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Transformations of *N*-Substituted Benzotriazoles into the Corresponding Carbanions by C−Benzotriazole Bond Scission[‡]

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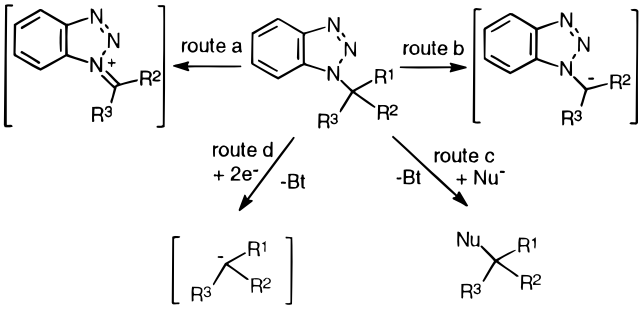
Various *N*-substituted benzotriazoles are transformed, by scission of the C-benzotriazole bond, into the corresponding carbanions by treatment with lithium. Thus, *N*-(diphenylmethyl)benzotriazole (**1**), *N*-benzylbenzotriazole (**6**), and *N*-allylbenzotriazole (**10**) all gave carbanions that reacted with diverse electrophiles to afford the corresponding products in good yields. This new methodology was successfully utilized to convert *N*-benzylbenzotriazole (**6**) and *N*-allylbenzotriazole (**10**) into dianion synthons by a sequential lithiation and reductive coupling and bis(benzotriazolyl)toluene (**18**) by double reductive couplings, demonstrating the synthetic potential of the present methodology.

Introduction

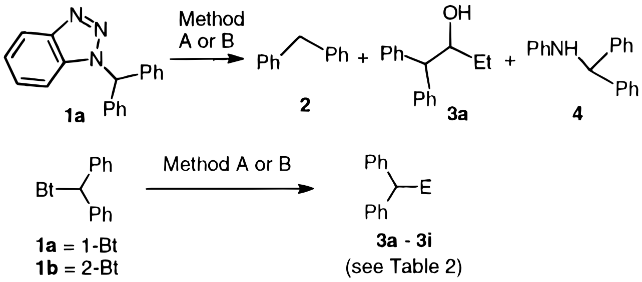
Scissions of various C−X bonds (C−halogen, C−chalcogen, and C−P) with the loss of the heteroatom functionality and formation of the corresponding carbanion are well documented.[1] However, the few examples of transformations of C−N bonds into carbanions reported by Yus *et al.*[2] all involve reductive ring opening of nitrogen-containing heterocycles, such as aziridines[2a,b] or azetidines,[2c] and take advantage of the high ring strain of these heterocycle rings. The conversion of acyclic C−N bonds into the corresponding carbanions by C−N scission has not previously been achieved.

In the past decade, our group has extensively investigated the use of the benzotriazolyl group (Bt) as an efficient leaving group.[3] Previous synthetic applications of benzotriazole chemistry have explored the now well-recognized ability of the benzotriazole group to stabilize both α-carbocations (Scheme 1, route a) and α-carbanions (route b) and, in addition, to act as a good leaving group (route c). In almost all cases where benzotriazole has acted as a leaving group it has behaved as a nucleofuge producing a carbocation as a reactive intermediate.[3] The only exception so far reported was that [α-(dialkylamino)alkyl]benzotriazoles could afford α-amino radicals.[4] Our previous experience prompted us to utilize *N*-substituted benzotriazoles as the substrate to transform acyclic C−N bonds into the corresponding carbanions. Herein, we disclose novel transformations of benzotriazole derivatives directly into the corresponding carbanions (Scheme 1, route d) when treated with lithium in tetrahydrofuran and demonstrate the considerable synthetic utility of trapping these intermediates.

Scheme 1



Scheme 2[a]



[a] Method A: (i) Li, E$^+$, THF, −78 °C, 2 h, (ii) H_2O. Method B: (i) Li, THF, −78 °C, 1 h, (ii) E$^+$, 30 min, (iii) H_2O.

