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The Chemistry of *N*-Substituted Benzotriazoles. Part 22 [1]: Transformations of 1-(Trimethylsilylmethyl)benzotriazole

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ABSTRACT

1-(Trimethylsilylmethyl)benzotriazole is readily prepared from benzotriazole and chloromethyltrimethylsilane. It undergoes fluoride-catalyzed desilylation with carbonyl compounds and forms an anion that can be alkylated and acylated readily and undergoes Peterson olefination. 1-(Cyclohexylidenemethyl)benzotriazole is lithiated exclusively at the α carbon atom, and the anion can be cleanly alkylated.

1-(α-Acylalkyl)benzotriazoles are reduced to ketones with zinc and acid. The stability of 1-alkenylbenzotriazoles to hydrolysis has been studied.

RESULTS AND DISCUSSION

1-(Trimethylsilylmethyl)azoles have been prepared by various methods [2–7]. However, alkylation of 1-(lithiomethyl)benzotriazole with trimethylsilyl chloride affords mainly the bis-silylated adduct [8]. We now find that multigram quantities of 1-(trimethylsilylmethyl)benzotriazole (**2**) can be synthesized readily by treating the sodium salt of benzotriazole with chloromethyltrimethylsilane in dry DMF. Some of the corresponding 2-(trimethylsilylmethyl)benzotriazole (ca. 20%) is also formed, but it is an oil and stays in solution.

Reactions of 1-(Trimethylsilylmethyl)benzotriazole with n-Butyllithium and Subsequently with Electrophiles

The treatment of **2** with *n*-butyllithium at −78°C affords a dark blue solution of the corresponding α-lithio derivative (**5**), which can be trapped with various electrophiles to give products, generally in good yields (Scheme 1). In particular, the alkylation of **5** succeeds with alkyl and silyl halides to give (**9a–9e**) in yields of above 80% (Table 1). Compound **9f** is prepared by treating the lithio derivative of 1-benzylbenzotriazole (**10a**) with trimethylsilyl chloride.

With ethyl 4-methylbenzoate and **5**, the ketone **1a** was obtained. Addition of aldehydes and ketones to **5** gives Peterson olefination products (**6a–6d**), although in the preparation of **6c** from acetophenone some unreacted starting material (ca. 6%) was also recovered (Table 2). With cyclohexenone, the Michael addition product (**8**) was obtained in 70% yield, although with ethyl 3,3-dimethylacrylate the expected ketone (**1b**) was formed.

Anion Formation from 1-α-(Trimethylsilylalkyl)benzotriazole and Subsequent Reactions with Electrophiles

The corresponding anions (**12**) derived from **9** are readily generated using *n*-butyllithium and in two typical cases were trapped with electrophiles to afford **16a** and **16b** in moderate to good yields. However low yields and a large number of side products are obtained on the treatment of **12** with esters or

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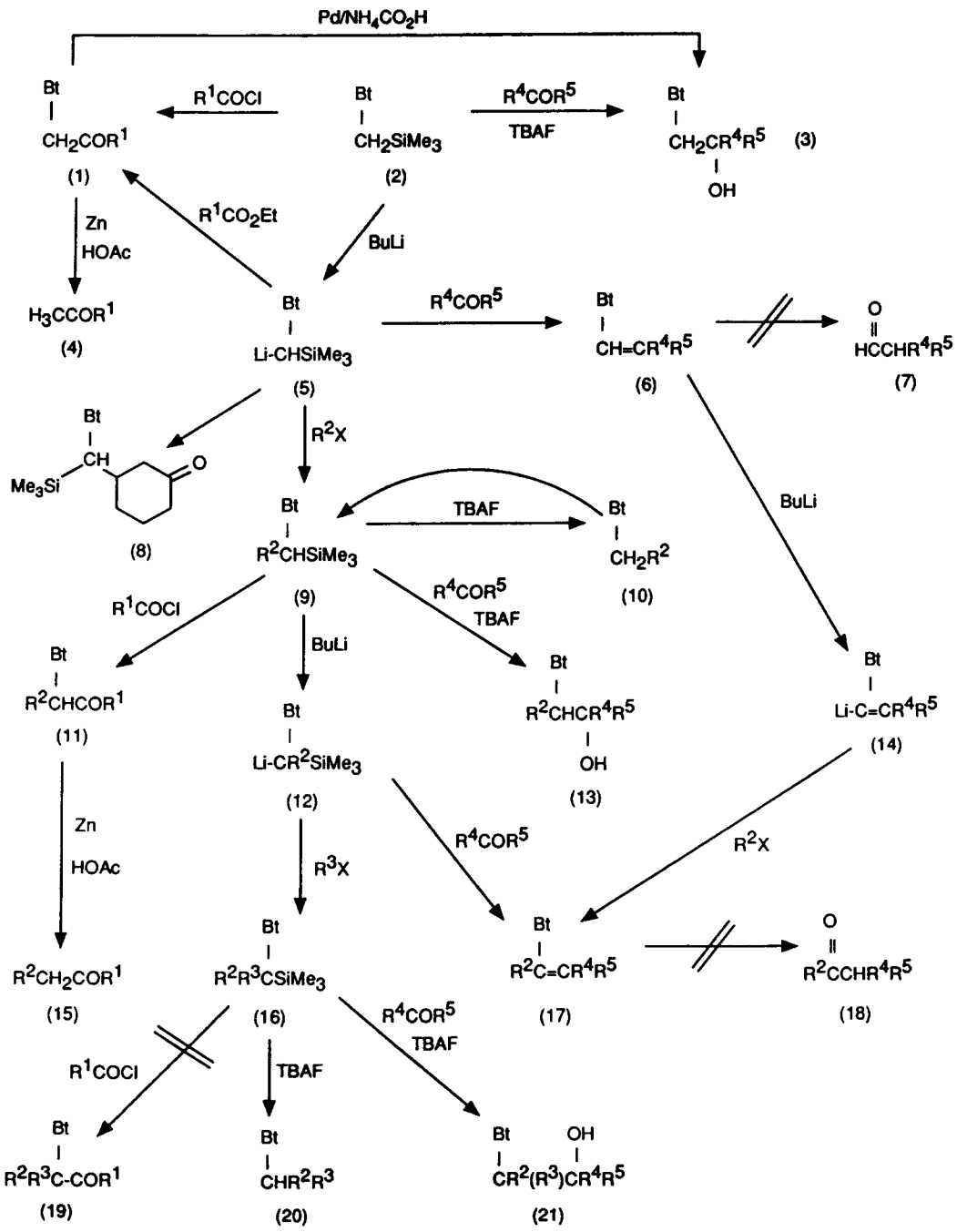


For designations of R^1, R^2, R^3, R^4, R^5 see Tables 1-6

SCHEME 1

acid chlorides. When the anions **12** derived from **9a,b** are treated with cyclohexanone, the reaction goes to only 80% completion; however, the olefinic products (**17b, 17c**) of these reactions can be obtained in a pure state by treating the lithio derivative of 1-(cyclohexylidenemethyl)benzotriazole (**6a**) with the corresponding alkyl halides (see next section). The phenyl derivative (**17e**) was prepared by the Peterson olefination on **9f** with cyclohexanone.

