Convenient Syntheses of Functionalized Dialkyl Ketones and Alkanoylsilanes: 1-(Benzotriazol-1-yl)-1-phenoxyalkanes as Alkanoyl Anion Equivalents

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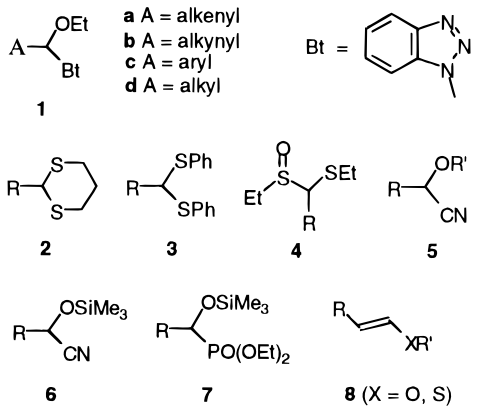
(Benzotriazol-1-yl)-1-phenoxyalkanes **10**, prepared by two-step transformations of the corresponding aldehydes, are readily deprotonated at the methine group by BuLi. Subsequent reactions with alkyl halides, aldehydes, ketones, and imines yield the corresponding substituted derivatives that undergo hydrolysis under acidic conditions to afford the expected functionalized ketones **13**, **15**, **17**, **19**, **21**, **24**, and **25**. Two successive lithiations of (benzotriazolyl)phenoxymethane, each followed by reaction with a trialkylsilyl chloride, alkyl halide, aldehyde, or ketone, generate similar intermediates **27**, **29**, **31**, **33**, and **36**. Subsequent hydrolyses of **27**, **29**, **31**, **33**, and **36** yield the functionalized ketones **28**, **30**, and **32** and the alkanoylsilanes **34** and **37** in good yields.

Introduction

We have recently demonstrated that alkenyl- (**1a**), alkynyl- (**1b**), and aryl- (including heteroaryl-)substituted (**1c**) *N*-(ethoxymethyl)benzotriazoles are versatile acyl anion equivalents, which can be used advantageously for the preparation of a wide variety of functionalized alkenyl,[1,2] alkynyl,[3] aryl,[4] and heteroaryl[4] ketones and alkenoyl-, alkynoyl-, aroyl-, and heteroaroylsilanes.[5] The benzotriazole-stabilized carbanions derived from **1a**−**c** all share the following features: convenient availability of starting materials, adequate reactivity toward various electrophiles including alkyl halides, aldehydes, ketones, and imines, and mild conditions for the hydrolysis of the intermediates thus produced. However, this methodology is not immediately applicable to alkyl-substituted *N*-(ethoxymethyl)benzotriazoles (**1d**) because the deprotonation of **1d** is difficult; this can be understood as the vinyl, ethynyl, and aryl groups of **1a**−**c** obviously play an important role in the stabilization of their corresponding anions. Previous work in our group has demonstrated that (carbazol-9-yl)(benzotriazol-1-yl)methane is an efficient acyl anion equivalent,[6] but its relatively large molecular weight (and occasional difficult reactions with sterically hindered electrophiles, such as triisopropylsilyl chloride) makes a smaller analog desirable. We now find that use of phenoxy compounds of type **10** in place of the ethoxy or carbazolyl analogs allows ready deprotonation to **11** and provides a convenient access to alkyl-substituted functionalized ketones, including bulky trialkylsilyl (R_3Si−)-substituted alkanoylsilanes that were difficult to prepare by previous methods.

The use of acyl anion equivalents has proven to be a powerful strategy in the synthesis of many carbonyl compounds, as referenced in previous papers[6,7] (for more general reviews see refs 8 and 9). The preparation of acyl anion precursors has commonly been carried out by one of two alternative strategies: (i) lithiation of a formyl anion equivalent such as **2**, **3**, **4**, or **7** (R = H) and subsequent alkylation with RX to give **2**, **3**, **4**, or **7** (R ≠ H). Use of such species as acyl anion equivalents is thus essentially a double-lithiation process, which provides flexibility for the introduction of two different substituents. (ii) An alternative strategy is the generation of acyl anion equivalents such as **2**−**8** directly from the corresponding aldehydes or their equivalents, which allows the conversions of available aldehydes into substituted ketones. In the present work, we have successfully utilized both of these strategies to provide novel acyl anion equivalents **10**.



Results and Discussion

Conversion of Aliphatic Aldehydes into Dialkyl Ketones and α-Hydroxy and α-Amino Functionalized Ketones. The intermediates 1-(benzotriazol-1-yl)-1-phenoxyalkanes **10** were prepared in two-step processes. Previously reported reactions of aldehydes, benzotriazole, and thionyl chloride in benzene yielded 1-(benzotriazol-1-yl)-1-chloroalkanes **9**.[10] We have now replaced the chloro atom in the α-(chloroalkyl)benzotri-

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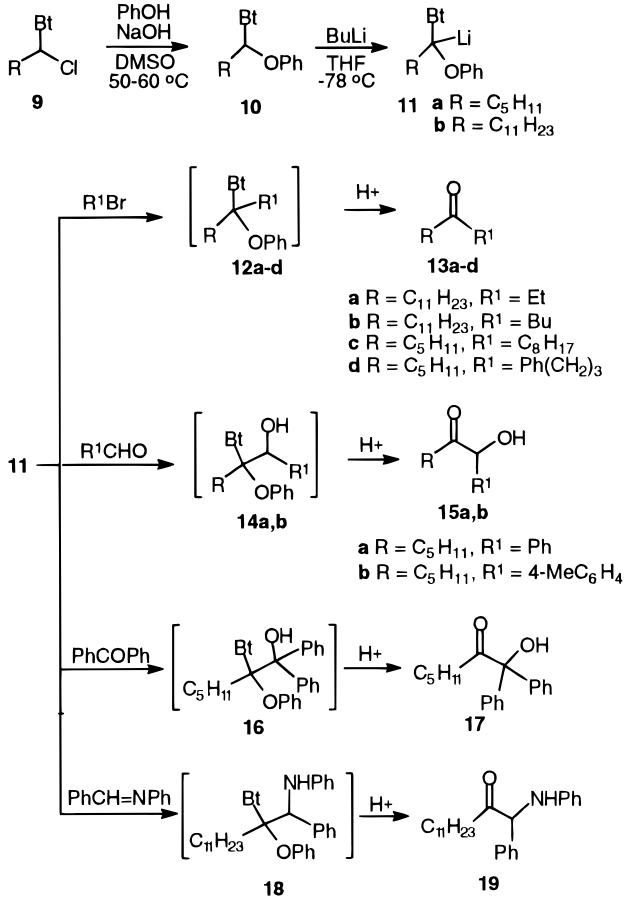
Scheme 1



azoles by phenoxide to give 1-(benzotriazol-1-yl)-1-phenoxyalkanes **10a**,**b** in 75% and 82% yields, respectively. Compounds **10a**,**b** are stable to storage at ambient temperature without special precautions.

Treatment of compound **10a** with 1 equiv of butyllithium at −78 °C for 2−5 min resulted in the formation of anion **11a** (Scheme 1). Subsequent reaction with (3-bromopropyl)benzene at −78 °C for a few minutes and then at room temperature for 10 min gave intermediate **12d** in 90% yield. The structure of **12d** was confirmed spectrally and by CHN analysis: ^{13}C NMR spectra clearly indicated that the methine carbon of **10a** was shifted downfield due to the introduction of the $Ph(CH_2)_3$ substituent. Hydrolysis of **12d** in refluxing aqueous ethanol (50%) containing 5% sulfuric acid for 10 min afforded **13d** in 96% yield. NMR spectra of **13d** showed the presence of a carbonyl group and the disappearance of the benzotriazolyl and phenoxy groups.