Results and Discussion

1-(Diphenylmethyl)benzotriazole (**1a**) was first employed as a substrate to transform the C−Bt bond into the corresponding carbanion. When compound **1a** was reacted with lithium in the presence of propionaldehyde in THF (Barbier-type reaction conditions) under argon at 0 °C (Scheme 2), only three compounds were detected from the reaction mixture by GC/MS (Table 1, entry 1). They were separated and characterized as diphenylmethane (**2**), 1,1-diphenyl-2-butanol (**3a**), and *N*-(diphenylmethyl)aniline (**4**) by ^{1}H and ^{13}C NMR. Compound **3a** was the product expected from the reaction of an intermediate carbanion and propionaldehyde. After a variety of reaction conditions were attempted, we found that it was possible to eliminate byproducts **4** from the reaction

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[‡] Part of this work has been presented at the 212th ACS National Meeting by M. Qi, Orlando, FL, Aug 1996.

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Table 1. Reactions of 1a with Lithium and Propionaldehyde under Various Conditions

entry	reagents	method[a]	solvent	*T* (°C)	GC/MS yield[b] (%)		
					2	**3a**	**4**
1	Li	A	THF	0	16	52	32
2	Li	A	THF	−20	31	52	<3
3	Li	A	PhH−HMPA	20	34	8	44
4	Li	A	THF	−78	19	72	0
5	Li/cat. DTBB	A	THF	−78	30	58	0
6	Li	B	THF	−78	28	50	0

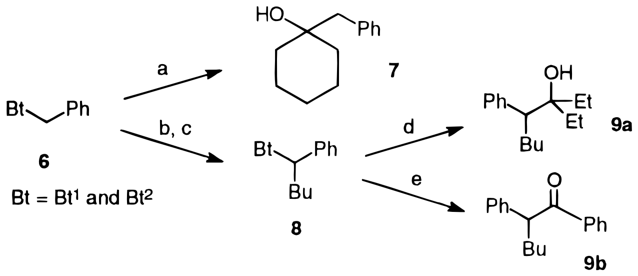
[a] Method A: compound **1a** reacted with lithium in the presence of propionaldehyde. Method B: compound **1a** was treated with lithium (1 h) before being quenched by the aldehyde. [b] GC/MS yields were taken directly from the GC/MS report. In most cases, the reaction mixtures contain a small amount of other compounds like benzeneamine.

Table 2. Reactions of (Diphenylmethyl)benzotriazole (1) with Electrophiles

electrophile	method	product	E	yield[a] (%)	charact
CH_3CH_2CHO	A	**3a**	$CH_3CH_2CH(OH)$	65	*b*
$(CH_2)_5CO$	A	**3b**	$(CH_2)_5C(OH)$	85	*c*
$CH_3(CH_2)_7CHO$	A	**3c**	$CH_3(CH_2)_7CH(OH)$	65	*c*
PhCHO	A	**3d**	PhCH(OH)	40	*b*
PhCHO	B	**3d**	PhCH(OH)	45	*b*
Me_3SiCl	A	**3e**	$SiMe_3$	85	*b*
$PhCO_2Me$	A	**3f**	PhCO	67	*b*
$PhCH_2Br$	B	**3g**	$PhCH_2$	60	*b*
MeI	B	**3h**[d]	Me	95	*b*
PhCH:NH(Ph)	B	**3i**[e]	PhCHNH(Ph)	48	*c*

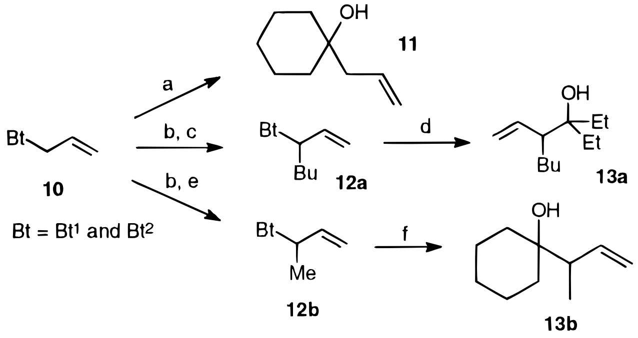
[a] Isolated yield. [b] Known compounds, for characterization see Experimental Section. [c] Novel compounds, which were characterized by ^1H and ^{13}C NMR spectroscopy and provided satisfactory elemental analyses (for details see the Supporting Information). [d] A mixture of compounds **2**, **3h**, and **5** was obtained (see text). [e] An imine dimer was also isolated (see Experimental Section).

Scheme 3[a]



[a] Key: (a) Li, $(CH_2)_5CO$, 88%; (b) BuLi; (c) BuBr; (d) Li, EtCOEt, 80%; (e) Li, $PhCO_2Me$, 46%.