Anion Formation from 1-Alkenylbenzotriazoles

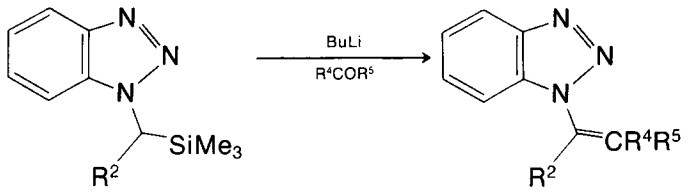
Metallation of 1-(cyclohexylidenemethyl)benzotriazole (**6a**) with *n*-butyllithium occurred readily and exclusively at the C-α position rather than at the allylic position in the cyclohexane ring. Treatment of the lithio compound (**14**) with deuterium oxide gave the expected monodeuterio derivative (**17a**), whereas compounds **17b–17d** were corre-

TABLE 1 Alkylation of 1-(Trimethylsilyl)methylbenzotriazole (**2** → **5** → **9**), of 1-Benzylbenzotriazole (**10a** → **9f**), of 1-(Cyclohexylidenemethyl)benzotriazole (**6a** → **14** → **17**), and of 1-(Benzotriazol-1-yl)-1-(trimethylsilyl)ethane (**9a** → **12** → **16**)

Substrate No.	*Electrophile*	*Reaction time*	*Product No.*	R^2	R^3	R^4	R^5	*Yield (%)*	*MP (°C)*[a]	*Formula*	*Found (%) (required)* C	H	N
2	MeI	4	**9a**	Me	—	—	—	86	71–72	$C_{11}H_{17}N_3Si$	60.3 (60.2	8.1 7.8	19.15 19.2)
2	HxI	6	**9b**	Hx	—	—	—	82	50–51	$C_{16}H_{27}N_3Si$	66.5 (66.4	9.4 9.4	14.5 14.5)
2	$PhCH_2Br$	4	**9c**	$PhCH_2$	—	—	—	81	108–108.5	$C_{17}H_{21}N_3Si$	69.1 (69.1	7.4 7.2	14.1 14.2)
2	Me_3SiCl	2	**9d**	Me_3Si	—	—	—	83	147–147.5[b]	$C_{13}H_{23}N_3Si_2$	56.3 (56.3	8.4 8.35)	
2	Me_3SiCH_2Cl	2	**9e**	Me_3SiCH_2	—	—	—	83	86–88[c]	$C_{14}H_{25}N_3Si_2$	57.8 (57.7	8.7 8.6	14.4 14.4)
10a	Me_3SiCl[6]	3	**9f**	Ph	—	—	—	91	127–128	$C_{16}H_{19}N_3Si$	68.0 (68.3	7.0 6.8	14.9 14.9)
6a	D_2O	0.5	**17a**	D	—	$—(CH_2)_5—$		94	99–101	$C_{13}H_{14}DN_3Si$	73.15 (72.9	7.7 7.5	19.3 19.6)
6a	MeI	2	**17b**	Me	—	$—(CH_2)_5—$		90	Oil[d]	$C_{14}H_{17}N_3Si$	—	—	—
6a	HxI	6	**17c**	Hx	—	$—(CH_2)_5—$		76	Oil[d]	$C_{19}H_{27}N_3Si$	—	—	—
6a	4-MeC_6H_4CHO	2	**17d**	4-$MeC_6H_4CH(OH)$	—	$—(CH_2)_5—$		74	151–152[d,e]	$C_{21}H_{23}N_3O$	75.3 (75.65	7.1 6.95	12.2 12.6)
9a	HxI	6	**16a**	Me	Hx	—	—	80	Oil[d]	$C_{17}H_{29}N_3Si$	—	—	—
9a	$PhCH_2Br$	4	**16b**	Me	$PhCH_2$	—	—	71	87–89	$C_{18}H_{23}N_3Si$	69.4 (69.9	7.9 7.5	13.7 13.6)

[a] Needles from hexanes unless otherwise stated.
[b] From MeOH.
[c] From MeOH–H_2O.
[d] Purified by chromatography.
[e] Microcrystals.

TABLE 2 Formation of Peterson'Olefination Products (**2** → **5** → **6** and **9** → **12** → **17**)



2, 9f **6, 17e**

Substrate No.	Electrophile	Reaction time (h)	Product No.	R^2	R^4	R^5	Yield (%)	MP (°C)	Formula	Found (%) (required) C	H	N
2	$C_6H_{10}O$	2	*6a*	—	—$(CH_2)_5$—		83	100–102	$C_{13}H_{15}N_3$	72.8 (73.2	7.4 7.1	19.7 19.7)
2	MeCOMe	6	*6b*	—	Me	Me	80	68–70[a]	$C_{10}H_{11}N_3$	—	—	—
2	PhCOMe	6	*6c*	—	Ph	Me	38	65–67	$C_{15}H_{13}N_3$	76.55 (76.6	5.7 5.6	17.6 17.9)
2	PhCOPh	6/12[b]	*6d*	—	Ph	Ph	45	76–79[c]	$C_{15}H_{20}N_3$	—	—	—
9f	$C_6H_{10}O$	6/12[b]	*17e*	Ph	—$(CH_2)_5$—		70	108–110	$C_{19}H_{19}N_3$	78.9 (78.9	6.8 6.6	14.6 14.5)

[a] Lit. [11] mp 70–71°C.
[b] 12 h at room temperature.
[c] Lit. [9] mp 78–80°C.

spondingly formed by treatment of **14** with alkyl halides and aldehydes (see Table 1, compounds **17a–17d**). The structures of products **17a–17d** were confirmed by analysis and by their NMR spectra, in particular by the disappearance of the vinyl proton at δ6.81 and the displacement of the carbon signal at 113.7 ppm in the ^1H and ^{13}C NMR spectra, respectively.

Fluoride-Catalyzed Desilylations

2-(Benzotriazol-1-yl)ethanols (**3, 13,** and **21**) are obtained in good yields when **2** or its derivatives, **9** and **16,** respectively, are treated with aliphatic and aromatic carbonyl compounds in the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF) in THF (Table 3). In all cases, the hydrolysis product (i.e., $SiMe_3$ replaced by H) was also obtained (ca. 10%). This latter type of byproduct was also observed in another investigation [7] in our laboratory and probably arises via protonation of the incipient carbanion by the solvent. In the case of 1-[bis(trimethylsilyl)methyl]benzotriazole (**9d**) selective electrophilic addition is followed by elimination to give rise to the corresponding alkylidene benzotriazoles [9].

Desilylations with replacement of $SiMe_3$ by H can be carried out using a slight excess of TBAF in refluxing THF. Thus the silyl derivatives **9** and **16** afforded the corresponding 1-alkylbenzotriazoles **10** and **20** in yields of greater than 70% (Table 4).

Acylative Desilylation

Desilylations can also be effected by treating **2** or **9** with acyl halides in the absence of F^- (Table 5). The aliphatic acyl halides were generally more reactive than those of the aryl series to afford the ketones **1** and **11** in yields of about 70%. However, steric hindrance plays an important factor, with the hydrolysis product being formed when compounds of type **16** were used. In contrast, sulfonyl halides failed to react in a similar manner, even in the presence of F^-.

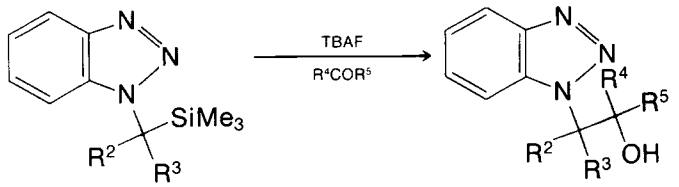
Reductive Elimination of Benzotriazole

Benzotriazole is readily eliminated when compounds of type **1** and **11** are treated with zinc in the presence of acetic acid to generate ketones **4** and **15** respectively (Table 6). On the other hand, when reduction was attempted with ammonium formate and activated palladium on carbon, the keto group was reduced to the alcohol. Thus **1a** afforded **3b** in over 80% yield.

