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Novel Routes to 4-Substituted N,N-Dialkylanilines, N-Alkylanilines and Anilines

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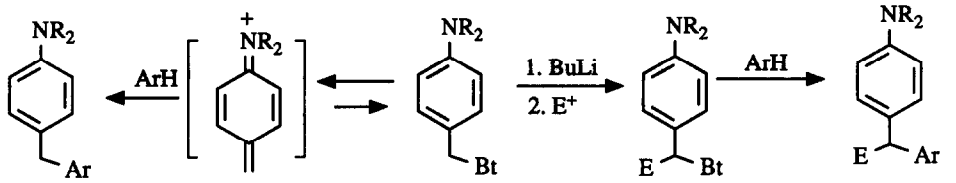
Abstract: *4-(Benzotriazol-1-ylmethyl)-N,N-dialkylanilines, -N-alkylanilines, -anilines and some substituted analogs obtained via lithiation are converted by lithium aluminum hydride or Grignard reagents into 4-substituted N,N-dialkylanilines, N-alkylanilines and anilines, respectively, in good yields.*

Previous work in our laboratory concerning the use of benzotriazole as a synthetic auxiliary[1] has demonstrated its utility in the elaboration of amines, ethers, thioethers, and other compounds. In particular, it has been shown that 4-(benzotriazol-1-ylmethyl)anilines **3**, readily available[2] from N,N-dialkylanilines by alkylation with 1-hydroxymethylbenzotriazole, undergo lithiation at the reactive methylene carbons α to the benzotriazolyl nitrogen followed by reaction with electrophiles to give **4**. The benzotriazole group in the parent **1a-b** and the derivatives **4** obtained via lithiation has been displaced by electron-rich aromatic compounds such as anilines, methoxybenzenes, 2-naphthol, and by heterocyclic compounds such as indoles and pyrroles, to afford diarylmethanes **1** and trisubstituted methanes **5**.[2,3] In these transformation, cation **2** and its analog are presumably the reactive intermediates, which are formed from **3** and **4** by the loss of benzotriazole anion with assistance from the aniline nitrogen lone pair acting through the benzene ring.

Displacements of the benzotriazole group in aniline derivatives of types **3** and **4** by hydride with lithium aluminum hydride ($LiAlH_4$) or by carbon anions with Grignard reagents should provide synthetic routes to 4-substituted N,N-dialkylanilines, N-alkylanilines and anilines. In the present work we have carried out a variety of such novel transformations, and have demonstrated that this methodology offers an attractive route for the *para* alkylation of anilines.

Previous methods for the ring alkylation of primary and secondary aromatic amines have included reactions with alkenes in the presence of aluminum powder, dust, or shavings, or in the presence of aluminum or sodium together with aluminum chloride which via the formation of catalytic amounts of aluminum anilide give *ortho* substituted mono-, di- or poly-alkylated aromatic amines.[4] High temperatures (250-330 °C) and high pressures (200-250 atm) are usually required.[4] For tertiary or N-acylated primary or secondary aromatic amines, these alkylations usually occur at the *para* position.[5] In the cases of propene and butene, secondary alkyl groups were introduced. Classical Friedel-Crafts methods have rarely been successfully applied to the alkylation of aromatic amines due to complex formation at the nitrogen atom which deactivates the ring.[6,7]

It has been demonstrated in our laboratory that heating aniline hydrochloride with 1-hydroxymethylbenzotriazole in acetic acid for 0.5 h gave 4-(benzotriazol-1-ylmethyl)aniline **6d** in 46% yield.[2] This work also showed that 4-(benzotriazol-1-ylmethyl)-N-methylaniline **6c** was readily available from heating N-methylaniline with 1-hydroxymethylbenzotriazole in a solution of acetic acid and conc.

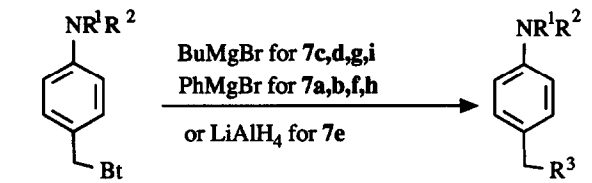


1 2 3 4 5

sulfuric acid for 0.5 h. The sulfuric acid was employed to protect the active hydrogen atom in the amino group by formation of a salt.

