).[16] The addition sequence in this reaction is very important. While addition of compound **1a** and cyclohexanone in THF solution to SmI_2 produced 71% (GC/MS, 65% isolated) of product **2aa** together with 29% (GC/MS) of methylaniline, the reverse mode of addition formed only 25% (GC/MS) of product **2aa** accompanied with the amine dimer **7** (10% GC/MS) due to the shortage of SmI_2 to reduce the radical to the desired carbanion.[17] Similarly, reaction of compound **1a** with other ketones formed the expected products **2ab**,**cc**,**gd**,**hb** in 54−75% isolated yield (Table 1). Isobutyraldehyde can be used under the same reaction conditions without any pinacol coupling problem, in contrast to a report[12b] that a two-step procedure is necessary to avoid pinacol coupling. Isopropyl isocyanate reacted with **1a** to produce amino acid derivative **8** in 68% yield (Scheme 4).

This samarium diiodide method possesses some advantages over the Li/LiBr reaction. First, the reaction

(14) (a) Reduction of (α-aminoalkyl)benzotriazoles in the absence of electrophiles to give diamines has been reported. Aurrecoechea, J. M.; Fernández-Acebes, A. *Tetrahedron Lett.* **1992**, *33*, 4763. (b) Giezendanner, H.; Hesse, M.; Schmid, H. *Org. Mass Spectrom.* **1970**, *4*, 405.

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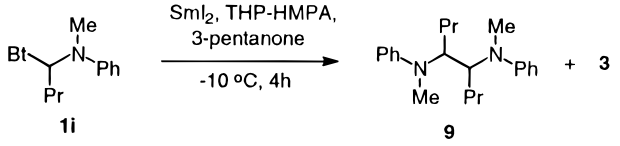
(16) Intramolecular cyclization of α-amino radicals derived from *N*-(α-benzotrizolylalkyl)alkenylamines and samarium diiodide has recently been reported. Aurrecoechea, J. M.; Fernández-Acebes, A. *Synlett* **1996**, 39.

(17) It has been proposed that many SmI_2-promoted reactions proceed by means of unstable organosamarium(III) intermediates: (a) Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050. (b) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943. (c) Walborsky, H. M.; Topolski, M. *J. Org. Chem.* **1992**, *57*, 370. (d) Molander, G. A.; Mckie, J. A. *J. Org. Chem.* **1991**, *56*, 4112.

Scheme 5



conditions are milder and the dissipation of the deep blue color of SmI_2/THF can be used as an indicator of complete reaction. Second, under these milder conditions, the scission of two C−N bonds creates higher selectivities, and alkylamine benzotriazole adducts (cyclic amine **1g** and acyclic amine **1h**) could be converted into the corresponding α-alkylaminocarbanions. Moreover, no *N*,*N*-dimethylaniline (**4**) was observed in any of these SmI_2 reactions.

However, the reaction of *N*-[(*N*-phenyl-*N*-methylamino)benzyl]benzotriazole (**1d**) with 3-pentanone using this SmI_2 procedure gave a complex mixture. When the reactions were repeated using SmI_2 in the mixed solvent THF−HMPA at 0 °C or −20 °C, *N*-benzyl-*N*-methylaniline was the only product obtained. Probably, SmI_2/THF−HMPA reduces the C−Bt bond and transforms **1d** into a secondary carbon radical, which abstracts a proton more quickly than being reduced further to the carbanion. Reportedly, carbon and nitrogen substituents stabilize α-aminoalkyl radicals,[18] and secondary carbon radicals are more difficult to reduce than their primary analogs.[19]

To overcome the problem of proton abstraction from solvent, SmI_2/THP−HMPA[12] was employed instead of SmI_2/THF−HMPA. The reaction of *N*-[(*N*-phenyl-*N*-methylamino)butyl]benzotriazole (**1i**), 3-pentanone (1 equiv), and SmI_2 (2.2 equiv)/THP−HMPA only gave *N*,*N*′-diphenyl-*N*,*N*′-dimethyl-1,2-dipropylethylenediamine (**9**, 75% GC/MS, 71% isolated) and *N*-methylaniline (**3**, 25% GC/MS) (Scheme 5). The absence of *N*-butylaniline in the GC/MS spectra showed that THP did suppress the hydrogen abstraction of radicals from solvent. However, the α-aminoalkyl radicals could not be reduced to the corresponding carbanions under these conditions but dimerized to give **9**. Therefore, for the α-alkyl-substituted benzotriazole reactions, Li/LiBr has to be used.