Attempted Hydrolysis of Benzotriazolylalkenes

Although the hydrolysis of 1,1-bis(benzotriazol-1-yl) derivatives of type **23** to the ketone **24** occur under very mild conditions [10] (Scheme 2), this

TABLE 3 Fluoride-Catalyzed Desilylations and Treatment with Carbonyl Compounds (**2** → **3**, **9** → **13**, and **16** → **21**)



2, 9, 16 **3, 13, 21**

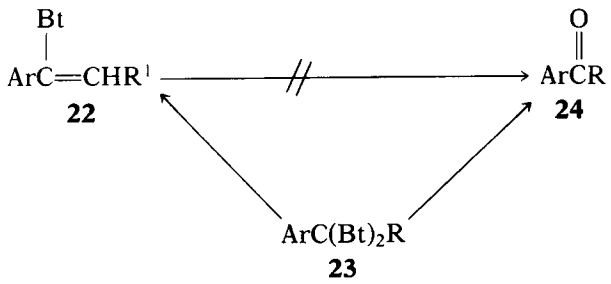
Substrate No.	*Carbonyl compound*	*Product No.*	R^2	R^3	R^4	R^5	*Yield (%)*	*mp (°C)*	*Formula*
2	$C_6H_{10}O$	**3a**	—	—	—$(CH_2)_5$—		39	132–134	$C_{13}H_{17}N_3O$
2	4-MeC_6H_4CHO	**3b**	—	—	H	4-MeC_6H_4	76	143–145	$C_{15}H_{17}N_3O$
9a	4-MeC_6H_4CHO	**13a**	Me	—	H	4-MeC_6H_4	72	Oil[a]	$C_{16}H_{17}N_3O$
9c	PrCHO	**13b**	$PhCH_2$	—	H	Pr	63	Oil	$C_{18}H_{21}N_3O$
9c	4-MeC_6H_4CHO	**13c**	$PhCH_2$	—	H	4-MeC_6H_4	57	Oil[a]	$C_{22}H_{21}N_3O$
16a	4-MeC_6H_4CHO	**21a**	Me	Hx	H	4-MeC_6H_4	65	Oil[a]	$C_{22}H_{29}N_3O$
16b	$C_6H_{10}O$	**21b**	Me	$PhCH_2$	—$(CH_2)_5$—		44	128–130	$C_{21}H_{25}N_3O$

[a] Mixture of diastereomers, which were further purified.

hydrolysis was shown not to involve intermediates of type **22.** Compound **22** was evidently formed in competition with **24** and did not hydrolyze [10]. Further attempts to effect the hydrolysis of **6** → **7** and **17** → **18** have also failed. Reaction conditions varied from treatment with 1–10*N* hydrochloric acid solutions, 10–98% sulfuric acid, trifluoromethanesulfonic acid with or without methanol and in refluxing hydrobromic acid solutions. Under the milder reaction conditions, only starting material was recovered, whereas with the more vigorous conditions, decompositions were generally observed.

CONCLUSIONS

The silicon-containing N substituent in 1-(trimethylsilylmethyl)benzotriazole allows a successive introduction of alkyl, alkylidene, and acyl groups at the α position to the benzotriazole ring. This enables the synthesis of a wide range of functionally substituted benzotriazoles, and suggests that similar methodology would be useful in the elaboration of N substituents in other heterocyclic ring systems.

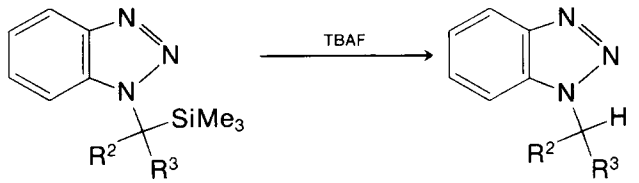


SCHEME 2

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Proton (200-MHz) NMR spectra were recorded on a Varian XL-200 (FT mode) spectrometer with Me_4Si as internal standard; ^{13}C (50-MHz) NMR on the above instrument, referring to the center signal of $CDCl_3$ (77.0). Mass spectra were obtained at 70 eV on a AEI MS 30 spectrometer operating with a DS-55 data sys-

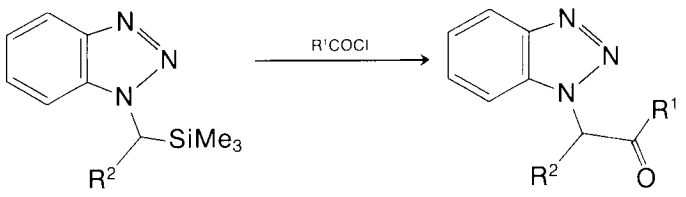
TABLE 4 Fluoride-Induced Desilylations: Formation of 1-Alkylbenzotriazoles (**9** → **10** and **16** → **20**)



9, 16 **10, 20**

Substrate No.	R^2	R^3	*Product No.*	*Yield (%)*	*Formula*
9b	Hx	—	**10b**	73	$C_{13}H_{19}N_3$
9c	$PhCH_2$	—	**10c**	79	$C_{14}H_{13}N_3$
16a	Me	Hx	**20a**	84	$C_{14}H_{21}N_3$
16b	Me	$PhCH_2$	**20b**	82	$C_{15}H_{15}N_3$

TABLE 5 Acylation of Trimethylsilylmethylbenzotriazole Derivatives with Acid Chlorides (R^1COCl) (**2** → **1** and **9** → **11**)



2, 9 **1, 11**

Substrate No.	Product No.	R^1	R^2	Reaction time (h)	Yield (%)	MP (°C)	Formula	Found (%) (required) C	H	N
2	**1a**	4-MeC_6H_4	—	72	72	133–135	$C_{15}H_{13}N_3O$	71.8 (71.7	5.2 5.2	16.8 16.7)
2	**1c**	Me	—	6	73	126–127	$C_9H_9N_3O$	61.9 (61.7	5.2 5.2	23.9 24.0)
2	**1d**	Ph	—	24	72	113–114	$C_{14}H_{11}N_3O$	71.0 (70.9	4.4 4.7	17.7 17.7)
2	**1e**	$BtCH_2CO(CH_2)_4$	—	6	63	197–200	$C_{20}H_{20}N_6$	64.0 (63.8	5.4 5.4	22.5 22.3)
2	**1f**	$PhCH_2$	—	6	70	141–142	$C_{15}H_{13}N_3O$	71.6 (71.7	5.2 5.2	16.8 16.7)
9a	**11a**	4-MeC_6H_4	Me	72	77	Oil	$C_{16}H_{15}N_3O$	—	—	—
9c	**11b**	4-MeC_6H_4	$PhCH_2$	96	55	97–98	$C_{22}H_{19}N_3$	77.4 (77.15	5.6 5.6	12.3 12.3)

tem. Elemental analyses were performed under the supervision of Dr. R. W. King of this department.

Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl. Dimethylformamide (DMF) was dried by azeotropic distillation with benzene followed by distillation under reduced pressure.

All moisture-sensitive reactions were carried out in a dry argon atmosphere.

Column chromatography was carried out with MCB silica gel (230–400 mesh).

