Convenient Preparations of Imines and Symmetrical Secondary Amines Possessing Primary or Secondary Alkyl Groups

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Hindered alkyl aldehydes react with benzotriazole and ammonia in dry ethanol or methanol to yield the corresponding bis[1-(benzotriazol-1-yl)alkyl]amines **2**. The reaction of aryl aldehydes, however, yields 1-(benzotriazol-1-yl)-*N*-alkylidenealkylamines **3**. The reactions of adducts **2** and **3** with lithium aluminum hydride furnishes dialkyl- and dibenzylamine derivatives **4**. Although the reactions of **2** and **3** with organometallic reagents are not as general, in several cases the reactions of amines **2** with Grignard reagents yield 1-alkyl or aryl substituted *N*-alkylidenealkylamines **5**. Similar reactions of amines **2** with phenyl lithium afford 1,1'-diphenyldialkylamines **7**.

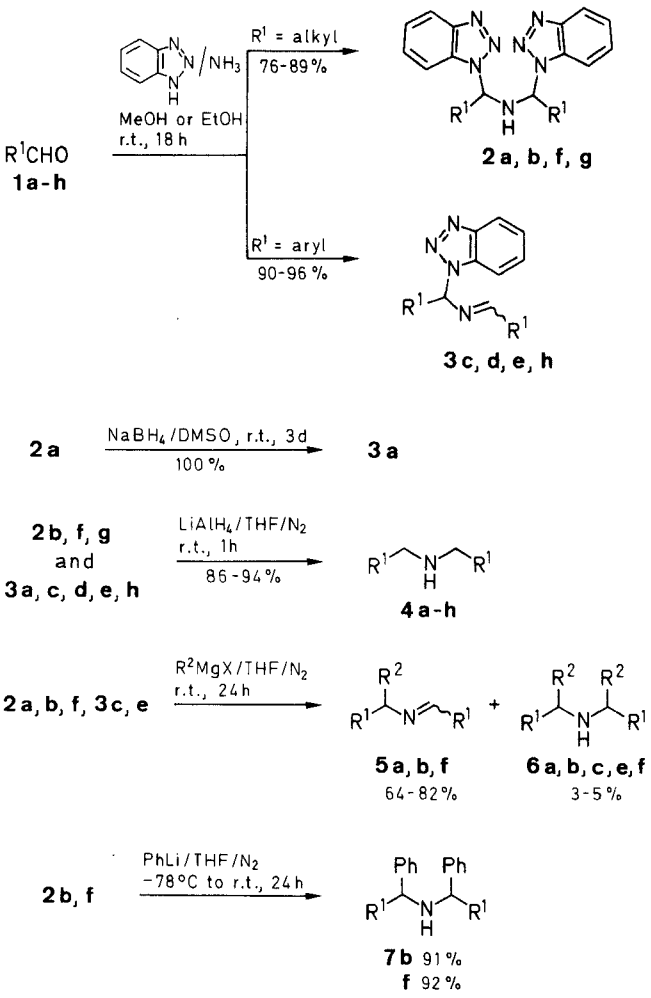
The many reported literature methods for the preparation of amines have been previously surveyed.[1,2]

The conversion of aldehydes to amines has been accomplished in a number of ways. In general, the aldehyde is used as an alkylating agent for an existing primary or secondary amine. Thus, the reaction of primary or secondary amines with aldehydes or ketones provides Schiff's bases which may be subsequently reduced to the higher amine, or undergo reaction with an organometallic reagent.[3-7] Oximes and hydrazones may be reduced in like manner.[8-11] Strecker adducts formed from the addition of cyanide or nitroalkanes to aldehydes, may also be reduced to amines under acidic conditions.[12-15] Several other less general techniques for the conversion of aldehyde to amine have also been reported.[16-23]

Recently the use of methodologies involving benzotriazole as a synthetic auxiliary have significantly extended the available methods for the synthesis of amines.[24] Treatment of adducts formed from the reaction of benzotriazole, an aldehyde, and a secondary amine with either sodium borohydride or an organometallic reagent has resulted in a general synthesis for tertiary amines.[2,25-27] Similarly, primary amines have been converted into secondary amines.[1,2,28,29] The reaction of benzotriazolylphosphine imide with Grignard reagents, and subsequent hydrolysis, also provides a route to primary amines.[30]

In all of these routes one molecule of an aldehyde has been employed to effect the monoalkylation of an existing nitrogen compound. However, two molecules of methanal are incorporated into its adduct with benzotriazole and ammonia,[31] and subsequent reaction of this adduct with two moles of a Grignard reagent furnishes symmetrical secondary amines possessing two primary alkyl substituents.[2] We now report the results of our attempts to generalize this method to other aldehydes.