Heating 4-(benzotriazol-1-ylmethyl)-N,N-dimethylaniline **6a** with an excess of phenylmagnesium bromide in benzene under reflux for 24 h gave 4-benzyl-N,N-dimethylaniline **7a** in 97% yield. Further, 4-alkyl-N,N-dialkylanilines **7b-d** were similarly obtained from both alkyl and aryl Grignard reagents in good to excellent yields (52-92%). The benzotriazole generated was readily extracted into the aqueous solution under basic conditions during work-up; the desired products were easily purified by passing the

Scheme 1

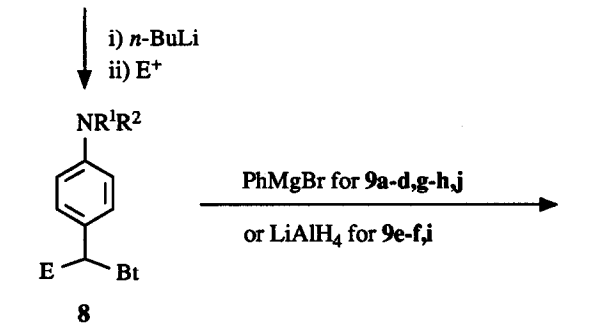


6a $R^1=R^2=Me$ **6c** $R^1=Me$, $R^2=H$

6b $R^1=R^2=Et$ **6d** $R^1=R^2=H$

7

7	R^1	R^2	R^3
a	Me	Me	Ph
b	Et	Et	Ph
c	Me	Me	*n*-Bu
d	Et	Et	*n*-Bu
e	Me	Me	H
f	Me	H	Ph
g	Me	H	*n*-Bu
h	H	H	Ph
i	H	H	*n*-Bu



8

8	R^1	R^2	E
a	Me	Me	Me
b	Me	Me	$PhCH_2$
c	Me	Me	$(CH_2)_5(OH)$
d	Me	Me	PhCH(OH)
e	Et	Et	Me
f	Me	H	*p*-MePhCH(OH)
g	Me	H	Bu
h	H	H	$PhCH_2$

9

9	R^1	R^2	E	R^3
a	Me	Me	Me	Ph
b	Me	Me	$PhCH_2$	Ph
c	Me	Me	$(CH_2)_5C(OH)$	Ph
d	Me	Me	PhCH(OH)	Ph
e	Me	Me	$PhCH_2$	H
f	Et	Et	Me	H
g	Me	H	*p*-MePhCH(OH)	Ph
h	Me	H	Bu	Ph
i	Me	H	Bu	H
j	H	H	$PhCH_2$	Ph

reaction mixture through a short column. The reactive cation **2** was considered to be the intermediate in the reaction. However, the analogous 4-alkyl-N-methylanilines **7f-g** and 4-alkylanilines **7h-i** were obtained by contrast in relative low yield (30-55%). This is possibly due to the low solubility or easy decomposition of the salts formed by the Grignard reagents and the aniline NH group.

As reported previously, the derivatives **8a-e**, were readily available from **6a-b** via lithiation.[3] While **8f-h** were also converted by reaction with Grignard reagents into compounds **9a-d, g-h, j**, it is noteworthy that the derivatives **8c-d, f**, obtained via lithiation after trapping with cyclohexanone, benzaldehyde or *p*-methylbenzaldehyde, reacted with phenylmagnesium bromide to give the expected products **9c**, **9d** and **9g**, respectively, in good yields (Table 1). The reaction required more vigorous conditions for the

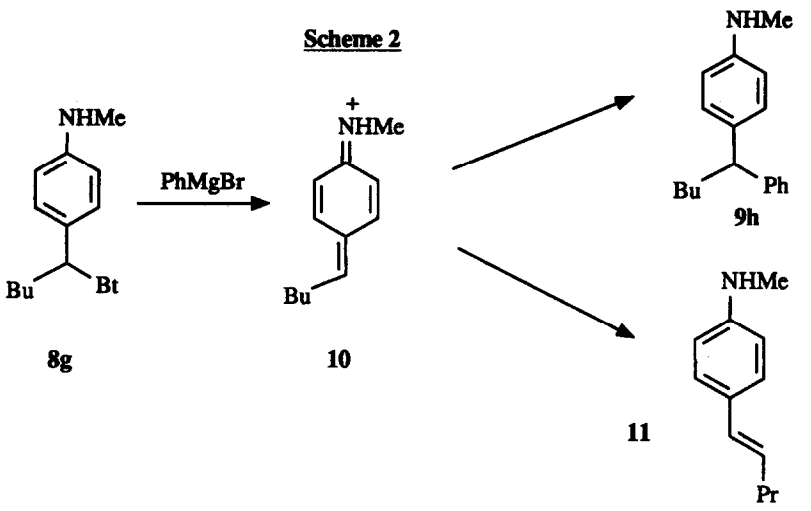
Table 1 4-Substituted anilines **7** and **9, 16**