The following compound was prepared by the known literature procedure: 1-benzylbenzotriazole (**10a**), mp 116–118°C (from MeOH) (lit. [11] mp 115–116°C).

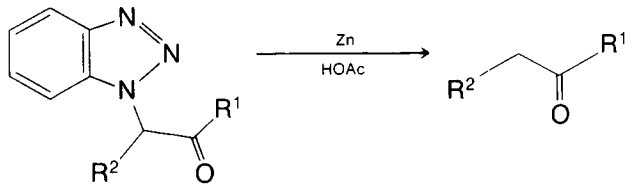
1-(Trimethylsilylmethyl)benzotriazole (**2**)

Benzotriazole (11.9 g, 100 mmol) was dissolved in sodium ethoxide (1 *M* in ethanol, 100 mL, 100 mmol). The solvent was then removed under vacuum and the resulting solid dried overnight in a vacuum oven at 50°C. The solid was then dissolved in DMF (100 mL) and chloromethyltrimethylsilane (13.9 mL, 100 mmol) added slowly. The mixture was stirred at ambient temperature for 24 h. Water (75 mL) was then added and the mixture was extracted with Et_2O (7 × 50 mL), and dried (Na_2SO_4); the solvent was then removed under vacuum to give a yellow oil. Crystallization from hexanes afforded colorless needles (13.75 g, 67%), mp 55–56°C. Analysis, found, C, 58.3; H, 7.6; N, 20.4; $C_{10}H_{15}N_3Si$ requires C, 58.5; H, 7.4; N, 20.5%. Results by ^1H NMR, δ 7.8–7.6 (1H, m), 7.2–6.8 (3H, m), 4.00 (2H, s), and 0.20 (9H, s); by ^{13}C NMR, δ 145.4, 133.6, 126.5, 123.4, 119.5, 109.4, 38.7, and −2.1.

General Procedure for Lithiation with n-Butyllithium and Reaction with Electrophiles

To a solution of the corresponding precursor (10 mmol) in dry THF (100 mL) at −78°C was added dropwise *n*-butyllithium (2.5 *M* in hexanes, 4.4 mL, 11 mmol) and the resulting colored solution or precipitate (as in the case of **6a**) was stirred at that temperature for 1 h. To the solution of the corresponding lithio derivative was added a solution of the electrophile (10.5 mmol) and the resulting solution was stirred at −78°C for the appropriate time (see Tables 1 and 2). The reaction mixture was then poured into saturated aqueous ammonium chloride (75 mL) and the layers were separated (it was sometimes necessary to add a little water to dissolve any inorganic precipitate). The aqueous layer was extracted with Et_2O (3 × 25mL), the combined organic extracts were washed with water, dried ($MgSO_4$), and the solvent was evaporated to give the crude product, which was purified as indicated in Tables 1 and 2.

TABLE 6 Reduction Elimination of Benzotraizole (**1** → **4** and **11** → **15**)



1, 11 **4, 15**

Substrate No.	Reaction time (h)	R^1	R^2	Product No.	Yield (%)	Formula	Bp (°C)	Lit. bp (°C)
1c	6	4-MeC_6H_4	—	**4a**	60	$C_9H_{10}O$	221–223	225[a]
11a	36	4-MeC_6H_4	Me	**15a**	71	$C_{10}H_{12}O$	236–239	239[a]
11b	36	4-MeC_6H_4	$PhCH_2$	**15b**	60	$C_{16}H_{16}O$	61–64	63–64[b]

[a] C.R. Noller, R. Adams, J. Am. Chem. Soc., 46, 1924, 1889.
[b] D.N. Kursanov, N.M. Loim, V.A. Baranova, L.V. Moiseeva, L.P. Zalukaev, Z.N. Parnes, Synthesis, 1973, 420.

The following compounds were thus prepared.

1-(Benzotriazol-1-yl)-1-(trimethylsilyl)ethane (**9a**). See Table 1. Results by ^1H NMR, δ 8.05–8.0 (1H, m), 7.6–7.3 (3H, m), 4.24 (1H, q, *J* 8 Hz), 1.67 (3H, d, *J* 8 Hz), and 0.16 (9H, s); by ^{13}C NMR, δ 145.6, 133.1, 126.4, 123.4, 119.7, 109.5, 45.6, 16.3, and −3.0.

1-(Benzotriazol-1-yl)-1-(trimethylsilyl)heptane (**9b**). See Table 1. Results by ^1H NMR, δ 8.15–8.1 (1H, m), 7.6–7.4 (3H, m), 4.19 (1H, dd, *J* 3.4 Hz, *J* 11.3 Hz), 3.5–1.8 (2H, m), 1.23 (8H, m), 0.87 (3H, m), 0.16 (9H, s); by ^{13}C NMR, δ 145.4, 134.0, 126.5, 123.3, 119.8, 109.5, 51.6, 31.4, 31.0, 28.7, 27.8, 22.4, 13.9, and −2.8.

1-(Benzotriazol-1-yl)-2-phenyl-1-(trimethylsilyl)ethane (**9c**). See Table 1. Results by ^1H NMR, δ 8.0–7.9 (1H, m), 7.3–7.1 (2H, m), 7.05–7.0 (3H, m), 6.90–6.8 (3H, m), 4.23 (1H, dd, *J* 4 Hz, *J* 10 Hz), 3.4–3.2 (2H, m), and 0.18 (9H, s); by ^{13}C NMR, δ 145.1, 139.3, 134.1, 128.4, 128.3, 126.4, 126.3, 123.2, 119.4, 109.2, 53.7, 37.9, and −2.7.

1-[Bis(trimethylsilyl)methyl]benzotriazole (**9d**). See Table 1. Results by ^1H NMR, δ 8.22 (1H, d, *J* 8 Hz), 7.5–7.3 (3H, m), 3.69 (1H, s), and 0.10 (18H, s); by ^{13}C NMR, δ 145.1, 133.8, 126.2, 123.3, 119.7, 109.7, 43.3, and −0.8.

1-(Benzotriazol-1-yl)-1,2-bis(trimethylsilyl)ethane (**9e**). See Table 1. Results by ^1H NMR, δ 7.90 (1H, d, *J* 8 Hz), 7.4–7.15 (3H, m), 4.20 (1H, dd, *J* 2.6, 13.6 Hz), 1.74 (1H, dd, *J* 13.6, 15.2 Hz), 0.97 (1H, dd, *J* 2.6, 15.2 Hz), 0.11 (9H, s), and −0.45 (9H, s); by ^{13}C NMR, δ 145.5, 133.2, 126.5, 123.4, 119.9, 109.6, 47.8, 17.3, −2.0, and −3.4.

1-(α-Trimethylsilylbenzyl)benzotriazole (**9f**). See Table 1. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.3–7.15 (6H, m), 7.05–7.0 (2H, m), 5.20 (1H, s), and 0.26 (9H, s); by ^{13}C NMR, δ 145.9, 138.4, 133.7, 128.5, 126.8, 126.6, 126.2, 123.7, 119.6, 110.2, 56.6, and −2.1.

1-(Cyclohexylidenemethyl)benzotriazole (**6a**). See Table 2. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.5–7.3 (3H, m), 6.81 (1H, s), 2.40 (2H, t, *J* 5 Hz), 2.17 (2H, t, *J* 5 Hz), and 1.85–1.5 (6H, m); by ^{13}C NMR, δ 145.4, 145.1, 133.3, 127.3, 123.7, 119.6, 113.7, 109.8, 33.4, 28.7, 27.9, 27.1, and 25.9.