The unsymmetric dialkyl ketones **13a**−**c** were similarly prepared in 64−90% overall yields (Table 1) without isolation of the corresponding intermediates **12a**−**c**. Compared to our previous BtCHAOEt (**1a**−**c**) cases,[1−5] in which the hydrolyses were carried out with a dilute acid (HCl, H_2SO_4, or oxalic acid) solution at room temperature, the hydrolyses of **13a**−**d** require stronger conditions due to the lack of the activation by a vinyl, alkynyl, or aryl group. All these reactions, including the alkylations and hydrolyses, were monitored by TLC until the starting materials were completely consumed. The benzotriazole and phenol generated by hydrolysis were easily removed by washing the organic extracts with 2N aqueous sodium hydroxide during workup.

Dialkyl ketones are usually prepared by oxidation of the corresponding alcohols. However, this route is subject to the availability of the alcohols. Preparations of dialkyl ketones (RCOR′) from two alkyl halides (RX and R′X) were effected *via* conversion of one alkyl halide into an aldehyde (RCHO) by treatment with disodium tetracarbonylferrate[11,12] or with the selenium compound $Me_3SiCH(Li)SePh$ followed by H_2O_2[13] and subsequent reaction with the Grignard reagent from another R′X and final oxidation of the hydroxy group. Use of a previous acyl anion equivalent strategy has been another common approach.[8]

Reactions of anion **11a** with 4-tolualdehyde for a few minutes at −78 °C generated intermediate **14b** in 80% yield. Unlike the preparations of **12a**−**d**, the reaction **11a** → **14b** was complete at −78 °C after 10 min without raising the temperature. The NMR spectra of **14b** indicated the presence of two diastereomers in a ratio of 4:1. Hydrolysis of **14b** under the same conditions as described for **12a**−**d** provided **15b** in 96% yield. The structure of **15b** was confirmed by NMR spectra and CHN analysis.

Reactions of **11a** with benzaldehyde or benzophenone and of anion **11b** with *N*-benzylideneaniline as electrophiles were carried out without isolation of intermediates **14a, 16**, and **18**, hydrolysis of which gave the corresponding α-hydroxy- and α-amino-substituted ketones **15a**, **17** and **19** in 65−74% yields.

α-Hydroxy ketones of types **15** and **17** have been prepared from 1,3-dithiane acyl anion equivalents (**2**).[8] However, as discussed in our recent papers,[4,6] hydrolyses of **2** require the irreversible removal of the dithiol, which is still most often accomplished by complex formation with heavy-metal salts (HgO and $HgCl_2$). Other routes to α-hydroxy ketones of types **15** and **17** include reduction of α-dicarbonyl ketones,[14] oxidation of 1,2-dihydroxy compounds,[15] oxidation of alkenes,[16] thiazolium-catalyzed dimerization of aldehydes,[17] and acyloin condensation.[18] However, these methods are frequently restricted to starting materials of appropriate symmetry and require careful control of the reaction conditions to avoid mixtures and overreduced or overoxidized products. α-Amino ketones of type **19** were previously prepared by reactions of α-chloro,[19] α-bromo,[20] or α-hydroxy ketones[21] with an amine. An alternative method for the preparation of compounds of type **19** is condensation of 1,2-dicarbonyl compounds with an amine followed by reduction.[21,22] All of these routes to compounds **19** are subject to the availability of the starting materials; for example, the direct halogenation of many ketones occurs on both sides of the carbonyl group. No previous report has been found on the preparation of an alkyl α-aminoalkyl ketone by an acyl anion equivalent approach.

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Table 1. Preparation of Ketones 13a–d, 15a,b, 17, 19, 21, 24, 25, 28a,b, 30a,b, and 32 and Alkanoylsilanes 34a–g and 37

						calcd/found	
compd	R	R^1	R^2	yield (%)	mp (°C)	C	H (or HR MS)
13a	*n*-$C_{11}H_{23}$	EtBr		88	oil[b]		
13b	*n*-$C_{11}H_{23}$	BuBr		90	oil[c]		
13c	*n*-C_5H_{11}	*n*-C_8H_{17}		81	oil[d]		
13d	*n*-C_5H_{11}	$Ph(CH_2)_3$		80[a]	oil	82.52/82.54	10.16/10.47
15a	*n*-C_5H_{11}	Ph		65	oil	75.69/75.46	8.80/9.20
15b	*n*-C_5H_{11}	4-Me-C_6H_4		76[a]	oil	76.33/76.07	9.15/9.43
17				76	oil	283.1620/283.1633	
19				74	50–51	366.2797/366.2740	
21				44[a]	oil[e]		
24				33	oil	309.1854/309.1897	
25				23	oil	309.1854/309.1859	
28a	*n*-C_8H_{17}	*n*-C_8H_{17}		97	48–50[f]		
28b	*n*-C_8H_{17}	*n*-$C_{10}H_{21}$		80	45–47[g]		
30a	$PhCH_2$	4-Me-C_6H_4		52[a]	92–93[h]		
30b	Me	$CH(CH_2)_5$		43[a]	oil	69.19/68.79	10.33/10.16
32				41	oil	72.67/72.82	11.19/11.49
34a	$PhCH_2$	Me	Me	84[a]	oil	67.22/67.05	12.22/12.21
34b	*n*-C_8H_{17}	Me	Me	82	oil	68.69/68.39	8.38/8.39
34c	*n*-C_7H_{15}	Ph	Me	96	oil	73.22/73.15	9.98/10.18
34d	Et	Ph	Ph	85	oil	79.70/79.94	6.37/6.45
34e	Et	*n*-C_8H_{17}	Me	71	oil	68.35/68.22	12.35/12.67
34f	*n*-C_8H_{17}	*t*-Bu	Me	56	oil	70.24/70.04	12.57/12.68
34g	Et	*i*-Pr	*i*-Pr	46	oil	67.22/67.00	12.22/12.44
37				66	oil	60.56/60.49	9.15/9.40

[a] Overall yields based on the starting materials **10a**,**b** or **26**. [b] Lit.[30] bp_{10} 148 °C. [c] Lit.[31] mp 32–34 °C. [d] Lit.[32] bp_{12} 147–148 °C. [e] Lit.[33] [f] Lit.[34] mp 53 °C. [g] Lit.[35] mp 47–48.5 °C. [h] Lit.[6] mp 90–91 °C.