Scheme 4[a]



[a] Key: (a) Li, $(CH_2)_5CO$, 82%; (b) BuLi; (c) BuBr; (d) Li, EtCOEt, 73%; (e) MeI; (f) Li, $(CH_2)_5CO$, 60%.

by lowering the reaction temperature (Table 1, entries 2 and 4). However, the second byproduct, diphenylmethane (**2**), was more difficult to avoid. Although replacing THF as solvent by benzene-HMPA can decrease the rate of hydrogen abstraction by radicals,[5] in the present case, higher yields for **2** and **4** but a lower yield for expected product **3a** resulted in using benzene−HMPA as solvent. One-step reaction conditions (method A) work better than the two-step procedure (Table 1, entries 4 *vs* 6). Also, lithium metal alone gave better results than by using 4,4′-di-*tert*-butylbiphenyl (DTTB) as a catalyst (Table 1, entries 4 *vs* 5). Benzotriazole rings probably assist the electron transfer in these reactions. No significant difference in the product slate was found on using 2-(diphenylmethyl)benzotriazole (**1b**) as starting material instead of the 1-isomer **1a**. Therefore, the mixture of the 1- and 2-(diphenylmethyl)benzotriazoles (**1**), which could be easily and quantitatively prepared from diphenylmethanol,[6] was used in subsequent reactions.

A variety of different classes of electrophiles worked well either under the conditions of method A or by using a two-step process (method B, Scheme 2). The results are summarized in Table 2. Small amounts of the pinacol coupling product were detected by GC/MS in the reaction of cyclohexanone. A low yield of an alkene was found in the GC/MS spectrum of the product of the nonanal reaction. Benzaldehyde gave a lower yield (40%) compared to aliphatic carbonyl compounds; a similar result was obtained when the two-step procedure was attempted (Table 2). The reaction of compound **1** with methyl benzoate gave the corresponding ketone **3f** in good yield, together with a trace (2% GC) of 1,2,2-triphenylethanol, evidently formed by the reduction of ketone **3f** by excess lithium.

The method B two-step process was applied when benzyl or alkyl halides were used as electrophiles. The reaction of compound **1** with benzyl bromide afforded 1,1,2-triphenylethane (**3g**) in good yield (Table 2). Excess lithium present in the reaction media converted a part of benzyl bromide to 1,2-diphenylethane (40% GC), as established by GC/MS. The reaction of compound **1** with methyl iodide gives a mixture of the methylated and dimethylated products, *i.e.*, 1,1-diphenylethane (**3h**) (30%) and 2,2-diphenylpropane (**5**) (44%), contaminated with diphenylmethane (**2**) (21%) in 95% total isolated yield. The dimethylated product could be formed from **3h** *via* further lithiation and methylation. The addition reaction of the preformed carbanion with the imine *N*-benzylideneaniline afforded amine **3i**, accompanied by the imine dimer, *N*,*N*′,1,2-tetraphenylethylenediamine.

N-Benzyl- (**6**) and *N*-allylbenzotriazoles (**10**) also reacted with cyclohexanone to give high yields of 1-benzylcyclohexanol (**7**) (Scheme 3) and 1-allylcyclohexanol (**11**) (Scheme 4) using the reaction conditions of method A. However, the simple alkyl-substituted *N*-pentylbenzotriazole could not be converted into the corresponding pentyllithium under the above conditions.

When samarium diiodide was used instead of lithium, it converted only part of *N*-(diphenylmethyl)benzotriazole (**1**) into diphenylmethane (**2**). The reaction of *N*-allylbenzotriazole (**10**) and cyclohexanone also gave a very low yield of the product **11**.