Product	Reactant	Reagent	Solvent	Reaction Time (h)	Yield (%)	M.p. (°C)	Lit. m.p. (°C) or b.p. (°C/mm) or Calcd. (Found) C	H	N	Purifying solvent[a]
7a	**6a**	PhMgBr	benzene	24	97	oil	126-128/0.3[8]			40 :1
7b	**6b**	PhMgBr	benzene	24	92	oil	85.31 (85.22)	8.84 (8.82)	5.85 (5.95)	50 :1
7c	**6a**	*n*-BuMgBr	benzene	25	52	oil	oil[9]			50 :1
7d	**6b**	*n*-BuMgBr	benzene	17	78	oil	-[b]			50 :1
7f	**6c**	PhMgBr	toluene	12	36	oil	-[10]			20 :1
7g	**6c**	*n*-BuMgBr	benzene	24	30	oil	-[c]			20 :1
7h	**6d**	PhMgBr	benzene	48	48	oil	179/picrate[11]			20 :1
7i	**6d**	*n*-BuMgBr	benzene	48	55	oil	104-106/5[12]			20 :1
9a	**8a**	PhMgBr	benzene	10	82	oil	132-135/0.55[13]			100 :1
9b	**8b**	PhMgBr	benzene	10	91	77-79	87.66 (87.30)	7.69 (7.42)	4.65 (4.50)	100 :1
9c	**8c**	PhMgBr	toluene	18	81	104-106	81.51 (81.86)	8.79 (8.92)	4.53 (4.41)	6 :1[a]
9d	**8d**	PhMgBr	toluene	18	69	99-101	83.24 (83.08)	7.30 (7.37)	4.41 (4.31)	10 :1
9e	**8b**	$LiAlH_4$	benzene	4	78	58-60	63[14]			-
9f	**8e**	$LiAlH_4$	toluene	13	77	oil	oil[15]			75 :1
9g	**8f**	PhMgBr	benzene	24	60	127-128	83.23 (83.22)	7.31 (7.38)	4.41 (4.29)	30 :1
9h	**8g**	PhMgBr	benzene	6	35	oil	-[d]			hexane
9i	**8g**	$LiAlH_4$	benzene	12	95	oil	-[c]			-
9j	**8h**	PhMgBr	benzene	17	68	oil	-[e]			20 :1
16	**8h**	$LiAlH_4$	toluene	28	90	152-154	152-156[16]			20 :1

[a]Column chromatography on alumina (neutral, Brockmann Activity I, 80-200 mesh). [b]HR MS Found: M = 219.1988. $C_{15}H_{25}N$ requires M=219.1587. [c]HR MS Found: M=177.1516; $C_{12}H_{19}N$ requires M=177.1517.
[d]HR MS Found: 253.1830. $C_{18}H_{23}N$ requires M=253.1830. [e]HRMS Found M=273.1517. $C_{20}H_{19}N$ requires M=273.1517.

conversion **8c** and **8d** into **9c** and **9d**, i.e. refluxing in toluene. The reaction of **8c** with phenylmagnesium bromide in benzene under reflux for 20 h gave only 40% of the desired product **9c** with 36% recovery of the starting material. On repeating the reaction in refluxing benzene for 3 days, TLC still showed the presence of the starting material. Finally, the reaction was completed by adding dry toluene, removing part of the benzene and refluxing for an additional 2 h until TLC indicated the disappearance of the starting material. In this way, **9c** was obtained in 81% yield. One of the reasons such vigorous conditions and an extended reaction time were required was because of the low solubilities of the salts formed from the