1-(Benzotriazol-1-yl)-2-methylpropene (**6b**). See Table 2. Results by ^1H NMR, δ 8.06 (1H, d, *J* 8 Hz), 7.5–7.3 (3H, m), 6.85 (1H, s), 2.03 (3H, s), and 1.77 (3H, s).

1-(Benzotriazol-1-yl)-2-phenylpropene (**6c**). This compound was purified by column chromatography (hexanes–ethyl acetate 9 : 1) (see Table 2). Results by ^1H NMR, δ 8.0–7.9 (1H, m), 7.25–6.9 (8H, m), and 2.36 (3H, s); by ^{13}C NMR, δ 145.2, 138.7, 137.6, 132.2, 128.3, 128.0, 127.2, 127.0, 123.6, 119.4, 118.3, 110.2, and 22.3.

1-(Benzotriazol-1-yl)-2,2-diphenylethene (**6d**). This compounds was purified by column chromatography (hexanes–chloroform, 2 : 1) (see Table 2). Results by ^1H NMR, δ 8.0–7.9 (1H, m), 7.63 (1H, s), 7.41 (5H, s), and 7.3–7.0 (8H, m).

[(Benzotriazol-1-yl)(phenyl)methylene]cyclohexane (**17e**). This compound is an oil purified by column chromatography (hexanes–chloroform, 2 : 1) (see Table 2). Results by ^1H NMR, δ 8.06 (1H, d, *J* 8 Hz), 7.4–7.2 (8H, m), 2.54 (2H, t, *J* 5 Hz), and

2.0–1.2 (8H, m); by ^{13}C NMR, δ 145.4, 144.0, 135.8, 133.6, 128.9, 128.3, 128.1, 127.5, 126.7, 123.7, 119.7, 110.2, 31.4, 30.9, 28.1, 28.0, and 26.2.

[*(Benzotriazol-1-yl)(deuterio)methylene*]*cyclohexane* (**17a**). See Table 1. Analysis, found, M^+, *m/z* 214.1331; $C_{13}H_{14}DN_3$ requires 214.1328. Results by ^1H NMR, δ 8.05 (1H, m), 7.6–7.3 (3H, m), 2.41 (2H, t, *J* 5 Hz) 2.18 (2H, t, *J* 5 Hz), 1.8–1.5 (6H, m); by ^{13}C NMR, δ 145.3, 145.1, 133.4, 127.4, 123.8, 119.7, 109.9, 33.4, 28.7, 27.9, 27.1, and 26.0 (the deuterated carbon signal was not observed).

[*1-(Benzotriazol-1-yl)ethylidene*]*cyclohexane* (**17b**). This compound was purified by column chromatography (hexane–chloroform, 1 : 1) to afford **17b** as a pale yellow oil (see Table 1). Analysis, found, M^+, *m/z* 227.1412; $C_{14}H_{17}N_3$ requires 227.1422). Results by ^1H NMR, δ 8.07 (1H, d, *J* 8 Hz), 7.5–7.3 (3H, m), 2.46 (2H, t, *J* 6 Hz), 2.20 (3H, s), and 1.8–1.3 (8H, m); by ^{13}C NMR, δ 145.1, 140.7, 132.9, 127.2, 123.6, 121.8, 119.6, 109.8, 30.3, 29.8, 27.5, 27.4, 26.0, and 17.8.

[*1-(Benzotriazol-1-yl)heptylidene*]*cyclohexane* (**17c**). This is a brown gum purified by column chromatography (hexane–chloroform, 3 : 2) to give a brown oil (see Table 1). Analysis, found, M^+, *m/z* 297.2204; $C_{19}H_{27}N_3$ requires M^+, *m/z* 297.2222). Results by ^1H NMR, δ 8.08 (1H, d *J* 8 Hz), 7.5–7.3 (3H, m), 2.61 (2H, m), 2.48 (2H, m), 1.8–1.4 (8H, m), 1.3–1.1 (8H, m), and 0.82 (3H, t, *J* 6 Hz); by ^{13}C NMR, δ 145.1, 141.0, 133.8, 127.3, 126.8, 123.6, 119.8, 110.0, 32.0, 31.4, 30.3, 30.0, 28.6, 27.8, 27.7, 27.6, 26.2, 22.4, and 13.9.

[*(4-Methyl-α-hydroxybenzyl)(benzotriazol-1-yl)methyl*]*cyclohexane* (**17d**). The crude mixture was purified by column chromatography (hexane–chloroform, 1 : 1) (see Table 1). Results by ^1H NMR, δ 7.9 (1H, m), 7.5–6.5 (7H, m), 6.18 (1H, d, *J* 5 Hz), 3.8 (1H, bs, OH), 2.75 (2H, bs), 2.15 (2H, bs), and 1.9–1.3 (8H, m); by ^{13}C NMR, 144.7, 144.4, 137.8, 136.7, 134.5, 128.6, 127.2, 124.9, 123.6, 119.2, 109.9, 69.7, 30.4, 27.8, 27.6, 26.0, and 20.8.

2-(Benzotriazol-1-yl)-2-(trimethylsilyl)octane (**16a**). This compound was purified by column chromatography (hexane–chloroform, 2 : 1) as a pale yellow oil (80%) (see Table 1). Analysis, found, M^+, *m/z* 303.2130; $C_{17}H_{29}N_3Si$ requires M^+, *m/z* 303.2130). Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.8–7.7 (1H, m), 7.4–7.25 (2H, m), 2.5–2.0 (2H, m), 1.85 (3H, m), 1.16 (8H, m), 0.80 (3H, t, *J* 6 Hz), and 0.18 (9H, s); by ^{13}C NMR, δ 146.5, 133.0, 126.1, 123.2, 120.1, 112.2, 57.3, 37.4, 31.4, 29.5, 23.6, 22.4, 22.1, 13.9, and −2.0.

2-(Benzotriazol-1-yl)-1-phenyl-2-(trimethylsilyl)propane (**16b**). See Table 1. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.3–6.95 (6H, m), 6.6–6.5 (2H, m), 3.64 (1H, d, *J* 14 Hz), 3.17 (1H, d, *J* 14 Hz), 1.84 (3H, s), and 0.19 (9H, s); by ^{13}C NMR, δ 146.2, 136.2, 133.9, 130.0, 127.9, 126.6, 126.0, 123.1, 119.9, 112.4, 57.7, 43.3, 20.1, and −2.2.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl) ethanone (**1a**). Ethyl 4-methylbenzoate and **5** gave after 6 h and the general workup a mixture that was purified by column chromatography (chloroform–hexanes, 1 : 3) and the resulting white solid stirred overnight in hexanes to furnish **1a** as colorless needles (51%), mp 134–135°C. Analysis, found, C, 71.8; H, 5.2; N, 16.8; $C_{15}H_{13}N_3O$ requires C, 71.7; H, 5.2; N, 16.7%. Results by ^1H NMR, δ 8.03 (1H, d, *J* 8 Hz), 7.9 (2H, d, *J* 7 Hz), 7.5–7.2 (5H, m), 6.03 (2H, s), and 2.40 (3H, s); by ^{13}C NMR, δ 189.9, 145.8, 145.4, 133.7, 131.3, 129.6, 128.2, 127.5, 123.8, 119.7, 109.5, 53.6, and 21.6.