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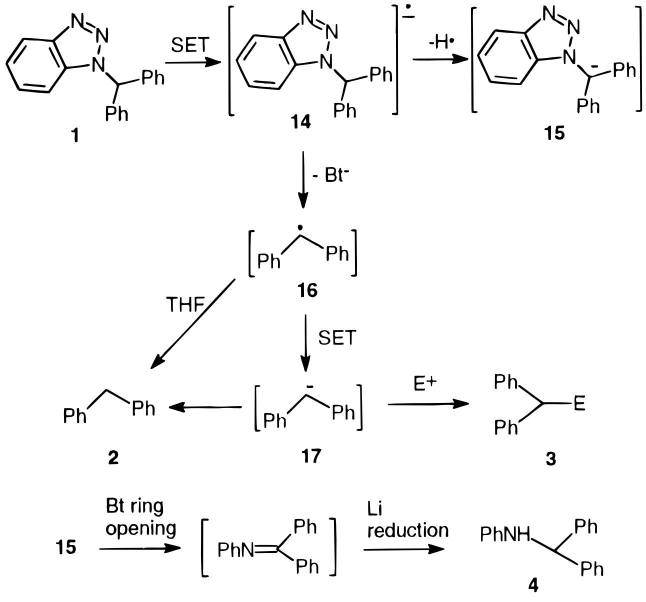
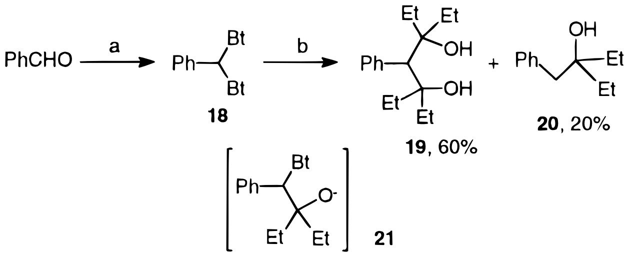
Scheme 5



These reactions may involve single-electron transfer (SET) from lithium to compounds **1**, **6**, or **10** to form the corresponding radical anions (*e.g.*, **14**, Scheme 5). The intermediate **14** could lose a proton radical affording a carbanion **15** when the reaction temperature is higher than −20 °C or lose a benzotriazolyl anion forming diphenylmethyl radical **16**. The carbanion **15** can convert to byproduct **4** through the ring opening of benzotriazole[7] and further reduction.[8] On the other hand, the diphenylmethyl radical **16** could be further reduced to diphenylmethyl anion **17** by a second SET process or abstract a hydrogen from THF[9] give another byproduct **2**. Byproduct **2** could also be formed from anion **17** by abstracting a proton from carbonyl compounds[10] or THF.[11] Both intermediates radical **16** and carbanion **17** could be reacted with electrophiles to afford the expected products. It is probably the carbanion, rather than the radical, that reacts with the electrophile to form the products. If the last step involved reaction of radicals, the aromatic carbonyl compounds should have given better results than their aliphatic analogues because it has previously been shown that the former are more easily reduced to ketyls and coupled with the radical.[12] The absence of diphenylmethyl or benzyl radical dimer in the GC/MS reaction mixture spectra supports our proposed reaction mechanism.

Synthetic Potential of This New Methodology. *N*-Benzyl- and *N*-allylbenzotriazoles can be lithiated at the α-carbon and the intermediates reacted with electrophiles to afford various classes of substituted benzotriazoles.[13] However, no convenient method was previously available for removing the Bt moiety. We have now demonstrated that two electrophiles can be introduced into these compounds by the technique of sequential lithiation and reductive coupling.

Scheme 6[a]



[a] Key: (a) BtH, $SOCl_2$, see ref 15; (b) Li/LiBr, Et_2CO.

N-Benzylbenzotriazole (**6**) (Scheme 3) was lithiated by butyllithium; the resulting carbanion reacted almost quantitatively with butyl bromide to form intermediate **8**. To introduce the second electrophile, intermediate **8** was treated *in situ* with lithium in the presence of 3-pentanone or methyl benzoate. The expected products alcohol **9a** and ketone **9b** were isolated in 80% and 46% overall yields, respectively.

In a similar manner, *N*-allylbenzotriazole (**10**) (Scheme 4) was treated with butyllithium and trapped with butyl bromide or iodomethane to afford intermediates **12a,b**, which were then each further treated with lithium and a ketone. Homoallylic alcohols **13a,b** were thus obtained by one-pot reactions from the simple starting material **10** in 73% and 60% overall yields, respectively. Most importantly, compound **12a,b** reacted with the ketones exclusively at the α-position. No product of γ-attack could be detected from the GC/MS spectra of the reaction mixture.

The umpolung of benzaldehyde to a toluene dianion synthon (previously effected using selenium methodology[14]) was achieved in two steps (Scheme 6): benzaldehyde was first converted to bis(benzotriazolyl)toluene **18** as previously reported,[15] and **18** was reacted with an electrophile in the presence of excess lithium in THF. In the second step, the two C−Bt bonds were sequentially transformed into carbanions and reacted with 3-pentanone as electrophile to give 1,3-diol **19** in 60% yield. 3-Benzyl-3-pentanol (**20**), the reductive product of the first reductive coupling intermediate **21** (Scheme 6), was detected by GC/MS and isolated as the only byproduct.