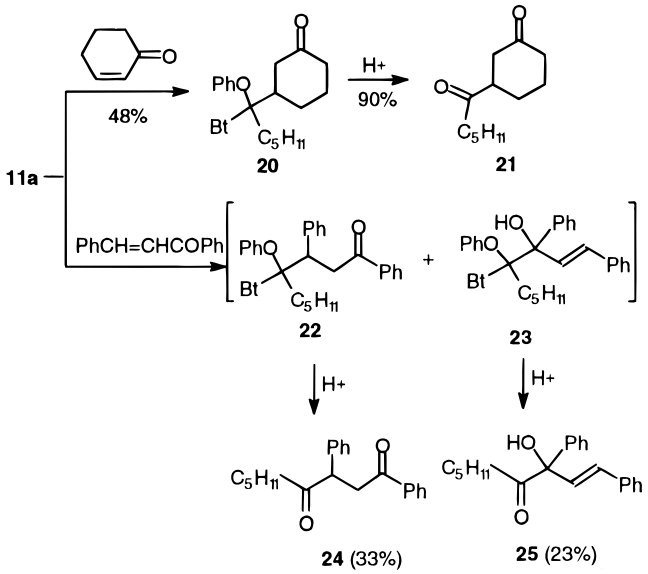
Conversion of Aliphatic Aldehydes into 1,4-Dicarbonyl Compounds. When anion **11a** was reacted with 2-cyclohexenone, it gave exclusively the γ-product **20** which was isolated in 48% yield. No 1,2-addition product was detected. The ^{13}C NMR of the crude products showed the carbonyl signals as expected for product **21**. Hydrolysis of **20** under conditions similar to those in the previous cases afforded the expected ketone **21** in 90% yield. The structures for the intermediate **20** and the final product **21** were confirmed by ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR spectra show two characteristic carbonyl signals at 209.8 and 210.5 ppm for **21**.

However, when *trans*-chalcone was used as electrophile to react with anion **11a**, both the α-alkylated **23** and the γ-alkylated products **22** were generated. The crude mixture was directly subjected to hydrolyses to afford the 1,4-dicarbonyl ketone **24** and α-hydroxy ketone **25** in 33% and 23% overall yields, respectively (Scheme 2). The loss of regioselectivity is probably due to the fact that the γ-position of *trans*-chalcone is sterically hindered, compared with 2-cyclohexenone.

Phenyl thioacetals **3** have been used for the synthesis of 1,4-diketones[23] by conversion of their lithiated species to copper reagents and subsequent reaction with α,β-unsaturated ketones. Previous work in our group reported the preparation of compounds of type **21** and **24** by using (carbazol-9-yl)(benzotriazol-1-yl)alkanes as acyl anion equivalents.[6] As stated earlier, the relatively high molecular weight of this compound is its major disadvantage.

Formation of Dialkyl Ketones and α-Hydroxy Functionalized Aliphatic Ketones by the Double-Lithiation Technique. (Benzotriazol-1-yl)phenoxymethane **26** was readily prepared in 87% yield from reaction of 1-(chloromethyl)benzotriazole with phenoxide ion according to the literature.[24] Compound **26** has previously been used in our group[25] as a one-carbon homologation reagent for the conversion of aldehydes to α-acetoxymethyl ketones.

Scheme 2



We have now found that **26** can also be used as the substrate in the double-lithiation technique with considerable flexibility. Successive treatment of (benzotriazol-1-yl)phenoxymethane **26** with 1 equiv of BuLi, followed by 1 equiv of benzyl bromide, then another equivalent of BuLi, and finally with *p*-tolualdehyde gave the intermediate **29a**, which was isolated in 64% yield. Hydrolysis of **29a** afforded the expected ketone **30a** in 81% yield. The intermediate **29b** and ketone **30b** were similarly prepared in 45% and 95% yields, respectively. The structures of **29a**,**b** and **30a**,**b** were fully supported by NMR spectra and elemental analyses.

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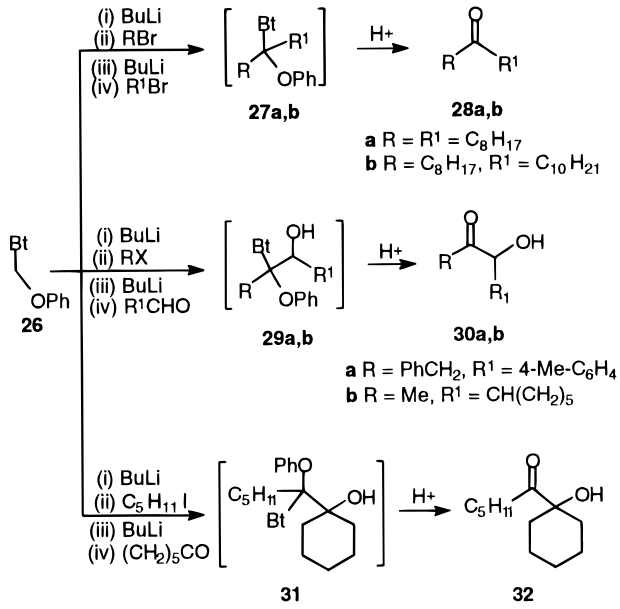
Scheme 3



Compounds **28a**,**b** and **32** were similarly prepared in 52−97% overall yields (Table 1) from **26** by treatment with the reagents given in Scheme 3 without isolation of the intermediates **27a**,**b** and **31**. In this approach, if two identical electrophiles are used, we can easily get the symmetrical ketones (*e.g.*, **28a**); if two different electrophiles are used, unsymmetrical ketones (**28b**) are readily prepared in high yields. A variety of α-hydroxy ketones of types **30** and **32** could thus easily be produced from starting material **26**.

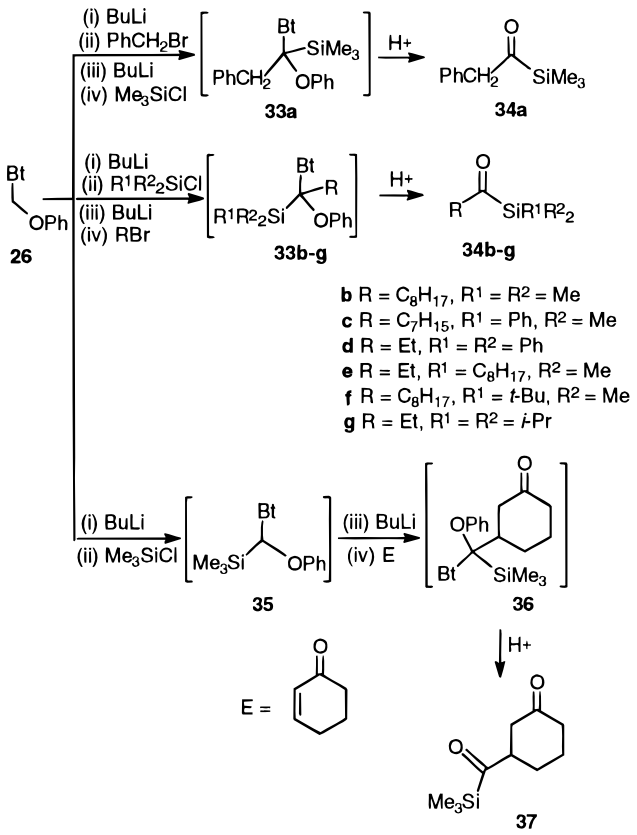
Preparation of Alkanoylsilanes. When a trialkylsilyl chloride or alkyl bromide was used as one of the electrophiles, double lithiation of compound **26** provided various bulky trialkylsilyl-substituted (*i*-Pr_3Si, Ph_3Si, and *t*-$BuMe_2Si$, *etc.*) alkanoylsilanes **34a**−**h** in 46−96% yields (Table 1). We have carried out the reaction sequence by both (i) adding the alkyl halide first and then introducing the trialkylsilyl group to give **34a** and (ii) using the reverse order to give **34b**−**h** (Scheme 4). Both approaches gave satisfactory results, and it appears to make little difference as to which electrophile (RX or R_3SiCl) is first introduced.

In the first approach, successive treatment of (benzotriazol-1-yl)phenoxymethane **26** with 1 equiv of BuLi followed by quenching with benzyl bromide then with another 1 equiv of BuLi and lastly with trimethylsilyl chloride gave the intermediate **33a** in 90% yield. Subsequent hydrolysis of **33a** afforded the expected ketone **34a** in 93% yield (Scheme 4).