The origin of byproduct *N*,*N*-dimethylaniline (**4**), formed only from the Li/LiBr reactions but not from SmI_2 reactions, is uncertain. However, the most probable pathway is the proton abstraction by an intermediate lithium species from THF[8a] or a carbonyl compound.[8b,11] This interpretation is based on the following facts: (i) the radical should not be the source of *N*,*N*-dimethylaniline because otherwise the radical dimer should be detected in the Li/LiBr reactions; in addition, no *N*,*N*-dimethylaniline was found in any of the SmI_2 reactions even in the one case when the dimer was detected; (ii) the organosamarium species are much softer and less basic than the lithium reagents, so it is reasonable that there is no *N*,*N*-dimethylaniline detected from the SmI_2 reactions. The above considerations also suggest that α-aminocarbanion intermediates rather than α-aminoalkyl radicals are involved in both the Li/LiBr and SmI_2 reactions. That only the radical dimer **9**, but no expected products, are obtained in the reaction of **1i** (Scheme 5) also supports this mechanistic interpretation.

In conclusion, the reaction presented here provided a general and easy route to α-aminocarbanions. Compared to previously available methods, this methodology has several advantages: (i) it gives access to various types of α-aminocarbanions; (ii) the starting materials are readily available directly from amines and easy to handle; and (iii) the main byproduct, benzotriazole, is a weak acid that can be easily washed away by basic aqueous solution and also recyclable. The drawback of our new method is the sometimes limited selectivity between two C−N bonds, which resulted in some amine byproducts; however, those amines can usually easily be separated from the desired products.

Experimental Section

General Comments. For general information, see the preceeding paper.[13] Benzotriazole derivatives **1a**−**i** were prepared easily from the corresponding amine, aldehyde, and benzotriazole in good yields.[20]

General Procedure for Li/LiBr Reactions. Lithium (0.68 g, 30 mmol, 30% dispersion in mineral oil, low content of sodium <0.05%) was washed twice with THF under argon. THF (10 mL) and 1,2-bromoethane (2.5 mmol) were added, and the suspension was stirred at room temperature for 5 min before being cooled to −78 °C. A solution of the appropriate α-amino benzotriazole derivatives (5 mmol) and electrophiles (6 mmol) in THF (25 mL) was added dropwise to the lithium suspension over 1 h and kept at the same temperature for another 3 h before being quenched with water (15 mL). The reaction mixture was separated, and the aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were washed with saturated NaCl solution, dried, and evaporated to give the crude product, which was purified by flash column chromatography on silica gel (eluent: hexanes−ethyl acetate−0.5−1% triethylamine) to afford the pure product.

1-[(Phenylmethylamino)methyl]-1-cyclohexanol (2aa): colorless oil; ^{1}H NMR δ 7.22 (t, J = 7.8 Hz, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 6.73 (t, J = 7.2 Hz, 1 H), 3.26 (s, 2 H), 3.0 (s, 3 H), 1.78 (s, 1 H), 1.42−1.71 (m, 9 H), 1.18−1.32 (m, 1 H); ^{13}C NMR δ 151.2, 128.9, 116.9, 112.7, 73.1, 64.5, 41.2, 36.0, 25.8, 21.7; MS *m*/*z* 219 (M^+, 9), 120 (100); HRMS (EI) calcd for $C_{14}H_{21}NO$ 219.1623, found 219.1625.

3,3-Dimethyl-1-(phenylmethylamino)-2-butanol (2ae): colorless oil; ^{1}H NMR δ 7.22−7.27 (m, 2 H), 6.83 (d, J = 7.9 Hz, 2 H), 6.78 (t, J = 7.3 Hz, 1 H), 3.55−3.59 (m, 1 H), 3.34 (dd, J = 14.3, 2.8 Hz, 1 H), 3.22 (dd, J = 14.3, 10.3 Hz, 1 H), 2.93 (s, 3 H), 2.36 (d, J = 2.2, 1 H), 1.0 (s, 9 H); ^{13}C NMR δ 151.0, 129.1, 117.8, 113.9, 75.8, 56.4, 39.1, 33.8, 25.7; MS *m*/*z* 207 (M^+, 10), 120 (100); HRMS (EI) calcd for $C_{13}H_{21}NO$ 207.1623, found 207.1623.

3,3-Dimethyl-1-(phenylamino)-2-butanol (2be): white solid; mp 45−46 °C; ^{1}H NMR δ 7.15−7.24 (m, 2 H), 6.71−6.76 (m, 1 H), 6.65 (d, J = 7.6 Hz, 2 H), 3.70 (br s, 1 H), 3.47 (dd, J = 10.3, 2.2 Hz, 1 H), 3.35 (dd, J = 12.6, 2.4 Hz, 1 H), 2.96 (dd, J = 12.7, 10.3 Hz, 1 H), 0.98 (s, 9 H), 2.10 (br s, 1 H); ^{13}C NMR δ 148.4, 129.3, 117.9, 113.5, 77.6, 45.8, 34.1, 25.8; MS *m*/*z* 193 (M^+, 15), 106 (100). Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.67; H, 9.94; N, 7.42.