Scheme 2

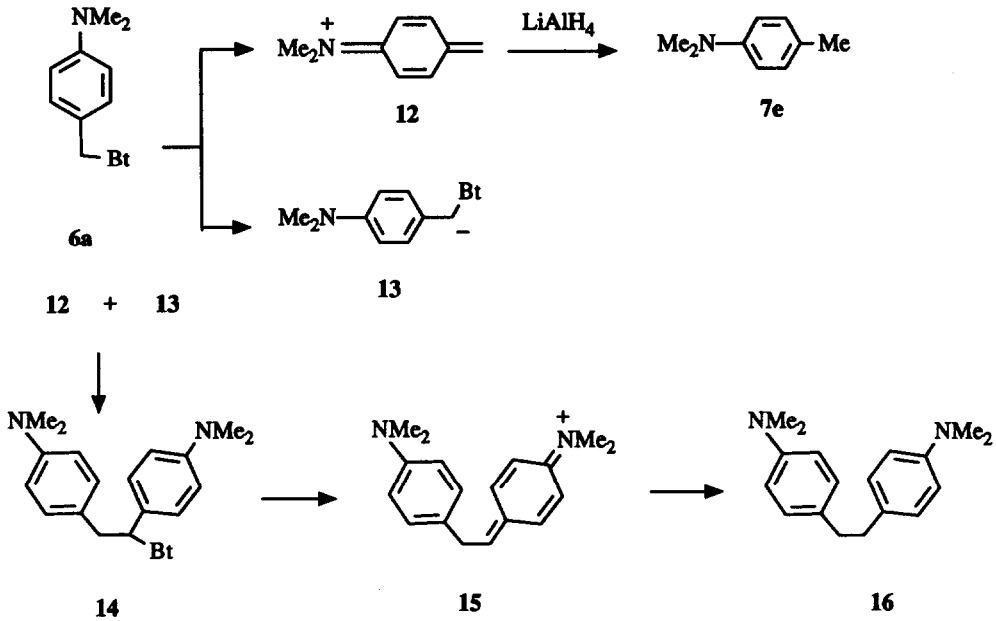


alcohols with phenylmagnesium bromide. However, such salts were stable under the conditions. Since different aldehydes or ketones could be used as electrophiles in the preparation of the substrates **8**, other alcohols of types **9c-d,g** should be obtained using this method.

The displacement of benzotriazole by Grignard reagents in substrate **6** and **8** usually goes smoothly. However, we did observe the case of elimination. Reaction of compound **8g** with PhMgBr in benzene under reflux gave **9h** and **11** in yields of 35% and 15%, respectively. This is because under the relatively vigorous conditions utilized, ionization of compound **8g** causes dissociation of the benzotriazolyl ion to give **10**, which reacts further with the Grignard reagent to yield **9h**, or via elimination of a β-hydrogen to give **11**.

The benzotriazolyl derivatives **6** and **8** also reacted with lithium aluminum hydride ($LiAlH_4$). For **8b** and **8e**, the reaction in benzene or toluene under reflux gave the desired products **9e-f** in good yields. However, similar to the case of **8g**, when compound **6a**, with an active hydrogen at the β-position, was heated in benzene with $LiAlH_4$ for 2 days, only unreacted starting material was recovered. When this reaction was repeated in toluene, it gave a mixture of 1,2-bis(4-N,N-dimethylaminophenyl)ethane **16** in 90% yield and only traces of the expected product, 4-methyl-N,N-dimethylaniline **7e**. The formation of 4-methyl-N,N-dimethylaniline **7e** and **16** can be explained as follows. The benzylic proton in **6a** was deprotonated by $LiAlH_4$ under the vigorous conditions to give **13**, in addition to the usual intermediate **12**; these combined to form **14**. Further reaction with elimination of benzotriazole gave reactive cation **15**,

Scheme 3



which was reduced by $LiAlH_4$ to **16**. Reduction of **12** gave the normal product **7e**.

The structure of the displacement products was confirmed by their NMR spectral data along with elemental analyses or mass spectroscopic data. Known compounds were compared with literature data. The NMR data clearly indicated the disappearance of the characteristic benzotriazolyl signals. The methylene bridge (in compounds **6**) or the methine bridge (in compounds **8**) signals in both ^1H and ^{13}C NMR spectra were correspondingly shifted upfield due to the loss of the electron-withdrawing benzotriazole group (see Table 2,3).

Many of the 4-substituted-N,N-dialkylanilines reported here are novel. 4-Benzyl-N,N-dimethylanilines (**7a**) and 4-pentyl-N,N-dimethylanilines (**7c**) were previously prepared via the reduction of 4-benzoyl-N,N-dimethylaniline and 1-(4-dimethylaminophenyl)pentanol with sodium borohydride/trifluoroacetic acid.[8] However, the poor availability of starting materials subtracts from the generality of this approach using $NaBH_4/CF_3COOH$. Compounds **7c**, **7d**, **7g** and **7i** with the normal alkyl chain are not accessible by conventional Friedel-Crafts alkylation.

Conclusions: The presently reported method shows many advantages over classical methods for the introduction of normal as well as branched alkyl ring substituents to N,N-dialkylanilines, N-alkylanilines and anilines. Our method is also versatile in the sense that different groups including (α-hydroxyalkyl)s are easily introduced via lithiation. In conclusion, we have developed a new and efficient process which significantly extends the available methodologies for the preparation of 4-substituted N,N-dialkylanilines, N-alkylanilines and anilines.

Table 2 ^{1}H NMR Spectral Data of Compounds **7**, **9** and **16** Prepared.