In conclusion, we found that easy scission of carbon−nitrogen bonds R−Bt allows transformation of benzotriazole derivatives into carbanions. As is well documented,[3] diverse benzotriazole derivatives are easily prepared and are of considerable use as synthetic intermediates. However, previous benzotriazole methodology has required substituent activation for effective removal of the benzotriazole moiety. The new transformations presented here offer advantageous benzotriazole removal for unactivated derivatives and further demonstrate the value of benzotriazole as a synthetic auxiliary as well as an alternative way to prepare a variety of lithium reagents.

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Experimental Section

Melting points were measured on a hot-stage microscope and are uncorrected. ^{1}H and ^{13}C NMR data were collected on a 300 NMR spectrometer (300 and 75 MHz, respectively) with TMS as internal reference in $CDCl_3$. All mass spectra were determined on a HP5890 Series II capillary GC operating in split mode with helium carrier gas and fitted with a mass selective detector (MSD). The column used was an HP5 capillary column 30 m × 0.25 mm, with 0.25 μm film thickness of 5% phenyl methyl silicone gum. The temperature program used an initial temperature of 50 °C for 1 min and then ramped at 10 °C min^{-1} to 250 °C. The GC yield was determined by integration areas of all the ions from GC/MS. Column chromatography was carried out using 230−400 mesh silica.

Compounds **1a** and **1b** were prepared as a mixture from benzotriazole, diphenylmethanol, and a catalytic amount of PTS in refluxing benzene, using a Dean−Stark trap to remove the formed water, in quantitative yield.[6] *N*-Benzyl-[6] and *N*-allylbenzotriazoles[16] were prepared from benzotriazole with benzyl bromide or allyl bromide, and potassium hydroxide in refluxing benzene or ethanol, both in greater than 90% yields. Compound **18** was prepared from benzotriazole, thionyl chloride, and benzaldehyde in 75% yield.[15] All these benzotriazole derivatives were used directly (without further purification) from the above reactions in the experiments now described. All other starting materials were supplied by Aldrich Chemical Co. or Fisher and used without further purification.

General Procedure for the Reactions of Compounds 1, 6, or 10 with Lithium and Electrophiles. Method A. Lithium (0.57 g, 25 mmol, 30% dispersion in mineral oil, low content of sodium <0.05%) was washed twice with THF under argon. THF (5 mL) was added, and the suspension was cooled to −78 °C. A solution of the appropriate benzotriazole derivatives (5 mmol) and electrophiles (7.5 mmol) in THF (25 mL) was added dropwise to the lithium suspension over 1 h and kept another hour before being quenched with water (15 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 (eluent: hexanes−ethyl acetate) to afford the pure product.

Method B. The same procedure was applied except that lithium was first treated with compound **1** (1 h) before being trapped by the electrophile (30 min).

1,1-Diphenyl-2-butanol (3a):[17] colorless oil; ^{1}H NMR δ 7.15−7.38 (10 H, m), 4.24 (1 H, dt, $J = 8.3$, 3.5 Hz), 3.87 (1 H, d, $J = 8.2$ Hz), 1.64 (1 H, s), 1.35−1.60 (2 H, m), 0.96 (3 H, t, $J = 7.4$ Hz); ^{13}C NMR δ 142.5, 141.5, 128.8, 128.7, 128.3, 128.2, 126.7, 126.4, 75.0, 58.3, 27.8, 10.0.

***N*-(Diphenylmethyl)aniline (4):**[18] ^{1}H NMR δ 7.20−7.36 (10 H, m), 7.09 (2 H, t, $J = 8.0$ Hz), 6.67 (1 H, t, $J = 7.3$ Hz), 6.52 (2 H, d, $J = 7.6$ Hz), 4.19 (1H, s); ^{13}C NMR: δ 147.3, 142.8, 129.1, 128.7, 127.4, 127.3, 117.6, 113.4; MS *m*/*z* 259 (M$^+$, 18), 182 (7), 167 (100).

1-(Diphenylmethyl)cyclohexanol (3b): colorless oil; ^{1}H NMR δ 7.54 (4 H, d, $J = 7.1$ Hz), 7.25−7.31 (4 H, m), 7.16−7.22 (2 H, m), 3.86 (1 H, s), 1.39−1.60 (9 H, m), 1.26−1.32 (2 H, m); ^{13}C NMR δ 141.5, 129.8, 128.2, 126.3, 73.5, 61.7, 37.2, 25.6, 22.1; MS *m*/*z* 266 (M$^+$, 0.2), 248 (4), 168 (100). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.30; H, 8.70.