In the second strategy, the trialkylsilyl chloride was introduced into the molecule prior to the alkyl group. Compounds **34b**−**g** were prepared in 46−96% yields without isolation of the intermediates **33b**−**g**. The relatively low yields for **34f**,**g** can be attributed to the steric hindrance of the electrophiles used [(*t*-Bu)Me_2SiCl and (*i*-$Pr)_3SiCl$].

We have also found that when trimethylsilyl chloride and cyclohexenone were used as electrophiles, a double-(lithiation + electrophile) sequence provided γ-oxo alkanoylsilane **37** in good yield. Thus, successive treatment of (benzotriazol-1-yl)phenoxymethane **26** with 1 equiv of BuLi followed by quenching with trimethylsilyl chloride and then with another 1 equiv of BuLi and lastly

Scheme 4



with cyclohexenone gave the intermediate **36**, which was then subjected to *in situ* hydrolysis to afford the expected ketone **37** in 66% overall yield. In the preparation of these alkanoylsilanes **34a**−**g** and **37**, the hydrolyses were accomplished under milder conditions than used above for the ketones: the intermediate **33a**−**h** and **36** were refluxed in aqueous THF/acetone containing 1% of 4 N dilute sulfuric acid. Structures were all confirmed by ^1H, ^{13}C NMR spectra and for novel compounds by elemental analyses. The known compounds have been compared with literature data. ^{13}C NMR clearly shows the carbonyl carbon resonance in the range of 243.1−248.3 ppm, which is typical for acylsilanes.

Previous preparations of alkanoylsilanes have mostly been restricted to examples with simple trialkylsilyl group (*e.g.*, Me_3Si) substituted compounds, and rarely are they extended to cases of bulky trialkylsilyl (R_3Si−) substituents. Lipshutz *et al.*[26] recently reported a novel route to the triisopropylacylsilanes of the type $NuCH_2COSiPr_3^i$ in overall yields of 50−80% *via* a two-step procedure: nucleophilic reaction with triisopropylsilylethylene oxide and subsequent oxidation of the hydroxy group. For comparison, Lipshutz[26] also utilized the "dithiane method", first reported by Corey[27] and Brook[28] in 1967 to synthesize the butyl triisopropylsilyl ketone in 32% yield. No previous report has been found of γ-oxo acylsilanes of type **37**: our method appears to be clearly more general than earlier approaches.

Comparison of 1-(Benzotriazol-1-yl)-1-phenoxyalkanes with Their Ethoxy Analogs. As mentioned

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earlier, 1-(benzotriazol-1-yl)-1-ethoxyalkanes (**1d**) do not undergo the easy deprotonation analogous to that which allows **1a**−**c** to be used as acyl anion synthons. However, as now demonstrated, replacement of the ethoxy group in the molecule of **1d** by a phenoxy group to give **10** allows deprotonation to proceed smoothly. The lower mesomeric electron-donor power of the phenoxy group combined with its larger electron-withdrawing inductive effect as compared to an ethoxy group evidently makes the methine proton of **10** more acidic than that of **1d**. A significant difference between the behavior of the phenoxy and an alkoxy group has also been observed by Wedler *et. al.*[29] in the Darzens reaction of phenyl esters of α-chlorocarboxylic acids with carbonyl compounds: whereas condensation of aldehydes or ketones with alkyl esters of α-chlorocarboxylic acids in the presence of a base generates α-chloro-*β*-hydroxy esters and α,*β*-epoxy esters, use of phenyl esters instead of alkyl esters led to α-chloro-*β*-lactones.

Conclusions

Novel acyl anion equivalents, 1-(benzotriazol-1-yl)-1-phenoxyalkanes, have been developed for the generation of functionalized alkyl ketones and bulky trialkylsilyl (R_3-Si−)-substituted alkanoylsilanes. The simplicity and generality of the procedures, coupled with the convenient availability of the starting materials, give these methods considerable potential importance in organic synthesis.

Experimental Section

General Comments. Melting points were determined on a hot stage apparatus without correction. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Gemini-300 spectrometer in $CDCl_3$ with TMS or $CDCl_3$, respectively, as the internal reference. Elemental analyses were performed using a Carlo Erba 1106 elemental analyzer. High-resolution mass spectra were measured on an AEI-30 mass spectrometer. Column chromatography was carried out on MCB silica gel (230−400 mesh). Tetrahydrofuran (THF) was freshly distilled from sodium−benzophenone. Lithiation reactions were carried out under the protection of dry nitrogen.

Compounds **9a**,**b** were prepared according to the literature procedure.[10]

1-(Benzotriazol-1-yl)-1-chlorohexane (9a) was obtained as a light brown oil: yield 70%; ^{1}H NMR δ 0.88 (t, 3 H, J = 7.1 Hz), 1.24−1.44 (m, 4 H), 1.48−1.63 (m, 2 H), 2.67−2.81 (m, 2 H), 6.77 (t, 1 H, J = 7.4 Hz), 7.44 (t, 1 H, J = 7.7 Hz), 7.57 (t, 1 H, J = 7.6 Hz), 7.78 (d, 1 H, J = 8.4 Hz), 8.12 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 13.6, 22.0, 25.6, 30.5, 37.5, 70.9, 110.4, 120.2, 124.5, 128.0, 131.3, 146.5. Anal. Calcd for $C_{12}H_{16}N_3Cl$: C, 60.63; H, 6.78; N, 17.68. Found: C, 60.90; H, 7.01; N, 17.48.

1-(Benzotriazol-1-yl)-1-chlorododecane (9b) was obtained as a light brown oil: yield 82%; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.6 Hz), 1.20−1.64 (m, 18 H), 2.60−2.83 (m, 2 H), 6.72 (t, 1 H, J = 7.5 Hz), 7.44 (t, 1 H, J = 7.7 Hz), 7.57 (t, 1 H, J = 7.7 Hz), 7.75 (d, 1 H, J = 8.4 Hz), 8.12 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.0, 22.6, 26.0, 28.5, 29.1, 29.2, 29.3, 29.4, 31.8, 37.7, 71.1, 110.4, 120.4, 124.6, 128.0, 131.4, 146.6; HRMS calcd for $C_{18}H_{28}N_3Cl$ 322.2050 (M + 1), found 322.2067.

General Procedure for the Preparation of 10a,b. Powdered sodium hydroxide (3.2 g, 80 mmol) was added to a solution of phenol (3.74 g, 40 mmol) in DMSO (20 mL). The suspension was stirred for 30 min, and the appropriate 1-(benzotriazol-1-yl)-1-chloroalkane **9a** or **9b** (40 mmol) was added. The mixture was heated at 50−60 °C for 1 h and was poured onto *ca.* 200 g of ice−water with stirring. The solution was extracted with diethyl ether (3 × 100 mL) and washed with NaOH solution (2 N, 100 mL) and water (3 × 150 mL). Evaporation of the solvent gave the crude product, which was chromatographed on silica gel (hexane/EtOAc 20:1).