3-[(Benzotriazol-1-yl)(trimethylsilyl)methyl]cyclohexanone (**8**). The reaction of **5** with 2-cyclohexen-1-one gave after 4 h and the general workup an oil purified by column chromatography (hexane–chloroform, 2 : 1) to afford the Michael addition product (**8**) as a colorless oil that slowly solidified into colorless plates (70%), mp 126–128°C. Analysis, found, C, 63.7; H, 7.7; $C_{16}H_{23}N_3OSi$ requires C, 63.75; H, 7.7%. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.5–7.35 (3H, m), 4.12 (1H, d, *J* 7 Hz), 2.7–2.5 (1H, m), 2.3–1.2 (8H, m), and 0.13 (9H, s); by ^{13}C NMR, δ 209.8, 145.2, 134.3, 127.1, 123.7, 119.9, 109.3, 56.0, 45.8, 41.5, 40.7, 30.6, 24.8, and −1.7.

1-(Benzotriazol-1-yl)-4-methyl-3-penten-2-one (**1b**). Ethyl 3,3-dimethylacrylate and **5** gave after 6 h and the general workup a mixture purified by column chromatography (chloroform–hexane, 1 : 1) to afford **1b** as colorless plates (45%), mp 78–80°C. Analysis, found, C, 66.6; H, 6.0; N, 19.6; $C_{12}H_{13}N_3O$ requires C, 67.0; H, 6.1; N, 19.5%. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.5–7.3 (3H, m), 6.08 (1H, s), 5.42 (2H, s), 2.15 (3H, s), and 1.90 (3H, s); by ^{13}C NMR, δ 190.3, 161.5, 145.7, 133.4, 127.5, 123.7, 119.7, 119.0, 109.3, 56.8, 27.8, and 21.2.

*General Procedure for the F^--Catalyzed Reaction of **2, 9,** and **16** with Carbonyl Compounds*

A 1 *M* solution of TBAF in THF (0.1 mL, 0.1 mmol) was added at ambient temperature to a solution of the carbonyl compound (10 mmol) and **2, 9,** or **16** (5 mmol) in dry THF (15 mL). After ca. 6 h, a further portion of TBAF (1 *M* in THF, 0.1 mL, 0.1 mmol) was added and the mixture stirred for another 18 h. Water (10 mL) and 1*N* HCl (10 mL) were then added and the mixture stirred until hydrolysis of

the silyl ether was complete (monitored by TLC). The layers were separated, the aqueous layer extracted with Et_2O (3 × 20 mL), and the combined organic extracts washed with water and dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was then purified to afford the alcohols **3**, **13**, and **21** respectively (see Table 3).

The following compounds were thus prepared.

1-(Benzotriazol-1-ylmethyl)cyclohexanol (**3a**). This compound was purified by column chromatography (hexanes–chloroform, 1 : 1). Analysis, found, C, 67.6; H, 7.7; N, 18.8; $C_{13}H_{17}N_3O$ requires C, 67.5; H, 7.4; N, 18.2%. Results by ^{1}H NMR, δ 7.93 (1H, d, *J* 8 Hz), 7.68 (1H, d, *J* 8 Hz), 7.45–7.25 (2H, m), 4.60 (2H, s), 2.97 (1H, s), and 1.7–1.2 (10H, m); by ^{13}C NMR, δ 145.2, 134.1, 127.1, 123.7, 119.3, 110.7, 72.0, 57.9, 35.1, 25.3, and 21.5.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl)ethanol (**3b**). The crude product was purified by column chromatography (hexanes–chloroform, 2 : 1). Analysis, found, C, 71.15; H, 6.2; N, 16.3; $C_{15}H_{15}N_3O$ requires C, 71.1; H, 6.0; N, 16.6%. Results by ^{1}H NMR, δ ($CDCl_3$) 7.8–7.5 (1H, m), 7.4–6.9 (7H, m), 5.4–5.2 (1H, m), 4.8–4.65 (2H, m), 3.9–3.6 (1H, bs, OH), and 2.40 (3H, m); by ^{13}C NMR, δ 145.2, 138.0, 137.5, 133.7, 129.3, 127.2, 125.8, 123.8, 119.2, 110.0, 73.0, 55.6, and 21.0.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl)propan-1-ol (**13a**). Column chromatography of the crude mixture (chloroform–hexanes, 1 : 2) furnished the alcohol **13a** as a colorless oil (5 : 3 mixture of diastereomers). The diastereomers were separated by column chromatography (chloroform–hexanes, 1 : 9) to give two products, A and B.

Compound A (R_f = 0.31) was a colorless oil. Analysis, found, C, 71.7; H, 6.45; $C_{16}H_{17}N_3O$ requires C, 71.9; H, 6.4%. Results by ^{1}H NMR, δ 7.80 (1H, d, *J* 8Hz), 7.4–7.15 (3H, m), 7.08 (2H, AB, J_{AB} 7.8 Hz), 6.96 (2H, AB, J_{AB} 7.8 Hz), 5.25–5.15 (1H, m), 4.97 (1H, m), 4.6–4.3 (1H, bs, OH), 2.20 (3H, s), and 1.73 (3H, d, *J* 7 Hz); by ^{13}C NMR, δ 145.2, 137.3, 132.7, 128.7, 126.8, 125.8, 123.6, 119.3, 110.0, 76.0, 61.2, 20.8, and 14.8.

Compound B (R_f = 0.22) was isolated as colorless prisms, mp 122–123°C. Analysis, found, C, 72.2; H, 6.2; N, 15.3; $C_{16}H_{17}N_3O$ requires C, 71.9; H, 6.4; N, 15.7%. Results by ^{1}H NMR, δ 7.7–7.5 (2H, m), 7.4–7.0 (6H, m), 5.3–5.15 (1H, m), 4.93 (1H, m), 4.5–4.3 (1H, bs, OH), 2.30 (3H, s), and 1.48 (3H, d, *J* 7 Hz); by ^{13}C NMR, δ 145.0, 137.7, 133.5, 129.1, 126.7, 126.4, 123.6, 119.0, 110.1, 77.0, 61.3, 21.0, and 17.2.

2-Benzotriazol-1-yl-1-phenylhexan-3-ol (**13b**). Column chromatography (chloroform) gave a 3 : 1 mixture of diastereomers. Analysis, found, M^+, *m/z* 295.1659; $C_{18}H_{21}N_3O$ requires M^+, *m/z* 295.1684). Results by ^{1}H NMR, δ 8.0–7.9 (1H, m), 7.4–6.9 (8H, m), 5.1–4.7 (1H, m), 4.4–4.1 (1H, m, OH), 4.0–3.5 (3H, m), 1.7–1.2 (4H, m), and 1.0–0.8 (3H, m); by ^{13}C NMR, δ 144.8, 137.4, 137.0, 134.0, 133.8, 128.7, 128.6, 128.3, 128.2, 127.2, 127.0, 126.6, 126.4, 123.8, 123.7, 119.5, 119.4, 109.6, 109.4, 73.4, 72.6, 66.4, 65.9, 38.4, 36.6, 36.4, 35.6, 18.9, and 13.8.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl) ethanone (**1a**). Ethyl 4-methylbenzoate and **5** gave column chromatography (chloroform–hexanes, 1 : 3) to afford **13c** (as a 5 : 3 mixture of diastereomers). Further separation of the mixture by column chromatography (chloroform) afforded the individual diastereomers A and B.