Compd.	NR^1R^2	$ArCH_2R^3$ or $ArCH(E)R^3$	E	R^3	Other groups
7a	2.85 (s, 6H)	3.86 (s, 2H)	-	7.1-7.3 (m,5H)	6.64 (d, 2H, J=8.8), 7.03 (d, 2H, J=8.8)
7b	1.09(t, 6H, J=7.0) 3.24(q, 4H, J=7.0)	3.84 (s, 2H)	-	7.1-7.3 (m,5H)	6.58 (d, 2H, J=8.8), 6.99 (d, 2H, J=8.8)
7c	2.86 (s, 6H)	2.50 (t, 2H, J=7.0)	-	0.88(t, 3H, J=7.0), 1.2-1.4 (m, 4H), 1.5-1.6(m, 2H)	6.66 (d, 2H, J=8.7), 7.03 (d, 2H, J=8.7)
7d	1.13(t, 6H, J=7.2) 3.30(q, 4H, J=7.2)	2.49 (t, 2H, J=7.0)	-	0.88(t, 3H, J=7.0), 1.2-1.4(m, 4H), 1.5-1.6(m, 2H)	6.62 (d, 2H, J=8.7), 7.02 (d, 2H, J=8.7)
7f	2.65(s, 3H)	3.82(s, 2H)	-	-[a]	3.3(s, 1H), 6.43(d, 2H, J=8.5) 6.94(d, 2H, J=8.4), 7.1-7.3(m, 5H)
7g(9l)	2.73(s, 3H)	2.48(t, 2H, J=7.9)	-	0.86(t, 3H, J=6.4), 1.2-1.4 (m, 4H), 1.5-1.6(m, 2H)	3.41(s, 1H), 6.51(d, 2H, J=8.5) 6.98(d, 2H, J=8.5)
7h	-	3.83(s, 2H)	-	-[a]	3.35(s, 2H), 6.51(d, 2H, J=8.5) 6.91(d, 2H, J=8.0), 7.1-7.3(m, 5H)
7l	-	2.51(t, 2H, J=7.2)	-	0.85(t, 3H, J=6.8),1.2-1.3 (m, 4H), 1.5-1.6(m, 2H)	3.40(s, 2H), 6.58(d, 2H, J=8.5) 6.91(d, 2H, J=8.5)
9a	2.79 (s, 6H)	4.02 (q, 1H, J=7.2)	1.58 (d, 3H, J=7.2)	-[a]	6.65 (d, 2H, J=8.5), 7.08(d, 2H, J=8.5) 7.1-7.3(m, 5H)
9b	2.86 (s, 6H)	4.13 (t, 1H, J=8.0)	3.32(d, d, 2H, J_1=8.0 J_2=3.0)[b]	-[a]	6.65 (d, 2H, J=8.7), 6.9-7.3 (m, 12H)
9c	3.00 (s, 6H)	3.94 (s, 1H)	1.5-1.7 (m, 10H)	7.3-7.5 (m, 3H)[b]	6.85 (d, 2H, J=8.6), 7.57 (d, 2H, J=8.4), 7.72 (d, 2H, J=7.8)
9d	2.76 (s, 6H)	4.15 (d, 1H, J=8.3)	2.25 (s, 1H), 5.26 (d, 1H, J=8.6)[b]	-[a]	6.51(d, 2H, J=7.5), 6.95 (d, 2H, J=7.6), 7.1-7.4 (m, 10H)
9e	-[a]	-[a]	-[a]	-	2.8-2.9 (m, 10H), 6.67 (d, 2H, J=7.0), 7.05(d, 2H, J=7.0), 7.0-7.3 (m, 5H)
9f	3.25(q, 4H, J=7.0)[b]	2.55 (q, 2H, J=7.5)	-[a]	-	1.0-1.3 (m, 9H), 6.61 (d, 2H, J=6.6) 7.03 (d, 2H, J=6.6)
9g	2.66(s, 3H)	4.10(d, 1H, J=9.0)	2.25(s, 3H), 5.28(d, 1H, J=8.8)	-	3.3(s, 1H), 6.37(d, 2H, J=8.5) 6.92(d, 2H, J=8.8), 7.01(d, 2H, J=8.1) 7.10(d, 2H, J=7.8), 7.2-7.4(m, 5H)
9h	2.73(s, 3H)	3.77(t, 1H, J=7.7)	0.85(t, 3H, J=6.8) 1.1-1.4(m, 4H), 2.0(q, 2H, J=7.2)	-[a]	3.47(s, 1H), 6.51(d, 2H, J=8.5) 7.0-7.3(m, 7H)
9j	-	4.0-4.1(m, 1H)	-[a]	-[a]	3.1-3.3(m, 3H), 6.3-6.5(m, 2H) 6.9-7.0(m, 4H), 7.0-7.3(m, 9H)
16	2.90(s, 12H)	2.79(s, 4H)	-	-	6.68(d, 4H, J=8.7), 7.05(d, 4H, J=8.7)

[a]Signals are overlapped and are reported in the column for other groups.