The reaction of ammonia with an aldehyde and benzotriazole in dry ethanol or methanol gives adducts **2** and **3** which, on reduction with lithium aluminum hydride, affords a further method for the preparation of symmetrical primary alkyl substituted amines **4**. The reaction of adducts **2** and **3** with organometallic reagents was not found to be a general reaction. Complex mixtures were obtained from the reaction of **3** with either Grignard reagents or organolithium reagents. In several cases, however, the reaction of adducts **2** with organometallic reagents did yield useful products. In these cases, the reaction of **2** with Grignard reagents furnished high yields of 1-alkyl or aryl substituted *N*-alkylidenealkylamines **5**. Similar reaction with phenyllithium resulted in the formation of 1,1'-diphenyldialkylamines **7**.



1–7	R^1	1–7	R^1	5,6	R^2
a	*t*-Bu	e	4-MeC_6H_4	a	Bn
b	*i*-Pr	f	*c*-C_6H_{11}	b	Bn
c	Ph	g	–CH(Me)Ph	c	Bn
d	4-ClC_6H_4	h	2,4-$(MeO)_2C_6H_5$	e	Ph
				f	Me

This technique for the synthesis of amines possesses several advantages over existing strategies. The overall conversion is achieved in two reaction steps, with the isolated yield of amine (based on the reagent aldehyde) being high. The secondary amines are formed as the sole products, avoiding the difficult separation procedures

necessary in many amine or ammonia alkylation procedures. The intermediate 1-(benzotriazol-1-yl)alkyl adducts need not be isolated prior to subsequent reaction, and overall yields are often improved if this is the case. Finally, the option of reduction or reaction with organometallic reagents of the intermediate 1-(benzotriazo-1-yl)alkyl adducts allows a variety of amine or imine products to be synthesised.

Aliphatic aldehydes not possessing α-methylene groups undergo reaction with alcoholic anhydrous ammonia and bezotriazole to furnish bis[1-(benzotriazol-1-yl)alkyl]-amines **2** (Table 1) (only polymeric material was obtained from the reaction of either butanal or ethanal under similar conditions). These products are analogous to *bis* Strecker adducts obtained from the condensation of aldehydes or ketones, ammonia and cyanide anion. In general, the primary aminonitriles obtained from the Strecker synthesis incorporate only mole of the carbonyl compound, although succin- and glutaraldehydes do react at both carbonyl groups with two moles of cyanide anion and one mole of ammonia (or a primary amine) in an intramolecular reaction to form 2,5-dicyanopyrrolidine[32] and 2,6-dicyanopiperidine,[33,34] respectively. An analogous condensation reaction leading to acyclic products occurs between primary amines, methanal and thiocarboxylic acids.[35]

Aryl aldehydes react with ammonia and benzotriazole to furnish the 1-(benzotriazol-1-yl)-*N*-alkylidenealkyl-amines **3** (Table 1). The product from the reaction of 2,2-dimethylpropanal (**1a**) could be purified by recrystallisation from ethanol to give a satisfactory C,H,N analysis for **2a**. However, in solution, some dissociation to **3a** and benzotriazole occured and the NMR spectrum was complex with clear signals for the *tert*-butyl groups of **3a**. Based on the integral for the $\delta = 5.71$ CH=N singlet, there was about 60% dissociation in $CDCl_3$ at room temperature. The ratio of aliphatic to aromatic integrals was correct for structure **2a**, suggesting that the compound is not dissociated in the solid state and no benzotriazole is lost during recrystallization. The preferential formation of the imines **3** is presumably due to either the increased steric hinderance of the tertiary alkyl group or to the increased stabilization of the C=N bond by aryl substitution. In each case the reactions proceed in