3-[(Diphenylamino)methyl]pentan-3-ol (2cb): white solid; mp 60−61 °C; ^{1}H NMR δ 7.29−7.24 (m, 4 H), 7.06 (d, J = 8.0 Hz, 4 H), 6.98 (t, J = 7.3 Hz, 2 H), 3.84 (s, 2 H), 1.85 (s, 1 H), 1.55−1.46 (m, 4 H), 0.79 (t, J = 7.4 Hz, 6 H); ^{13}C NMR δ 150.2, 129.3, 121.9, 121.8, 76.4, 60.6, 29.3, 7.7. Anal. Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20. Found: C, 80.05; H, 8.74; N, 5.18.

1-[1-(Phenylmethylamino)-1-phenylmethyl]-1-cyclohexanol (2da): colorless oil; ^{1}H NMR δ 7.49 (d, J = 6.7 Hz, 2 H), 7.18−7.34 (m, 5 H), 6.86 (d, J = 8.3 Hz, 2 H), 6.69 (t, J = 7.1 Hz, 1 H), 4.71 (s, 1 H), 3.08 (s, 3 H), 1.90−1.95 (m, 1 H),

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1.40−1.65 (m, 9 H), 1.20−1.30 (m, 1 H); ^{13}C NMR δ 151.2, 138.2, 129.9, 129.0, 128.0, 127.1, 116.6, 113.1, 75.8, 69.6, 37.0, 35.9, 34.9, 25.6, 21.9, 21.6. Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53. Found: C, 81.21; H, 8.65.

1-[1-(Phenylamino)ethyl]-1-cyclohexanol (2ea): colorless oil; ^{1}H NMR δ 7.10−7.18 (m, 2 H), 6.60−6.70 (m, 3 H), 3.60 (br s, 1 H), 3.38 (q, J = 7.0 Hz, 1 H), 2.05 (br s, 1 H), 1.38−1.65 (m, 9 H), 1.16−1.30 (m, 1 H), 1.08 (d, J = 7.0 Hz, 3 H); ^{13}C NMR δ 148.0, 129.2, 117.3, 113.6, 73.2, 56.8, 34.7, 33.2, 25.7, 21.9, 21.6, 14.8. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.22; H, 9.99; N, 6.09.

General Procedure for SmI_2 Reactions. A solution of the appropriate α-amino benzotriazole derivatives (2.2 mmol) and electrophiles (2 mmol) in THF or THP (10 mL) was added dropwise to the SmI_2 solution in THF, THF−HMPA (20:1), THP,[12b] or THP−HMPA (20:1) at 0 °C under argon. The reaction was kept stirring until the deep blue (or purple) color disappeared and then quenched with saturated aqueous Na_2CO_3 solution (20 mL) at the same temperature. The reaction mixture was separated, and the aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were washed with saturated NaCl solution, dried, and evaporated to give the crude product, which was purified by flash column chromatography on silica gel (eluent: hexanes−ethyl acetate−0.5−1% triethylamine) to afford the pure product.

3-[(Phenylmethylamino)methyl]-3-pentanol (2ab): colorless oil; ^{1}H NMR δ 7.23 (t, J = 8.0 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.74 (t, J = 7.2 Hz, 1 H), 3.30 (s, 2 H), 2.99 (s, 3 H), 1.76 (s, 1 H), 1.58 (q, J = 7.4 Hz, 4 H), 0.95 (t, J = 7.5 Hz, 6 H); ^{13}C NMR δ 151.5, 129.0, 117.1, 112.9, 76.2, 61.2, 41.1, 29.2, 7.9. Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 74.86; H, 10.47; N, 6.86.

1-(Phenylmethylamino)-3-methyl-2-butanol (2af): colorless oil; ^{1}H NMR δ 7.27 (t, J = 7.8 Hz, 2 H), 6.85 (d, J = 8.3 Hz, 2 H), 6.79 (t, J = 7.5 Hz, 1 H), 3.67−3.74 (m, 1 H), 3.34 (dd, J = 14.4, 3.5 Hz, 1 H), 3.25 (dd, J = 14.4, 9.4 Hz, 1 H), 2.96 (s, 3 H), 2.27 (s, 1 H), 1.72−1.85 (m, 1 H), 1.05 (d, J = 6.9 Hz, 3 H), 1.02 (d, J = 6.9 Hz, 3 H); ^{13}C NMR δ 150.7, 129.1, 117.6, 113.7, 73.4, 58.4, 39.2, 31.8, 18.7, 17.7; HRMS (EI) calcd for $C_{12}H_{19}NO$ 193.1467, found 193.1466.