1-(Benzotriazol-1-yl)-1-phenoxyhexane (10a) was obtained as a colorless oil: yield 75%; ^{1}H NMR δ 0.86 (t, 3 H, J = 6.8 Hz), 1.20−1.40 (m, 4 H), 1.45−1.60 (m, 2 H), 2.25−2.38 (m, 1 H), 2.43−2.58 (m, 1 H), 6.80−7.00 (m, 4 H), 7.17 (t, 2 H, J = 8.1 Hz), 7.32 (t, 1 H, J = 8.4 Hz), 7.44 (t, 1 H, J = 7.2 Hz), 7.82 (d, 1 H, J = 8.1 Hz), 8.03 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 13.7, 22.3, 24.3, 30.9, 34.7, 88.2, 111.0, 111.1, 116.1, 120.0, 122.8, 124.2, 127.6, 129.6, 146.6, 156.1. Anal. Calcd for $C_{18}H_{21}N_3O$: C, 73.18; H, 7.17; N, 14.23. Found: C, 73.23; H, 7.38; N, 14.61.

1-(Benzotriazol-1-yl)-1-phenoxydodecane (10b) was obtained as a colorless oil: yield 82%; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.6 Hz), 1.10−1.61 (m, 18 H), 2.22−2.40 (m, 1 H), 2.42−2.59 (m, 1 H), 6.80−7.08 (m, 4 H), 7.13−7.26 (m, 2 H), 7.34 (t, 1 H, J = 7.7 Hz), 7.45 (t, 1 H, J = 7.7 hz), 7.82 (d, 1 H, J = 8.4 Hz), 8.04 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.1, 22.6, 24.7, 28.8, 29.3, 29.4, 29.5, 31.8, 34.8, 88.3, 111.2, 116.2, 120.1, 122.8, 124.2, 127.6, 129.6, 131.1, 146.7, 156.2. Anal. Calcd for $C_{24}H_{33}N_3O$: C, 75.95; H, 8.76; N, 11.07. Found: C, 75.95; H, 8.98; N, 10.94.

General Procedure for the Preparation of Intermediates 12d, 14b, and 20, and Ketones 13d, 15b, and 21. To a solution of 1-(benzotriazol-1-yl)-1-phenoxyalkane **10a**,**b** (5 mmol) in THF (70 mL) was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5.0 mmol) at −78 °C. The solution was stirred at this temperature for 5 min, and the appropriate electrophile ($Ph(CH_2)_3Br$, 4-tolualdehyde, or 2-cyclohexenone, 5 mmol) was added. The solution was kept at this temperature for 5 min (for **12d**, the reaction mixture was warmed to 20 °C and kept at this temperature for an additional 2 min). Then the solution was quenched with water (10 mL), extracted with diethyl ether (3 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues, that were purified by column chromatography on silica gel to give the corresponding intermediates **12d**, **14b**, and **20**, which were separately dissolved in a mixture of ethanol (20 mL), water (20 mL), and H_2SO_4 (2 mL) and refluxed for 10−15 min. Water (80 mL) was then added, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues that were chromatographed on silica gel (hexane/EtOAc 30:1) to give the ketones **13d**, **15b**, and **21**. Elemental analyses and high resolution mass spectra measurements for **13d**, **15b**, and **21** are shown in Table 1.

3-(Benzotriazol-1-yl)-3-phenoxy-1-phenylnonane (12d) was obtained as a colorless oil: yield 83%; ^{1}H NMR δ 0.78 (t, 3 H, J = 6.6 Hz), 1.00−1.55 (m, 6 H), 1.69−1.87 (m, 2 H), 2.42−2.75 (m, 6 H), 6.37 (d, 2 H, J = 8.1 Hz), 6.91 (t, 1 H, J = 7.5 Hz), 7.01−7.06 (m, 4 H), 7.10−7.24 (m, 3 H), 7.26−7.37 (m, 2 H), 7.87 (d, 1 H, J = 7.7 Hz), 8.10 (d, 1 H, J = 7.4 Hz); ^{13}C NMR δ 13.8, 22.2, 22.4, 24.5, 31.4, 34.3, 35.0, 35.2, 98.0, 112.9, 119.6, 119.9, 123.3, 124.1, 125.9, 127.5, 128.2, 128.3, 129.3, 132.3, 141.2, 146.8, 153.7; HRMS calcd for $C_{27}H_{31}N_3O$ 414.2545 (M + 1), found 414.2546.

2-(Benzotriazol-1-yl)-2-phenoxy-1-hydroxy-1-(4-methylphenyl)heptane (14b) was obtained as a colorless solid: yield 80%; mp 146−149 °C (a mixture of two diasteromers, ratio: *ca.* 4:1); ^{1}H NMR δ 0.70−0.80 (m, 3 H), 1.05−1.25 (m, 4 H), 1.42−1.55 (m, 2 H), 2.21 (s) and 2.26(s) (total 3 H), 2.62−2.72 (m, 2 H), 3.36 (d, J = 4.5 Hz) and 3.54 (d, J = 2.7 Hz) (total 1 H), 5.44 (d, J = 4.6) and 5.57 (d, J = 2.9 Hz) (total 1 H), 6.50−7.32 (m, 11 H), 7.85−7.92 (m, 1 H), 8.00−8.05 (m, 1

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H); ^{13}C NMR δ 13.7, 15.2, 21.0, 21.1, 21.9, 22.0, 22.2, 22.7, 31.7, 32.8, 77.3, 78.1, 99.0, 113.3, 114.5, 119.1, 119.2, 119.3, 119.4, 123.3, 123.4, 123.7, 123.9, 127.0, 127.1, 127.4, 128.4, 128.6, 129.3, 129.4, 134.1, 134.2, 138.0, 138.3, 146.0, 153.9. Anal. Calcd for $C_{26}H_{29}N_3O_2$: C, 75.15; H, 7.03; N, 10.11. Found: C, 75.07; H, 7.36; N, 9.99.

3-[1-Phenoxy-1-(benzotriazol-1-yl)hexyl]cyclohexanone (20) was obtained as a colorless oil: yield 48% (a mixture of two diasteromers, ratio *ca.* 3:1); ^{1}H NMR δ 0.72 (t, 3 H, J = 6.9 Hz), 0.81−1.70 (m, 9 H), 1.86−2.48 (m, 5 H), 2.52−3.24 (m, 3 H), 6.56 (d, J = 8.1 Hz) and 6.66 (d, J = 8.3 Hz) (total 2 H), 6.93 (t, 1 H, J = 7.4 Hz), 7.07 (t, 2 H, J = 7.8 Hz), 7.78(d, J = 8.7 Hz) and 7.87 (d, J = 8.7 Hz) (total 1 H), 8.08 (d, 1 H, J = 6.9 Hz); ^{13}C NMR δ 13.2, 21.3, 21.7, 23.9, 25.1, 30.9, 31.9, 40.2, 42.4, 47.2, 99.1, 113.6, 119.1, 119.3, 123.0, 123.5, 127.3, 128.8, 133.4, 145.4, 153.1, 208.6. Anal. Calcd for $C_{24}H_{29}N_3O_2$: C, 73.61; H, 7.47; N, 10.74. Found: C, 73.80; H, 7.66; N, 10.38.

1-Phenylnonan-4-one (13d) was obtained as a colorless oil: yield 96%; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.9 Hz), 1.18−1.37 (m, 4 H), 1.50−1.60 (m, 2 H), 1.84−1.95 (m, 2 H), 2.30−2.40 (m, 4 H), 2.60 (t, 2 H, J = 7.5 Hz), 7.14−7.19 (m, 3 H), 7.23−7.29 (m, 2 H); ^{13}C NMR δ 13.8, 22.3, 23.4, 25.1, 31.3, 35.0, 41.7, 42.7, 125.8, 128.2, 128.3, 141.5, 210.8.