Compound A (R_f = 0.36) was isolated as colorless prisms, mp 137–138°C. Analysis, found, C, 76.45; H, 6.2; N, 12.0; $C_{22}H_{21}N_3O$ requires C, 76.9; H, 6.2; N, 12.2%. Results by ^{1}H NMR, δ 7.9–7.75 (1H, m), 7.3–6.7 (12H, m), 5.38 (1H, d, *J* 5.5 Hz), 5.0–4.9 (1H, m), 4.18 (1H, bs, OH), 3.60 (2H, d, *J* 6.5 Hz), and 2.21 (3H, s); by ^{13}C NMR, δ 144.8, 137.7, 137.4, 137.2, 133.7, 129.0, 128.7, 128.2, 126.8, 126.4, 125.9, 123.5, 119.2, 109.3, 75.8, 67.8, 35.9, and 20.9.

Compound B (R_f = 0.24) was a colorless gum. Analysis, found, C, 77.3; H, 6.0; $C_{22}H_{21}N_3O$ requires C, 76.9; H, 6.2. Results by ^{1}H NMR, δ 7.69 (1H, d, *J* 8 Hz), 7.3–6.8 (12H, m), 5.40 (1H, t, *J* 5.5 Hz), 4.98 (1H, m), 4.2–4.1 (1H, m, OH), 3.44 (1H, dd, *J* 10.9, 13.7 Hz), 3.16 (1H, dd, *J* 4.5, 13.7 Hz), and 2.28 (3H, s); by ^{13}C NMR, δ 144.8, 137.9, 137.7, 137.0, 134.4, 129.3, 128.5, 128.3, 126.8, 126.5, 126.1, 123.6, 119.1, 109.5, 75.6, 67.9, 38.0, and 21.0.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl)octan-1-ol (**21a**). The alcohol **21a** was obtained as a colorless gum (7 : 5 ratio of diastereomers) after purification by column chromatography (chloroform–hexanes, 1 : 2). Further chromatography (ethyl acetate–hexanes, 1 : 6) of the diastereomers afforded two compounds, A and B.

Compound A (R_f = 0.42) was isolated as colorless microcrystals, mp 86–88°C. Analysis, found, C, 75.2; H, 8.35; $C_{22}H_{29}N_3O$ requires C, 75.2; H, 8.3%. Results by ^{1}H NMR, δ 7.85 (1H, d, *J* 8 Hz), 7.40 (1H, d, *J* 8 Hz), 7.21 (2H, m), 6.83 (2H, AB, J_{AB} 8.1 Hz), 6.68 (2H, AB, J_{AB} 8.1 Hz), 5.07 (1H, s), 3.35 (1H, bs, OH), 2.8–2.6 (1H, m), 2.14 (3H, s), 2.1–1.9 (1H, m), 1.78 (3H, s), 1.08 (8H, m), and 0.72 (3H, t, *J* 6 Hz); by ^{13}C NMR, δ 146.1, 137.6, 136.4, 133.8, 128.4, 127.0, 126.6, 123.2, 119.8, 112.7, 80.1, 70.3, 35.9, 31.5, 29.4, 23.1, 22.4, 20.9, 20.2, and 13.9.

Compound B (R_f = 0.33) was a colorless oil. Analysis, found, C, 75.0; H, 8.4; $C_{22}H_{29}N_3O$ requires C, 75.2; H, 8.3%. Results by ^{1}H NMR, δ 7.6 (2H, t, *J* 8 Hz), 7.25–7.0 (2H, m), 6.86 (2H, AB, J_{AB} 8.6 Hz), 6.83 (2H, AB, J_{AB} 8.6 Hz), 5.10 (1H, d, *J* 3.7 Hz), 3.70 (1H, d, *J* 3.7 Hz, OH), 2.5–2.3 (1H, m), 2.13 (3H, s), 1.71 (3H, s), 1.7–1.5 (1H, m), 0.95 (8H, m), and 0.61

(3H, t, *J* 7 Hz); by ^{13}C NMR, δ 146.0, 137.5, 136.4, 133.6, 128.4, 127.5, 126.6, 123.3, 119.6, 112.7, 79.5, 70.7, 37.1, 31.3, 29.2, 22.8, 22.3, 20.9, 19.7, and 13.8.

1-[1-(Benzotriazol-1-yl)-1-(phenylmethyl)ethyl]cyclohexanol (**21b**). This compound was purified by column chromatography (hexanes–chloroform, 1 : 1) to give an oil. Analysis, found, C, 74.9; H, 7.7; N, 12.3; $C_{21}H_{25}N_3O$ requires C, 75.2; H, 7.5; N, 12.5%. Results by ^1H NMR, δ 8.1–8.0 (1H, m), 7.65–7.55(1H, m), 7.4–7.25 (2H, m), 7.05–6.9 (3H, m), 6.7–6.6 (2H, m), 4.46 (1H, d, *J* 14 Hz), 3.39 (1H, bs, OH), 3.06 (1H, d, *J* 14 Hz), 1.85 (3H, s), and 2.1–1.0 (10 H, m); by ^{13}C NMR, δ 145.9, 136.5, 135.0, 130.1, 127.8, 127.2, 126.3, 123.4, 120.1, 113.1, 77.7, 74.8, 40.8, 32.4, 31.6, 25.6, 21.5, and 21.2.

*General Procedure for the F^--Induced Desilylations of **9** and **16***

To a solution of the corresponding silyl derivative (5 mmol) in THF (10 mL) was added TBAF (1 *M* in THF, 5.5 mL, 5.5 mmol). The solution was heated under reflux for 12 h. Water (15 mL) was then added and the organic material extracted with chloroform (3 × 10 mL), dried ($MgSO_4$), and the solvent removed in vacuo. The crude oil was then purified by column chromatography (chloroform–hexanes, 2 : 3) (see Table 4).

The following compounds were prepared in this manner.

1-Heptylbenzotriazole (**10b**). Analysis, found, C, 71.7; H, 8.8; $C_{13}H_{19}N_3$ requires C, 71.85; H, 8.8%. Results by ^1H NMR, δ 8.06 (1H, d, *J* 8 Hz), 7.6–7.3 (3H, m), 4.63 (2H, t, *J* 7 Hz), 2.05–1.95 (2H, m), 1.4–1.2 (8H, m), and 0.86 (3H, t, *J* 7 Hz); by ^{13}C NMR, δ 145.8, 132.8, 127.0, 123.6, 119.8, 109.2, 48.1, 31.4, 29.5, 28.5, 26.5, 22.4, and 13.9.

1-(2-Phenylethyl)benzotriazole [12] (**10c**). Results by ^1H NMR, δ 8.1–7.9 (1H, m), 7.4–7.0 (8H, m), 4.82 (2H, t, *J* 7 Hz), and 3.27 (2H, t, *J* 7 Hz).

2-(Benzotriazol-1-yl)octane (**20a**). Analysis, found, M^+, *m/z* 231.1724; $C_{14}H_{21}N_3$ requires M^+, *m/z* 231.1735). Results by ^1H NMR, δ 8.06 (1H, d, *J* 8 Hz), 7.6–7.3 (3H, m), 4.92 (1H, m), 1.70 (3H, d, *J* 7 Hz), 2.3–1.2 (10H, m), and 0.81 (3H, t, *J* 6 Hz); by ^{13}C NMR, δ 145.9, 132.2, 126.6, 123.5, 119.8, 109.5, 55.9, 36.1, 31.3, 28.6, 26.0, 22.2, 20.6, and 13.8.