1,1-Diphenyl-2-decanol (3c): colorless oil; ^{1}H NMR δ 7.37−7.39 (2 H, m), 7.23−7.33 (6 H, m), 7.16−7.21 (2 H, m), 4.30−4.36 (1 H, m), 3.88 (1 H, d, $J = 8.3$ Hz), 1.64 (1 H, s), 1.24−1.52 (14 H, m), 0.88 (3 H, t, $J = 6.6$ Hz); ^{13}C NMR δ 142.6, 141.5, 128.8, 128.7, 128.5, 128.2, 126.7, 126.4, 73.7, 58.7, 35.0, 31.8, 29.5, 29.2, 25.8, 22.6, 14.1. Anal. Calcd for $C_{20}H_{30}O$: C, 85.11; H, 9.74. Found: C, 84.80; H, 10.25.

1,2,2-Triphenylethanol (3d):[19] white solid; mp 87−89 °C (lit.[19] 86−88 °C); ^{1}H NMR δ 7.39 (2 H, d, $J = 7.1$ Hz), 7.32 (2 H, t, $J = 7.4$ Hz), 7.05−7.25 (11 H, m), 5.36 (1 H, dd, $J = 8.8$, 3.0 Hz), 4.23 (1 H, d, $J = 8.8$ Hz), 2.16−2.18 (1 H, m); ^{13}C NMR δ 142.2, 141.5, 140.9, 128.9, 128.7, 128.6, 128.2, 128.0, 127.5, 126.8, 126.3, 76.7, 60.2.

Trimethyl(diphenylmethyl)silane (3e):[20] white solid; mp 72−74 °C (lit.[20] mp 73−75 °C); ^{1}H NMR δ 7.21−7.28 (8 H, m), 7.10−7.16 (2 H, m), 3.51 (1 H, s), 0.03 (9 H, s); ^{13}C NMR δ 142.9, 128.7, 128.3, 125.0, 46.1, −1.7; MS *m*/*z* 240 (M$^+$, 20), 165 (23), 73 (100).

1,2,2-Triphenylethanone (3f):[19] white solid; mp 134−135 °C (lit.[19] mp 133−134 °C); ^{1}H NMR δ 8.03 (2 H, d, $J = 7.5$ Hz), 7.53 (2 H, t, $J = 6.9$ Hz), 7.25−7.45 (11 H, m), 6.07 (1 H, s); ^{13}C NMR δ 198.2, 139.1, 133.0, 129.9, 129.2, 129.0, 128.7, 128.6, 128.4, 127.1, 59.4; MS *m*/*z* 272 (M$^+$, 0.5), 167 (34), 105 (100).

1,2,2-Triphenylethane (3g):[19] white solid; mp 53−54 °C (lit.[19] mp 54 °C); ^{1}H NMR δ 7.07−7.25 (13 H, m), 6.98 (2 H, d, $J = 6.3$ Hz), 4.22 (1 H, t, $J = 7.8$ Hz), 3.35 (2 H, d, $J = 7.9$ Hz); ^{13}C NMR δ 144.4, 140.2, 129.0, 128.3, 128.2, 128.0, 126.2, 125.9, 53.1, 42.1. MS *m*/*z* 258 (M$^+$, 0.5), 167 (100).

Diphenylmethane (2),[17] **1,1-diphenylethane (3h),**[17] and **2,2-diphenylpropane (5):**[21] light yellow syrup; ^{1}H NMR δ 7.14−7.30 (10 H, m), 4.14 (1 H, q, $J = 7.4$ Hz, **3h**), 3.97 (2 H, s, **2**), 1.67 (6 H, s, **5**), 1.63 (3 H, d, $J = 7.3$ Hz, **3h**); ^{13}C NMR δ 150.6 (**5**), 146.3 (**3h**), 140.8 (**2**), 128.9, 128.4, 128.3, 128.0, 127.6, 126.8, 126.0, 125.6, 44.8 (**3h**), 42.9 (**5**), 41.9 (**2**), 30.7 (**5**), 21.8 (**3h**); MS *m*/*z* for **2**, 168 (M$^+$, 94), 167 (100); for **3h**, 182 (M$^+$, 33), 167 (100); for **5**, 196 (M$^+$, 22), 181 (100), 166 (19).