1-Hydroxy-1-(4-methylphenyl)heptan-2-one (15b) was obtained as a colorless oil: yield 95%; ^{1}H NMR δ 0.82 (t, 3 H, J = 7.2 Hz), 1.10−1.28 (m, 4 H), 1.45−1.55 (m, 2 H), 2.30−2.38 (m, 5 H), 4.30 (br s, 1 H), 5.05 (s, 1 H), 7.19 (s, 5 H); ^{13}C NMR δ 13.7, 21.1, 22.2, 23.3, 31.0, 37.7, 79.4, 127.2, 129.5, 135.2, 138.3, 209.8.

3-Hexanoylcyclohexanone (21) was obtained as a colorless oil: yield 90%; ^{1}H NMR δ 0.89 (t, 3 H, J = 6.6 Hz), 1.20−1.38 (m, 4 H), 1.52−1.88 (m, 5 H), 2.01−2.18 (m, 2 H), 2.28−2.59 (m, 6 H), 2.86−2.97 (m, 1 H); ^{13}C NMR δ 13.6, 22.2, 23.0, 24.7, 27.1, 31.1, 40.7, 40.8, 42.3, 49.9, 209.8, 210.5.

General Procedure for the Preparation of Ketones 13a−c, 15a, 17, and 19. To a solution of 1-(benzotriazol-1-yl)-1-phenoxyalkane **10a** or **10b** (5 mmol) in THF (70 mL) was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5.0 mmol) at −78 °C, and the solution was stirred at this temperature for 2 min. The appropriate electrophile (EtBr, BuBr, PhCHO, PhCOPh, or PhCH=NPh, 5 mmol) was added, and the solution was kept at this temperature for 5 min (for **13a−c**, the reaction mixture was warmed to 20 °C and kept at this temperature for additional 2 min). The reaction was then quenched with water (10 mL) and evaporated *in vacuo* to give a residue, which was dissolved in a mixture of ethanol (20 mL), water (20 mL), and H_2SO_4 (2 mL) and refluxed for 10−15 min. Water (80 mL) was added, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvents and purification by column chromatography (hexane/AcOEt 30:1) gave the ketones **13a−c**, **15a**, **17**, and **19**. Elemental analyses and high resolution mass measurements for **13a−c**, **15a**, **17**, and **19** are given in Table 1.

3-Tetradecanone (13a) was obtained as a colorless oil: yield 88%; ^{1}H NMR δ 0.89 (t, 3 H, J = 6.6 Hz), 1.05 (t, 3 H, J = 7.4 Hz), 1.20−1.26 (m, 16 H), 1.51−1.60 (m, 2 H), 2.35−2.45 (m, 4 H); ^{13}C NMR δ 7.8, 14.0, 22.6, 23.9, 29.3, 29.4, 29.5, 29.6, 31.9, 35.8, 42.4, 211.7.

5-Hexadecanone (13b) was obtained as a colorless oil: yield 90%; ^{1}H NMR δ 0.86−0.94 (m, 6 H), 1.20−1.38 (m, 18 H), 1.51−1.61 (m, 4 H), 2.37−2.42 (m, 4 H); ^{13}C NMR δ 13.8, 14.0, 22.3, 22.6, 23.8, 25.9, 29.2, 29.3, 29.4, 29.5, 29.6, 31.8, 42.4, 42.8, 211.6.

6-Tetradecanone (13c) was obtained as a colorless oil: yield 81%; ^{1}H NMR δ 0.86−0.91 (m, 6 H), 1.20−1.48 (m, 14 H), 1.50−1.62 (m, 2 H), 1.80−1.90 (m, 2 H), 2.38 (t, 2 H, J = 7.5 Hz), 3.39 (t, 2 H, J = 6.8 Hz); ^{13}C NMR δ 13.7, 13.9, 22.4, 22.5, 23.4, 23.8, 29.1, 29.2, 29.3, 31.4, 31.5, 31.7, 42.6, 210.9.

1-Hydroxy-1-phenylheptan-2-one (15a) was obtained as a colorless oil: yield 63%; ^{1}H NMR δ 0.82 (t, 3 H, J = 7.1 Hz), 1.10−1.25 (m, 4 H), 1.40−1.60 (m, 2 H), 2.25−2.40 (m, 2 H), 4.42 (br s, 1 H), 5.08 (s, 1 H), 7.30−7.40 (m, 5 H); ^{13}C NMR δ 13.7, 22.1, 23.3, 31.0, 37.7, 79.6, 127.3, 128.5, 128.8, 138.1, 209.6.

1-Hydroxy-1,1-diphenylheptan-2-one (17) was obtained as a colorless oil: yield 76%; ^{1}H NMR δ 0.79 (t, 3 H, J = 7.1 Hz), 1.08−1.25 (m, 4 H), 1.40−1.50 (m, 2 H), 2.55 (t, 2 H, J = 7.7 Hz), 4.93 (s, 1 H), 7.25−7.33 (m, 10 H); ^{13}C NMR δ 13.6, 22.1, 23.9, 31.0, 38.2, 85.4, 127.9, 128.2, 141.5, 211.1.

1-(Phenylamino)-1-phenyltridecan-2-one (19) was obtained as a colorless solid: yield 74%; mp 50−51 °C; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.10−1.55 (m, 18 H), 2.41 (t, 2 H, J = 7.4 Hz), 4.99 (d, 1 H, J = 4.5 Hz), 5.48 (d, 1 H, J = 4.5 Hz), 6.56 (d, 2 H, J = 8.7 Hz), 6.64 (t, 1 H, J = 7.4 Hz), 7.08(t, 2 H, J = 7.4 Hz), 7.30−7.40 (m, 3 H); 7.44 (d, 2 H, J = 8.1 Hz); ^{13}C NMR δ 14.1, 22.7, 23.9, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 39.1, 67.7, 113.3, 117.6, 127.9, 128.3, 129.1, 138.2, 146.1, 206.4.

Preparation of Ketones 24 and 25. To a solution of 1-(benzotriazol-1-yl)-1-phenoxyhexane (**10a)** (5 mmol) in THF (70 mL) was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5.0 mmol) at −78 °C. The solution was stirred at this temperature for 5 min, and then *trans*-chalcone (1.05 g, 5 mmol) was added. The solution was kept at this temperature for 5 min and then quenched with water (10 mL), extracted with diethyl ether (3 × 100 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues, which underwent a short column on silica gel to give the corresponding intermediates **22** and **23**. The intermediates **22** and **23** were separately dissolved in a mixture of ethanol (20 mL), water (20 mL), and H_2SO_4 (2 mL) and refluxed for 10−15 min. Water (80 mL) was then added, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues, that were chromatographed on silica gel (hexane/AcOEt 50:1) to give the ketones **24** and **25**. Elemental analyses and high-resolution mass measurements are given in Table 1.

1,3-Diphenylnonane-1,4-dione (24) was obtained as a colorless oil: yield 33%; ^{1}H NMR δ 0.81 (t, 3 H, J = 7.1 Hz), 1.10−1.30 (m, 4 H), 1.45−1.65 (m, 2 H), 2.40−2.70 (m, 2 H), 3.12 (dd, 1 H, J = 18.1, 3.6 Hz), 4.04 (dd, 1 H, J = 18.0, 10.2 Hz), 4.43 (dd, 1 H, J = 10.2, 3.6 Hz), 7.26−7.57 (m, 8 H), 7.94−7.98 (m, 2 H); ^{13}C NMR δ 13.8, 22.3, 23.3, 31.1, 41.7, 42.3, 53.3, 127.4, 128.0, 128.3, 128.5, 129.0, 133.1, 136.5, 138.2, 198.1, 209.3.