1-(Diphenylamino)-2,3-dimethylbutan-2-ol (2cc): colorless oil; ^{1}H NMR δ 7.29−7.24 (m, 4 H), 7.06 (d, J = 7.9 Hz, 4 H), 6.98 (t, J = 7.4 Hz, 2 H), 3.89 (s, 2 H), 1.92 (s, 1 H), 1.81 (septet, J = 6.9 Hz, 1 H), 1.07 (s, 3 H), 0.97 (d, J = 6.9 Hz, 3 H), 0.86 (d, J = 6.9 Hz, 3 H); ^{13}C NMR δ 150.3, 129.4, 121.9, 121.8, 76.4, 61.4, 36.3, 21.8, 17.7, 17.0; MS m/z 269 (M^+, 6), 251 (6), 182 (100), 169 (99); HRMS (EI) calcd for $C_{18}H_{23}NO$ 270.1858, found 270.1792.

1,1-Dicyclohexyl-2-pyrrolidinoethanol (2gd): white solid; mp 51−2 °C; ^{1}H NMR δ 2.62−2.68 (m, 4 H), 2.48 (s, 2 H), 1.67−1.82 (m, 9 H), 1.55−1.66 (m, 5 H), 1.35−1.45 (m, 2 H), 0.95−1.25 (m, 10 H), 0.84−0.89 (m, 1 H); ^{13}C NMR δ 57.2, 55.8, 44.7, 27.0, 26.9, 26.8, 26.6, 24.1; HRMS (EI) calcd for $C_{18}H_{33}NO$ 279.2562, found 279.2595.

3-[(Dibenzylamino)methyl]-3-pentanol (2hb): white solid; mp 54−55 °C; ^{1}H NMR δ 7.26−7.39 (m, 10 H), 3.70 (s, 4 H), 2.64 (br s, 1 H), 2.57 (s, 2 H), 1.41 (q, J = 7.2 Hz, 4 H), 0.73 (t, J = 7.5 Hz, 6 H); ^{13}C NMR δ 139.2, 129.1, 128.3, 127.1, 73.7, 60.4, 59.9, 29.8, 7.7. Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.88; H, 9.34; N, 4.72.

***N*-Isopropyl-(phenylmethylamino)acetamide (8):** white solid; mp 92−94 °C; ^{1}H NMR δ 7.27 (t, J = 7.8 Hz, 2 H), 6.84 (t, J = 6.3 Hz, 2 H), 6.74 (d, J = 8.4 Hz, 1 H), 6.42 (br s, 1 H), 4.13 (septet, J = 6.6 Hz, 1 H), 3.80 (s, 3 H), 2.99 (s, 3 H), 1.11 (d, J = 6.6 Hz, 6 H); ^{13}C NMR δ 169.2, 149.3, 129.5, 129.2, 118.6, 113.1, 59.0, 41.0, 39.6, 22.5; MS m/z 206 (M^+, 7), 120 (100). Anal. Cacld for $C_{12}H_{18}N_2O$: C, 69.87; H, 8.79; N, 13.58. Found: C, 69.88; H, 9.16; N, 13.57.

***N*,*N*′-Diphenyl-*N*,*N*′-dimethyl-1,2-dipropylethylenediamine (9).** 1,2-Diiodoethane (5 mmol) was added to a suspension of samarium powder (6.5 mmol) in tetrahydropyran (THP, 50 mL) under argon at room temperature. After the mixture was stirred for 3 h, the suspension of SmI_2 in THP so formed was cooled (−10 °C), and then *N*-[α-(phenylmethylamino)-butyl]benzotriazole (**1i**, 2.2 mmol), 3-pentanone (2 mmol), and HMPA (4 mL) were added successively. After the mixture had been stirred for 4 h, saturated aqueous Na_2CO_3 was added, followed by usual workup as described above. Column chromatography of the crude product gave 71% of **9** as a white powder: mp 117−118 °C ; ^{1}H NMR δ 7.23 (t, J = 7.6Hz, 2 H), 7.14 (t, J = 7.6 Hz, 2 H), 6.77 (d, J = 8.2 Hz, 2 H), 6.57−6.75 (m, 4 H), 3.92−4.02 (m, 1 H), 3.81−3.91 (m, 1 H), 2.79 (s, 3 H), 2.40 (s, 3 H), 1.0−1.68 (m, 8 H), 0.90 (t, J = 7.2 Hz, 3 H), 0.77 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 151.1, 150.7, 129.2, 128.7, 115.8, 115.4, 112.2, 112.0, 60.2, 60.0, 33.8, 32.1, 31.2, 20.1, 19.8, 14.4, 14.1. Anal. Calcd for $C_{22}H_{32}N_2$: C, 81.43; H, 9.94; N, 8.63. Found: C, 81.34; H, 9.91; N, 8.70.

Supporting Information Available: ^{1}H and ^{13}C NMR and HRMS spectra for products **2aa**,**ab**,**ae**,**af**,**cc**,**ea**,**gd** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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