[b]Other signals are overlapped and are reported in the column for other groups.

Experimental Section

General: Melting points were determined with a Köfler hot stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer in $CDCl_3$ using TMS as an internal reference for ^{1}H spectra and $CDCl_3$ for ^{13}C NMR spectra (abbreviations used: s singlet; d doublet; t triplet; q quartet; m multiplet; and dd doublet of doublets). Elemental analyses were performed on a Carlo Erba-1106 instruments. High resolution mass measurement were recorded on an AEI MS-30 mass spectrometer. Tetrahydrofuran, diethyl ether, benzene, and toluene were predried and freshly distilled from

Table 3 ^{13}C NMR Spectral Data of Compounds 7, 9 and 16 prepared.

Compd.	NR^1R^2	$ArCH_2R^3$ or $ArCH(E)R^3$	E	R^3	Other groups
7a	40.7	40.9	-	125.7, 128.3, 128.7, 142.0	112.9, 129.2, 129.5, 149.1
7b	12.5, 44.3	40.8	-	125.6, 128.7, 129.6, 142.1	112.1, 127.9, 128.2, 146.1
7c	40.8	34.8	-	14.0, 22.5, 31.4, 31.5	112.9, 128.9, 131.1, 148.8
7d	12.6, 44.4	34.8	-	14.0, 22.6, 31.5, 31.6	112.3, 129.1, 130.0, 146.0
7f	30.6	40.9	-	_[b]	112.2, 112.3, 125.6, 128.2, 128.6, 129.5, 141.9, 147.5
7g(9l)	30.9	34.9	-	14.0, 22.5, 31.4, 31.5	112.4, 129.0, 131.6, 147.2
7h	-	40.9	-	_[b]	115.1, 125.7, 128.2, 128.6, 129.6, 130.9, 141.0, 144.4
7i	-	34.9	-	13.9, 22.4, 31.3	115.1, 128.9, 132.8, 143.9
9a	40.5	43.7	22.0	125.6, 127.4, 128.0, 147.1	112.6, 128.1, 134.4, 148.9
9b	40.7	52.0	42.3[a]	_[b]	112.7, 125.7, 125.8, 127.9, 128.2, 128.5, 128.7, 129.1, 132.6, 140.6, 145.2, 148.9
9c	40.4	60.6	22.0, 25.6, 36.8, 37.1, 73.4	125.8, 127.9, 129.6, 142.2	112.4, 129.2, 130.3, 148.9
9d	40.4	59.1	76.8[a]	_[b]	112.4, 126.5, 126.8, 127.2, 127.8, 128.5, 128.8, 129.1, 129.6, 141.6, 142.6, 148.9
9e	40.8	38.2	36.9, 125.7, 128.2, 128.9, 142.1	-	112.9, 128.4, 129.9, 149.0
9f	12.5, 44.4	27.7	15.8	-	112.3, 128.4, 131.2, 145.9
9g	30.6	59.2	21.1, 76.7[a]	_[b]	112.2, 126.5, 126.8, 128.5, 128.6, 128.8, 129.2, 130.4, 136.8, 140.0, 141.9, 147.5
9h	30.8	50.4	14.0, 22.7, 30.3, 35.6	_[b]	112.4, 125.6, 127.7, 128.2, 128.5, 134.1, 146.2, 147.4
9j	-	51.9	42.0[a]	_[b]	114.8, 125.5, 125.7, 127.6, 127.7, 128.0 128.5, 128.8, 134.3, 140.3, 144.3, 144.9
16	40.9	37.3	-	-	113.1, 129.0, 130.6, 149.0

[a]Other signals are indistinguishable from signals in other groups and are reported in the column for other groups.

[b]Signals are indistinguishable and are reported in the column for other groups.

sodium and benzophenone. Column chromatography was carried out on MCB silica gel (230-400 mesh) unless stated otherwise.

The benzotriazole adducts **6a-b**[2], **6d**,[2] **8a-c**[3], **8e**,[3] were prepared according to the previously described methods. The novel compound **8d** was also prepared by adaptation of literature procedures. Compounds **6c**, **8f-h** were prepared with improved procedures separately.