1,3-Diphenyl-3-hydroxy-1-nonen-4-one (25) was obtained as a colorless oil: yield 23%; ^{1}H NMR δ 0.82 (t, 3 H, J = 6.9 Hz), 1.10−1.30 (m, 4 H), 1.45−1.65 (m, 2 H), 2.40−2.60 (m, 2 H), 4.89 (s, 1 H), 6.87 (d, 1 H, J = 15.8 Hz), 7.04 (d, 1 H, J = 15.8 Hz), 7.20−7.50 (m, 10 H); ^{13}C NMR δ 13.7, 22.2, 23.8, 31.0, 37.0, 83.1, 126.7, 126.8, 127.0, 128.0, 128.2, 128.6, 128.7, 132.5, 136.3, 141.2, 209.2.

General Procedure for the Lithiation of Compound 26. Preparation of the Intermediates 29a,b and 33a, Ketones 30a,b, and Alkynoylsilane 34a. To a solution of 1-(phenoxymethyl)benzotriazole (**26**) (1.13 g, 5 mmol) in THF (70 mL) at −78 °C was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5 mmol) and the solution stirred for 2 min at this temperature. The appropriate electrophile ($PhCH_2$-Br or MeI, 5 mmol) was added, and the mixture was stirred at this temperature for 5 min and then at room temperature for an additional 5 min. The solution was cooled to −78 °C again, and a second equivalent of BuLi (2.2 M in cyclohexane, 2.3 mL, 5 mmol) was added. After addition of a second electrophile (*p*-tolualdehyde, cyclohexanal, or Me_3SiCl, 5 mmol), the solution was kept at −78 °C for 5 min and then quenched with water (20 mL) (for **33a** the reaction was quenched at room temperature), extracted with diethyl ether (3 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues, that were purified by column chromatography on silica gel (hexane/AcOEt 100:1) to give **29a**,**b** and **33a**. Then **29a (**or **29b**, **33a)** was dissolved in a mixture of ethanol (20 mL), water (20 mL), and H_2SO_4 (2 mL) and refluxed for 10−15 min. Water (80 mL) was added, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 100 mL × 2) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue that was chromatographed on silica gel (hexane/AcOEt 200:1) to give **30a**,**b** or **34a**. Elemental analyses and high-

resolution mass spectra measurements for **30a**,**b** and **34** are shown in Table 1.

2-(Benzotriazol-1-yl)-1-hydroxy-1-(4-methylphenyl)-3-phenyl-2-phenoxypropane (29a) was obtained as a colorless solid: yield 64%; mp 165−167 °C; ^{1}H NMR δ 2.28 (s, 3 H), 3.86 (d, 1 H, J = 15.1 Hz), 4.17 (d, 1 H, J = 15.1 Hz), 4.83 (d, 1 H, J = 3.0 Hz), 6.01 (s, 1 H), 6.48 (dd, 2 H, J = 7.7, 1.1 Hz), 6.84−7.15 (m, 15 H), 7.93 (dd, 1 H, J = 8.4, 0.9 Hz); ^{13}C NMR δ 21.0, 39.5, 76.4, 98.7, 114.0, 117.8, 119.0, 122.6, 123.8, 126.9, 127.2, 127.9, 128.0, 128.4, 129.5, 131.1, 133.9, 134.2, 134.3, 138.1, 145.2, 154.2. Anal. Calcd for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 77.11; H, 5.70; N, 9.61.

2-(Benzotriazol-1-yl)-2-phenoxy-1-hydroxy-1-cyclohexylpropane (29b) was obtained as a colorless solid: yield 45%; mp 150−151 °C; ^{1}H NMR δ 1.12−1.54 (m, 5 H), 1.62−2.00 (m, 6 H), 2.16 (s, 3 H), 2.90 (d, 1 H, J = 5.7 Hz), 4.15−4.20 (m, 1 H), 6.45 (d, 2 H, J = 7.5 Hz), 6.98 (t, 1 H, J = 8.1 Hz), 7.10 (t, 2 H, J = 8.0 Hz), 7.30 (t, 1 H, J = 7.7 Hz), 7.39 (t, 1 H, J = 8.3 Hz), 7.95 (t, 2 H, J = 8.4 Hz); ^{13}C NMR δ 18.6, 26.0, 26.2, 26.5, 28.1, 32.0, 39.5, 79.5, 98.4, 113.2, 119.6, 120.4, 123.9, 124.1, 127.4, 129.4, 132.4, 146.4, 153.3. Anal. Calcd for $C_{21}H_{25}N_3O_2$: C, 71.77; H, 7.17; N, 11.96. Found: C, 72.08; H, 7.35; N, 12.08.

[1-(Benzotriazol-1-yl)-1-phenoxy-2-phenylethyl]trimethylsilane (33a) was obtained as a colorless solid: yield 90%; mp 115−117 °C; ^{1}H NMR δ 0.20 (s, 9 H), 3.52 (d, 1 H, J = 14.1 Hz), 3.72 (d, 1 H, J = 14.1), 6.45 (d, 2 H, J = 7.5 Hz), 6.88−7.40 (m, 11 H), 7.98 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 0.2, 45.7, 95.8, 113.6, 119.1, 123.3, 123.8, 126.8, 127.0, 129.0, 129.1, 131.2, 133.8, 135.0, 145.6, 156.3. Anal. Calcd for $C_{23}H_{25}N_3OSi$: C, 71.28; H, 6.50; N, 10.84. Found: C, 71.04; H, 6.58; N, 10.86.

1-Hydroxy-1-(4-methylphenyl)-3-phenylpropan-2-one (30a) was obtained as a colorless solid: yield 82%; mp 92−93 °C; ^{1}H NMR δ 2.39 (s, 3 H), 3.65 (s, 2 H), 4.23 (d, 1 H, J = 4.5 Hz), 5.17 (d, 1 H, J = 4.8 Hz), 7.02−7.07 (m, 2 H), 7.21 (s, 3 H), 7.24−7.32 (m, 4 H); ^{13}C NMR δ 21.2, 44.5, 78.9, 127.2, 127.6, 128.6, 129.4, 129.7, 133.0, 134.6, 138.7, 207.1.

1-Cyclohexyl-1-hydroxy-2-propanone (30b) was obtained as a colorless oil: yield 95%; ^{1}H NMR δ 1.15−1.90 (m, 11 H), 2.22 (s, 3 H), 3.51 (br s, 1 H), 4.07 (d, 1 H, J = 2.4 Hz); ^{13}C NMR δ 25.0, 25.5, 25.8, 25.9, 26.4, 29.9, 41.0, 81.1, 209.9.

(Phenylacetyl)trimethylsilane (34a) was obtained as a yellow oil: yield 91%; ^{1}H NMR δ 0.12 (s, 9 H), 3.85 (s, 2 H), 7.13 (d, 2 H, J = 8.4 Hz), 7.23−7.31 (m, 3 H); ^{13}C NMR δ −2.9, 55.4, 126.8, 128.5, 129.9, 133.1, 243.8.