***N*,1,2,2-Tetraphenylethylamine** (3i): white solid; mp 177−179 °C; ^{1}H NMR δ 7.21−7.30 (5 H, m), 6.99−7.16 (12 H, m), 6.61 (1 H, t, $J = 7.2$ Hz), 6.42 (2 H, d, $J = 7.6$ Hz), 4.98 (1 H, d, $J = 8.7$ Hz), 4.23 (1 H, d, $J = 8.8$ Hz), 4.15 (1 H, br s); ^{13}C NMR δ 147.1, 142.3, 141.9, 140.5, 129.0, 128.7, 128.2, 128.0, 127.4, 127.0, 126.9, 126.4, 117.5, 113.6, 61.4, 59.6. Anal. Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 89.57; H, 6.85; N, 3.96.

***N,N*′,1,2-Tetraphenylethylenediamine:**[8] yellow solid; mp 137−142 °C (lit.[8] mp 134−140 °C); ^{1}H NMR ($CDCl_3$−D_2O) δ (two isomers in a ratio of 1.5:1, peaks in minor isomer in square brackets) 6.92−7.23 (14 H, m), 6.62−6.68 (2 H, m), 6.48−6.52 (4 H, m), 4.53 (4 H, s) [4.95 (s)]; ^{13}C NMR: δ 147.0 [146.5], 139.9 [138.2], 129.1 [129.2], 128.4 [128.2], 127.5 [127.3], 118.1 [117.8], 114.1 [113.7], 64.0 [62.0]. Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.91; H, 6.77; N, 7.57.

1-Benzylcyclohexanol (7):[22] colorless oil; ^{1}H NMR δ 7.20−7.31 (5 H, m), 2.75 (2 H, s), 2.17 (1 H, s), 1.26−1.60 (10 H, m); ^{13}C NMR: δ 137.2, 130.6, 128.1, 126.4, 71.1, 48.7, 37.3, 25.8, 22.1; MS *m*/*z* 190 (M$^+$, 0.2), 172 (5), 99 (100), 81 (75).

1-Allylcyclohexanol (11):[23] colorless oil; ^{1}H NMR δ 5.81−5.95 (1 H, m), 5.06−5.16 (2 H, m), 2.20 (2 H, d, $J = 7.5$ Hz), 1.38−1.65 (10 H, m), 1.24−1.34 (1 H, m); ^{13}C NMR δ 133.7, 118.6, 70.9, 46.7, 37.4, 25.8, 22.2; MS *m*/*z* 122 (M$^+$ − H_2O), 99 (100), 81(90).

Synthesis of 9a,b and 13a,b *via* Lithiation and Reductive Coupling: General Procedure. *N*-Benzylbenzotriazole (**6**) or *N*-allylbenzotriazole (**10**) (5 mmol) was dissolved in THF (25 mL) and cooled to −78 °C under argon. BuLi (5.5 mmol, 1.6 M in hexanes) was introduced *via* a syringe. The resulting deep blue solution was treated with butyl bromide (5 mmol, for **9a**,**b** and **13a**) or iodomethane (5 mmol, for **13b**), and the reaction temperature was allowed to warm to rt over 3 h (solution A, light yellow). In another reaction flask (B), 25 mmol of lithium (0.57 g, 30% dispersion in mineral oil) was washed twice with THF (2 × 20 mL) under argon. Fifteen mL of THF was added, and the suspension was cooled to −78 °C. The solution A was transferred to a dropping funnel

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connected to flask B and mixed with 3-pentanone (6 mmol, for **9a** and **13a**), methyl benzoate (6 mmol, for **9b**), or cyclohexanone (6 mmol, for **13b**). The mixed solution was dropped into the lithium suspension over 1 h and kept another hour before being quenched by water (15 mL), at the same temperature. The reaction mixture was separated, and the aqueous phase was extracted with ether (2 × 20 mL). The combined organic solution was washed with saturated NaCl solution, dried, and evaporated to give the crude product, which was purified by flash column chromatography (eluent: hexanes−ethyl acetate) to afford the pure product.

3-Ethyl-4-phenyl-3-octanol (9a): colorless oil; ^{1}H NMR δ 7.20−7.35 (5H, m), 2.67 (1H, dd, J = 10.6, 4.8 Hz), 1.70−1.86 (2H, m), 1.60 (2H, q, J = 7.0 Hz), 1.20−1.42 (4H, m), 0.98−1.16 (3H, m), 0.80−0.96 (9H, m); ^{13}C NMR: δ 141.6, 129.8, 128.0, 126.2, 76.2, 52.1, 30.4, 29.2, 28.4, 28.0, 22.8, 14.0, 8.0, 7.6; HRMS (CI) calcd for $C_{16}H_{26}O + H$ 235.2062, found 235.2059.