2-(Benzotriazol-1-yl)-2-(4-dimethylaminophenyl)-1-phenylethanol (8d): Prepared according to the literature procedure[3] and purified by column chromatography on silica gel with hexane:EtOAc (8:1). Yield: 61%. M.p. 162-164 °C. (Found: C, 73.35; H, 6.15; N, 15.42. $C_{22}H_{22}N_4O$ requires C, 73.72; H, 6.19; N, 15.63.). Mixture of two diastereomers (7:1 represented as ma: major, and mi: minor): ^1H NMR 2.81 (s,

ma) and 2.87 (s, mi) (total 6 H), 4.05 (s, 1 H), 5.68 (d, J = 8.7, mi) and 5.74 (d, 1 H, J = 8.7, ma) (total 1 H), 5.93 (d, 1 H, J = 7.3), 6.46 (d, 2 H, J = 8.6), 6.92 (d, 2 H, J = 8.8), 7.1 - 7.4 (m, 8 H), 8.0 (d, 1 H, J = 7.6). ^{13}C NMR 40.2, 70.2 (69.0), 76.4 (75.0), 110.2, 112.0, 119.6, 124.0 (123.3), 127.1 (126.6), 127.3, 127.8, 128.1 (128.0), 128.2, 128.4 (129.5), 133.5, 139.7, 145.7, 150.1.

4-(Benzotriazol-1-ylmethyl)-N-methylaniline (6c): To a solution of N-methylaniline (10.7 g, 100 mmol) in conc. sulfuric acid (7 ml) and acetic acid (50 ml) was added 1-hydroxymethyl-(1H)-benzotriazole (14.9 g, 100 mmol) at 0-10 °C. The mixture was heated for 30 minutes under reflux. Then, the solution was poured into ice-water (200 ml) and neutralized with NaOH. A sticky stuff was formed and separated from the aqueous solution. Recrystalization from benzene gave 10.9 g product. Yield: 46%. M.p. 92 - 93 °C. (Found: C, 70.59; H, 5.93; N, 23.78. $C_{14}H_{14}N_4$ requires C, 70.55; H, 5.93; N, 23.52). ^{1}H NMR 2.72 (s, 3 H), 3.96 (s, 1 H), 5.65 (s, 2 H), 6.50 (d, 2 H, J = 8.6), 7.12 (d, 2 H, J = 8.6), 7.2 - 7.4 (m, 3 H), 8.0 (d, 1 H, J = 8.1). ^{13}C NMR 30.2, 52.0, 110.0, 112.1, 119.4, 122.4, 123.5, 126.8, 128.8, 132.4, 146.0, 149.2.

General Procedure for Preparation of Compounds 8f-h

A solution of **6c** or **6d** (5 mmol) in dry tetrahydrofuran (100 ml) in a Schlenk type reactor under a nitrogen atmosphere was cooled to -78 °C in a dry ice-acetone bath. *n*-Butyllithium (4.1 ml of 2.5 *M* solution in hexanes, 10.25 mmol) was added dropwise, slowly. The mixture developed an intense dark blue color and was kept at this temperature for 2 hours. Then appropriate electrophile (5 mmol) was added slowly by syringe. The color of the solution changed to pale yellow. The chilled solution was stirred for a further 2 hours. Cold water (50 ml) was then added. The resulting mixture was extracted with diethyl ether (3 x 150 ml), and washed with water (150 ml) and dried over magnesium sulfate (30 g). Removal of the solvent under vacuum (25 °/25 mm Hg) yielded crude product which was purified by column chromatography.

2-(Benzotriazol-1-yl)-2-(4-methylaminophenyl)-1-(4-methylphenyl)ethanol (8f): Eluent: hexane:EtOAc (20:1). Yield: 53%. M.p. 119 - 121 °C. (Found: C, 73.65; H, 6.19; N, 15.30. $C_{22}H_{22}N_4O$ requires C, 73.71; H, 6.37; N, 15.64). Mixture of two diastereomers (4:1 represented as ma: major, and mi: minor): ^{1}H NMR 2.16 (s, ma) and 2.23 (s, mi) (total 3 H), 2.60 (s, ma) and 2.66 (s, mi) (total 3 H), 3.8 - 3.9 (s, 1 H), 5.6-5.9 (m, ma + mi, total 1 H), 6.31 (d, J = 8.6, ma) and 6.42 (d, J = 8.6, mi) (total 1 H), 6.8 - 7.0 (m, 4 H), 7.1 - 7.4 (m, 6 H), 7.90 (d, 1 H, J = 7.3). ^{13}C NMR 20.9 (20.9), 30.1 (30.2), 70.0 (68.8), 75.9 (74.8), 110.2 (110.0), 111.9, 119.3, 123.8, (122.9), 124.0 (123.6), 126.9 (126.4), 127.0, 128.5, 128.6 (129.5), 133.4 (133.3), 136.7, 137.2 (136.9), 145.5 (145.4), 148.9 (149.3).