2-(Benzotriazol-1-yl)-1-phenylpropane (**20b**). Analysis, found, C, 75.8; H, 6.4; $C_{15}H_{15}N_3$ requires C, 75.9; H, 6.4%. Results by ^1H NMR, δ 7.99 (1H, d, *J* 8 Hz), 7.5–6.9 (8H, m), 5.05 (1H, m), 3.40 (1H, dd, *J* 8.2, 13.7 Hz), 3.22 (1H, dd, *J* 6.4, 13.7 Hz), and 1.75 (3H, d, *J* 6 Hz); by ^{13}C NMR, δ 145.6, 137.1, 132.5, 128.6, 128.2, 126.58, 126.53, 123.4, 119.5, 109.2, 57.1, 42.8, and 20.1.

General Procedure for Desilylation with Acid Chlorides

By method A, the trimethylsilyl derivative **2** (10 mmol) and the acid chlorides (12 mmol) were dissolved in dry THF or CCl_4 (10 mL) and the mixture was heated under reflux. On cooling the colorless needles were filtered and dried.

By method B, 1-(trimethylsilylalkyl)benzotriazole (**9**) (10 mmol) and 4-methylbenzoyl chloride were dissolved in dry carbon tetrachloride (10 mL) and the mixture was heated under reflux. Hydrochloric acid (2N, 5 mL) was then added and the mixture washed with methylene chloride (3 × 15 mL); the combined organic fractions were washed with 5% aqueous Na_2CO_3 (2 × 10 mL), with water (1 × 10 mL), and dried (Na_2SO_4). Evaporation of the solvent gave the crude product, which was then purified by column chromatography (see Table 5).

The following compounds were thus prepared.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl) ethanone (**1a**). This compound is identical in all respects to the ketone prepared earlier.

1-(Benzotriazol-1-yl)propan-2-one (**1c**). Results by ^1H NMR, δ 8.1–8.05 (1H, m), 7.6–7.3 (3H, m), 5.44 (2H, s), and 2.21 (3H, s); by ^{13}C NMR, δ 199.8, 145.9, 133.4, 127.9, 124.1, 120.0, 109.0, 56.7, and 27.0.

2-(Benzotriazol-1-yl)-1-phenylethanone (**1d**). Results by ^1H NMR, δ 8.1–8.0 (3H, m), 7.7–7.25 (5H, m), and 6.09 (2H, s); by ^{13}C NMR, δ 190.3, 146.0, 134.5, 133.9, 133.8, 129.1, 128.2, 127.8, 124.0, 120.0, 109.5, and 53.8.

1,8-Bis(benzotriazol-1-yl)-octane-2,7-dione (**1e**). This compound was isolated as colorless needles (CH_3CN). Results by ^1H NMR, δ(DMSO-d_6) 8.06 (2H, d, *J* 8 Hz), 7.73 (2H, d, *J* 8 Hz), 7.54 (2H, t, *J* 8 Hz), 7.40 (2H, t, *J* 8 Hz), 5.87 (4H, s), 2.72 (4H, m), and 1.58 (4H, m).

1-(Phenylacetyl)methylbenzotriazole (**1f**). Results by ^1H NMR, δ 8.05 (1 H, d, *J* 8 Hz), 7.45–7.1 (8H, m), 5.44 (2H, s), and 3.79 (2H, s); by ^{13}C NMR, δ 199.5, 145.9, 133.4, 132.1, 129.2, 129.0, 127.8, 127.6, 124.0, 120.0, 109.0, 55.4, and 47.3.

2-(Benzotriazol-1-yl)-1-(4-methylphenyl)-1-propanone (**11a**). This was a colorless oil purified by column chromatography (chloroform–hexanes, 1 : 1). Analysis, found, M^+, *m/z* 265.1187; $C_{16}H_{15}N_3O$ requires M^+, *m/z* 265.1215). Results by ^1H NMR, δ 8.02 (1H, d, *J* 8 Hz), 7.91 (2H, d, *J* 8 Hz), 7.55–7.25 (3H, m), 7.19 (2H, d, *J* 8 Hz), 6.69 (1H, q, *J* 7 Hz), 2.33 (3H, s), and 1.96 (3H, d, *J* 7 Hz); by ^{13}C NMR, δ 193.3, 146.5, 145.1, 132.0, 131.6, 129.5, 128.8, 127.6, 123.9, 120.1, 110.4, 59.3, 21.6, and 16.2.

2-(Benzotriazol-1-yl)-4'-methyl-3-phenylpropiophenone (**11b**). Results by ^{1}H NMR, δ 7.98 (1H, d, *J* 8 Hz), 7.88 (2H, d, *J* 8 Hz), 7.58 (1H, d, *J* 8 Hz), 7.5–7.25 (2H, m), 7.2–7.1 (5H, m), 7.0–6.9 (2H, m), 6.74 (1H, ABX, J_{AX} 6 Hz, J_{BX} 9 Hz), 3.78 (1H, ABX, J_{AB} 14 Hz, J_{AX} 6 Hz), 3.61 (1H, ABX, J_{AB} 14 Hz, J_{BX} 9 Hz), and 2.29 (3H, s); by ^{13}C NMR, δ 192.3, 146.3, 145.2, 136.0, 132.1, 131.9, 129.5, 128.85, 128.81, 128.5, 127.7, 127.0, 124.0, 120.1, 110.4, 64.7, 36.1, and 21.5.

General Procedure for the Formation of Ketones **4** *and* **15.**

To a mixture of **1** or **11** (2 mmol) in acetic acid (5 mL) and dry ethanol (10 mL) was added zinc metal (granular, 20 mesh) (1.30 g, 20 mmol) and the mixture was stirred at ambient temperature. Ethanol (10 mL) was then added. The insoluble materials were filtered off and the solvent was evaporated. The residue was then purified by column chromatography (hexane–chloroform 2 : 1) (see Table 6).

The following compounds were thus prepared.

4'-Methylacetophenone (**4a**). This is a colorless liquid. Results by ^{1}H NMR, δ 7.73 (2H, d, *J* 8 Hz), 7.13 (2H, d, *J* 8 Hz), 2.50 (3H, s), and 2.33 (3H, s).

4'-Methylpropiophenone (**15a**). This also is a colorless liquid. Results by ^{1}H NMR, δ 7.96 (2H, d, *J* 8 Hz), 7.33 (2H, d, *J* 8 Hz), 3.00 (2H, q, *J* 7 Hz), 2.40 (3H, s), and 1.20 (3H, t, *J* 7 Hz).

4'-Methyl-3-phenylpropiophenone (**15b**). This was isolated as colorless plates. Results by ^{1}H NMR, δ 7.96 (2H, d, *J* 8 Hz), 7.5–7.2 (7H, s), 3.3–3.0 (4H, m), and 2.36 (3H, s).

2-(Benzotriazole-1-yl)-1-(4-methylphenyl) ethanol (**3b**). To a solution of 2-(benzotriazol-1-yl)-1-(4-methylphenyl)ethanone (**1a**) (0.50 g, 2 mmol) and ammonium formate (0.65 g, 10 mmol) in dry methanol (15 mL) was added palladium on carbon (palladium content 10%, 0.5 g). The mixture was then heated under reflux for 3 h. The catalyst was filtered off through a celite pad and to the filtrate was added chloroform (40 mL). The mixture was washed with water (3 × 15 mL) and dried ($MgSO_4$). Then the solvent was removed in vacuo to give a white solid (0.45 g, 90%), the physical and spectral properties of which were similar to the alcohol prepared earlier.

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