General Procedure for the Lithiation of Compound 26. Preparation of 28a,b and 32. To a solution of 1-(phenoxymethyl)benzotriazole (**26**) (1.13 g, 5 mmol) in THF (70 mL) at −78 °C was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5 mmol) and the solution stirred for 2 min at this temperature. The appropriate electrophile (n-$C_8H_{17}Br$, $PhCH_2Br$, or n-$C_5H_{11}I$) was added, and the mixture was stirred at this temperature for 5 min and then at room temperature for an additional 5 min. The solution was cooled to −78 °C again, and a second equivalent of BuLi (2.2 M in cyclohexane, 2.3 mL, 5 mmol) was added. After addition of a second electrophile (n-$C_8H_{17}Br$, n-$C_{10}H_{21}Br$, or cyclohexanone), the solution was kept at −78 °C for 5 min and then at room temperature for an additional 5 min. Then the solution was quenched with water (20 mL) (in the case **32**; it was quenched at −78 °C) and evaporated under reduced pressure to give a residue, which was directly hydrolyzed by refluxing in a mixture of ethanol (20 mL), water (20 mL), and H_2SO_4 (2 mL) for 10−15 min. Water (80 mL) was then added, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues that were purified by column chromatography on silica gel (hexane/EtOAc 50:1). Elemental analyses and high-resolution mass spectra measurements are shown in Table 1.

9-Heptadecanone (28a) was obtained as a colorless solid: yield 97%; mp 48−50 °C; ^{1}H NMR δ 0.91 (t, 6 H, J = 6.8 Hz), 1.17−1.47 (m, 20 H), 1.50−1.71 (m, 4 H), 2.41 (t, 4 H, J = 7.4 Hz); ^{13}C NMR δ 14.0, 22.6, 23.9, 29.1, 29.2, 29.3, 31.8, 42.8, 211.4.

9-Nonadecanone (28b) was obtained as a colorless solid: yield 80%; mp 45−47 °C; ^{1}H NMR δ 0.87 (t, 6 H, J = 6.8 Hz), 1.15−1.40 (m, 24 H), 1.50−1.67 (m, 4 H), 2.37 (t, 4 H, J = 7.5 Hz); ^{13}C NMR δ 14.0, 22.6, 23.8, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.7, 31.8, 42.7, 211.4.

1-(1-Hydroxycyclohexyl)hexan-1-one (32) was obtained as a colorless oil: yield 41%; ^{1}H NMR δ 0.89 (t, 3 H, J = 6.9 Hz), 1.20−1.38 (m, 5 H), 1.40−1.50 (m, 2 H), 1.53−1.78 (m, 9 H), 2.57 (t, 2 H, J = 7.4 Hz), 3.63 (br s, 1 H); ^{13}C NMR δ 13.7, 21.0, 22.3, 23.3, 25.2, 31.3, 33.7, 35.5, 77.8, 214.8.

General Procedure for the Lithiation of Compound 26. Preparation of 34b−g and 37. To a solution of 1-(phenoxymethyl)benzotriazole (**26**) (1.13 g, 5 mmol) in THF (70 mL) at −78 °C was added *n*-butyllithium (2.2 M in cyclohexane, 2.3 mL, 5 mmol) and the solution stirred for 2 min at this temperature. The appropriate trialkylsilyl chloride [Me_3SiCl, $PhMe_2SiCl$, Ph_3SiCl, (n-C_8H_{17})Me_2SiCl, (t-Bu)Me_2-SiCl, (i-Pr)$_3$SiCl] was added, and the mixture was stirred at this temperature for 5 min, adding a second equiv of BuLi (2.2 M in cyclohexane, 2.3 mL, 5 mmol). The solution was kept at −78 °C for an additional 2 min before a second electrophile (n-$C_8H_{17}Br$, $PhCH_2Br$, n-$C_7H_{15}Br$, EtBr, or cyclohexenone). Then the solution was stirred at −78 °C for 5 min and then at room temperature for an additional 5 min. Water (20 mL) and HCl (5 N, 15 mL) were added, and the mixture was refluxed for 7 h. After cooling, the solution was extracted with diethyl ether (3 × 100 mL), and the combined extracts were washed with NaOH solution (2 N, 2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave residues, that were purified by column chromatography on silica gel (hexane/EtOAc 50:1). Elemental analysis data are shown in Table 1.

Nonanoyltrimethylsilane (34b) was obtained as a yellow oil: yield 82%; ^{1}H NMR δ 0.21 (s, 9 H), 0.89 (t, 3 H, J = 6.9 Hz), 1.20−1.35 (m, 10 H), 1.48−1.54 (m, 2 H), 2.60 (t, 2 H, J = 7.4 Hz); ^{13}C NMR δ −3.2, 14.0, 22.1, 22.6, 29.1, 29.3, 29.4, 31.8, 48.4, 248.3.

Dimethylphenyloctanoylsilane (34c) was obtained as a yellow oil: yield 96%; ^{1}H NMR δ 0.48 (s, 6 H), 0.84 (t, 3 H, J = 6.9 Hz), 1.10−1.30 (m, 8 H), 1.41−1.46 (m, 2 H), 2.55 (t, 2 H, J = 7.2 Hz), 7.35−7.39 (m, 3 H), 7.53−7.56 (m, 2 H); ^{13}C NMR δ −4.7, 14.0, 22.2, 22.5, 29.0, 29.2, 31.6, 48.8, 128.1, 129.8, 133.9, 134.6, 246.3.

Triphenylpropionylsilane (34d) was obtained as a yellow oil: yield 85%; ^{1}H NMR δ 0.96 (t, 3 H, J = 7.1 Hz), 2.75 (q, 2 H, J = 7.1 Hz), 7.36−7.48 (m, 9 H), 7.58−7.61 (m, 6 H); ^{13}C NMR δ 6.2, 44.0, 128.2, 130.2, 131.4, 136.1, 243.1.

Dimethyloctylpropionylsilane (34e) was obtained as a yellow oil: yield 71%; ^{1}H NMR δ 0.19 (s, 6 H), 0.68−0.73 (m, 2 H), 0.86−0.91 (m, 3 H), 0.98 (t, 3 H, J = 7.2 Hz), 1.20−1.37 (m, 12 H), 2.62 (q, 2 H, J = 7.2 Hz); ^{13}C NMR δ-4.9, 6.0, 13.5, 14.0, 22.6, 23.5, 29.1, 31.8, 33.3, 41.9, 248.2.

***tert*-Butyldimethylnonanoylsilane (34f)** was obtained as a yellow oil: yield 56%; ^{1}H NMR δ 0.17 (s, 6 H), 0.87 (t, 3 H, J = 6.6 Hz), 0.92 (s, 9 H), 1.17−1.33 (m, 10 H), 1.42−1.53 (m, 2H), 2.58 (t, 2 H, J = 7.2 Hz); ^{13}C NMR δ −7.0, 14.0, 16.5, 21.9, 22.6, 26.4, 29.1, 29.3, 29.5, 31.8, 50.3, 247.9.

Propionyltriisopropylsilane (34g) was obtained as a yellow oil: yield 46%; ^{1}H NMR δ 0.99 (t, 3 H, J = 7.1 Hz); 1.12-(d, 18 H, J = 6.9 Hz); 1.29 (hept, 3 H, J = 6.9 Hz), 2.61 (q, 2 H, J = 7.1 Hz); ^{13}C NMR δ 5.7, 10.7, 18.5, 44.3, 247.4.

3-[(Trimethylsilyl)carbonyl]cyclohexanone (37) was obtained as a yellow oil: yield 66%; ^{1}H NMR δ 0.25 (s, 9 H), 1.50−2.50 (m, 8 H), 3.28−3.38 (m, 1 H); ^{13}C NMR δ −3.0, 24.8, 25.5, 40.9, 53.9, 210.4, 245.8.

Supporting Information Available: The NMR spectra of compounds **9b, 12d, 17, 19, 24,** and **25** (12 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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