1-(Benzotriazol-1-yl)-1-(4-methylaminophenyl)pentane (8g): Eluent: hexanes:EtOAc (20:1). Yield: 85%. M.p. 53 - 54 °C. (Found: C, 73.19; H, 7.65; N, 19.04. $C_{18}H_{22}N_4$ requires C, 73.42; H, 7.54; N, 19.04). ^{1}H NMR 0.81 (t, 3 H, J = 7.1), 1.1 - 1.4 (m, 4 H), 2.3 - 2.5 (m, 1 H), 2.6 - 2.8 (m, 4 H), 4.05 (s, 1 H), 5.71 (t, 1 H, J = 7.0). 6.49 (d, 2 H, J = 8.6), 7.1 - 7.5 (m, 5 H), 8.0 (d, 1 H, J = 7.3). ^{13}C NMR 13.5, 21.9, 28.3, 30.0, 33.9, 63.2, 110.0, 111.8, 119.2, 123.3, 126.4, 126.7, 127..5, 132.2, 145.8, 148.9.

2-(Benzotriazol-1-yl)-2-(4-aminophenyl)-1-phenylethane (8h): Eluent: hexanes:EtOAc (10:1). Yield: 88%. M.p. 121 - 122 °C (Found: C, 76.43; H, 5.78; N, 17.95. $C_{20}H_{18}N_4$ requires C, 76.40; H, 5.77; N, 17.83). ^{1}H NMR 3.6 - 3.7 (m, 3 H), 4.0 - 4.1 (m, 1 H), 5..8 - 5.9 (m, 1 H). 6.51 (d, 2 H, J = 8.3), 7.0 - 7.3 (m, 10 H), 7.96 (d, 1 H, J = 7.8). ^{13}C NMR 40.7, 64.3, 109.3, 114.4, 119.1, 123.1, 126.0, 126.3, 127.5, 127.6, 127.7, 128.5, 132.2, 136.8, 145.4, 146.1.

Reaction of Benzotriazole Adducts with Grignard Reagents: General Procedure

To a solution of the benzotriazole adduct **6, 8,** (5 mmol) in benzene or toluene (30 ml) under nitrogen was added the appropriate Grignard reagent solution in Et_2O (20 ml; 1 mmol/ml; freshly prepared from magnesium and the appropriate alkyl bromide). The ether was distilled off and the mixture was refluxed for appropriate time (Table 1). The reaction was monitored by TLC until the starting material had been consumed. The reaction mixture was cooled, poured into ice-water (30 ml), and acidified with 2 N HCl and the solution was then made alkaline (pH 9) with 10% NaOH solution. The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 60 ml). The combined organic extracts were washed with H_2O (50 ml), and dried ($MgSO_4$). Evaporation of the solvent gave the crude product which was purified by column chromatography using the stated eluent (Table 1). Preparative details and the NMR spectral data of the products are given in Tables 1-3.

Reaction of Benzotriazole Adducts with $LiAlH_4$: General Procedure

Lithium aluminum hydride (0.5 g, 13 mmol) was added in one portion to a solution of the benzotriazole adduct **6a** or **8b, 8e, 8g** (5 mmol) in the appropriate solvent (80 ml) under nitrogen. The solution was heated under reflux for the appropriate time given in Table 1. The reaction was monitored by TLC until the starting material had been consumed. The reaction mixture was cooled, poured into ice-water (30 ml), the solution was made slightly acidic with 2 N HCl. The organic layer was then separated and the aqueous layer extracted with Et_2O (3 × 100 ml). The combined extracts were washed with H_2O (50 ml), and dried over $MgSO_4$. Evaporation of the solvent gave the crude product which was purified by column chromatography using the eluent given in Table 1. Preparative details and the NMR spectral data of the products are given in Tables 1-3.

1-(4-Methylaminophenyl)-1-pentene (11): It was obtained as a by-product (an oil) with the same procedure as **9h**. Yield: 15%. HR MS Found: M=175.1361. $C_{12}H_{17}N$ requires M=175.1361. ^{1}H NMR 0.93 (t, 3 H, J = 7.3), 1.4 - 1.6 (m, 2 H), 2.12 (q, 2 H, J = 7.8), 2.80 (s, 3 H), 3.40 (s, 1 H), 5.9 - 6.1 (m, 1 H), 6.24 (d, 1 H, J = 15.8), 6.51 (d, 2 H, J = 8.7), 7.21 (d, 2 H, J = 8.3). ^{13}C NMR 13.7, 22.8, 30.7, 35.1, 112.4, 126.6, 126.8, 127.5, 129.6, 148.3.

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