Phenyl 1-phenylpentyl ketone (9b):[24] colorless oil; ^{1}H NMR δ 7.97 (2H, d, J = 7.2 Hz), 7.20−7.49 (8H, m), 4.54 (1H, t, J = 7.3 Hz), 2.14−2.26 (1H, m), 1.78−1.90 (1H, m), 1.16 - 1.40 (4H, m), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR δ 200.1, 132.7, 129.6, 128.8, 128.6, 128.5, 128.2, 126.9, 126.4, 53.7, 33.8, 29.9, 22.7, 13.9; MS *m/z* 252 (M$^+$, 1), 196 (8), 105 (100).

3-Ethyl-4-ethenyl-3-octanol (13a): colorless oil; ^{1}H NMR δ 5.65 (1H, dt, J = 17.1, 9.9 Hz), 5.15 (1H, dd, J = 10.2, 2.5 Hz), 5.06 (1H, dd, J = 17.1, 2.4 Hz), 2.09 (1H, dt, J = 10.2, 2.5 Hz), 1.44−1.60 (5H, m), 1.10−1.38 (6H, m), 1.84−1.92 (9H, m); ^{13}C NMR δ 139.2, 117.6, 75.2, 51.5, 30.3, 28.6, 28.4, 27.8, 22.7, 14.0, 7.5, 7.4; HRMS (CI) calcd for $C_{12}H_{24}O + H$ 185.1905, found 185.1907.

1-(1-Methylallyl)-1-cyclohexanol (13b):[23] colorless oil; ^{1}H NMR δ 5.77−5.89 (1H, m), 5.03−5.09 (2H, m), 2.15−2.20 (1H, m), 1.39−1.66 (10H, m), 1.29 (1H, s), 1.20 (3H, d, J = 7.0 Hz); ^{13}C NMR δ 140.4, 115.8, 72.4, 48.3, 35.0, 34.4, 25.9, 21.8, 14.1; MS *m/z* 136 (M$^+$ − H_2O, 1.5), 99 (100).

Synthesis of 3,5-Diethyl-4-phenyl-3,5-heptanediol *via* Double Reductive Couplings. Lithium (0.57 g, 25 mmol, 30% dispersion in mineral oil) was washed twice with THF (2 × 20 mL) under argon. THF (10 mL) was added, and the suspension was treated with 1,2-dibromoethane (2.5 mmol) and then cooled to −78 °C. The solution of α,α-bis(benzotriazolyl)toluene (2.5 mmol) and 3-pentanone (6 mmol) in THF (30 mL) was dropped into the lithium suspension over 1 h and kept another hour before being quenched by water (15 mL), at the same temperature. The reaction mixture was separated, and the aqueous phase was extracted with ether (2 × 20 mL). The combined organic solution was washed with saturated NaCl solution, dried, and evaporated to give the crude product, which was purified by flash column chromatography (eluent: hexanes−ethyl acetate) to afford the pure product **19** (60%) and byproduct 3-benzyl-3-pentanol (**20**, 20%).

3,5-Diethyl-4-phenyl-3,5-heptanediol (19): white solid; mp 110−112 °C; ^{1}H NMR δ 7.74 (1H, d, J = 7.0 Hz), 6.95−7.36 (4H, m), 3.34 (2H, s), 2.96 (1H, s), 1.74−1.90 (4H, m), 1.40−1.52 (2H, m), 1.08−1.20 (2H, m), 0.92 (6H, t, J = 7.2 Hz), 0.70 (6H, t, J = 7.2 Hz); ^{13}C NMR δ 140.6, 132.0, 130.1, 127.4, 126.1, 79.6, 55.1, 31.2, 31.0, 8.4, 7.6. Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.49; H, 11.06.

3-Benzyl-3-pentanol (20):[25] colorless oil; ^{1}H NMR δ 7.12−7.36 (5H, m), 2.75 (2H, s), 1.44 (4H, q, J = 7.0 Hz), 1.30 (1H, br s), 0.96 (6H, t, J = 7.0 Hz); ^{13}C NMR: δ 137.5, 130.5, 128.1, 126.3, 74.5, 44.7, 30.4, 8.0.

Supporting Information Available: ^{1}H and ^{13}C NMR and HRMS spectra for products **3c**, **9a**, and **13a** (11 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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