Table 1. Compounds **2**, **3** Prepared

Educt	Product[a]	Yield (%)	mp (°C)	IR ν (cm^{-1})	MS (70 eV) *m/z* (%)
1a	**2a**	84	131–132	–	273 (M^+-118, 1), 215 (6), 154 (20), 119 (30), 104 (22)
	3a[b]	100	97 (dec)	1650 (w), 1625 (w, C=N)	273 (M^+-1, 1), 215 (6), 154 (20), 119 (30), 104 (22)
1b	**2b**	76	130–131	–	245 (M^+-118, 4), 175 (13), 174 (20), 132 (18), 126 (100), 119 (34), 104 (43), 91 (26)
1c	**3c**	92	129–130	1638 (s), 1578 (s, C=N)	208 (M^+-32, 12), 195 (15), 194 (100), 180 (42), 152 (21)
1d	**3d**[c]	90	oil	1701 (m), 1643 (s), 1595 (s, C=N)	353 (M^+-27, 8), 351 (15), 278 (19), 263 (37), 362 (21), 262 (M^+-118, 58), 214 (27), 127 (28), 125 (100)
1e	**3e**[c]	90	oil	1701 (s), 1687 (s), 1639 (s), 1605 (s, C=N)	311 (M^+-29, 12), 223 (19), 222 (100), 194 (21)
1f	**2f**	89	159–160	–	382 (M^+-61, 2), 241 (7), 215 (11), 214 (22), 206 (41), 132 (26), 131 (19), 119 (56), 104 (100), 95 (31), 91 (77)
1g	**2g**	84	166–167	1607 (s, C=N)	410 (M^+-77, 1), 382 (3), 263 (17), 250 (6), 235 (5), 119 (48), 91 (100)
1h	**3h**	96	166–167	1632 (s), 1603 (s, C=N)	433 (M^+-1, 2), 403 (3), 315 (12), 314 (100), 269 (16), 268 (42), 240 (53)

[a] Satisfactory microanalyses obtained for all new compounds (**2a,b,f,g, 3a,c,h**): C ±0.5, H ±0.3, N ±0.3.
[b] **2a** Converted into **3a** on treatment with $NaBH_4$ in DMSO for 3 d at r.t.
[c] Products isolated as oils conservatively estimated at 90% purity by NMR analysis. Attempts to purify the products by chromatography resulted in decomposition. Subsequent reactions were carried out on the crude oil and yields are calculated from this estimated yield.

Table 2. Compounds **4** Prepared

Educt	Product	Yield (%)[a]	Molecular Formula[b]	MS (70 eV) *m/z* (%)
3a	**4a**	93	$C_{10}H_{23}N$ (157.3)	157 (M^+, 5), 142 (15), 100 (100), 71 (21)
2b	**4b**[c]	90	$C_8H_{19}N$ (129.2)	129 (M^+, 8), 114 (8), 86 (100), 84 (13)
3c	**4c**[c]	94	$C_{14}H_{15}N$ (197.3)	197 (M^+, 12), 196 (16), 106 (63), 92 (22), 91 (100)
3d	**4d**[33, 36]	91	$C_{14}H_{13}Cl_2N$ (266.2)	266 (M^+ + 1, 9), 265 (M^+, 16), 264 (17), 140 (43), 127 (24), 125 (100)
3e	**4e**[37]	86	$C_{16}H_{19}N$ (225.3)	225 (M^+, 9), 224 (10), 120 (56), 105 (87)
2f	**4f**[38]	91	$C^z{}_{14}H_{27}N$ (209.4)	209 (M^+, 12), 127 (22), 126 (100), 97 (13)
2g	**4g**[d, 39]	93	$C_{18}H_{22}N$ (252.4)	252 (M^+-1, 2), 149 (9), 148 (100), 105 (18), 92 (18), 91 (99)
3h	**4h**[40]	89	$C_{18}H_{23}NO_4$ (317.4)	318 (M^+ + 1, 16), 317 (M^+, 3), 179 (31), 166 (21), 151 (100), 121 (27)

[a] All products were isolated as oils.
[b] Satisfactory HRMS data obtained: *m/z* ±0.0009, except for **4h**: *m/z* −0.066.
[c] Comercially available; Aldrich Chemical Company, Inc.
[d] HRMS obtained of M^+-1 ion (*m/z* −0.0002).

high yield, and isolation of the products is frequently aided by their quantitative precipitation from solution. Purification of the 1-benzotriazolylalkyl intermediates is unnecessary prior to subsequent reduction or reaction with organometallic reagents. The crude product of the reaction, simply obtained by evaporation of the alcohol solvent, is suitable for these purposes.

Both adducts **2** and **3** are reduced with lithium aluminum hydride to yield symmetrical secondary amines **4** (Table 2). Compounds **2** and **3** could not be reduced with sodium borohydride. Indeed, treatment with this reagent was found to convert **2a** to a sample of 1-(benzotriazol-1-yl)-2,2-dimethyl-*N*-(2,2-dimethylpropylidene)propylamine **(3a)** alone.

^{1}H- and ^{13}C-NMR data for products **2, 3,** and **4** are give in Table 3. Compound **2b** showed a clear diastereotopic effect with the methyl doublets at $\delta = 0.56$ (6 H) and 1.30 (6 H). In addition, several of the new compounds (e.g., **2a, 2b, 7b, 7f**) showed line broadening due to the presence of diastereoisomers.

The nucleophilic substitution of benzotriazolate with organometallic reagents has previously been demonstrated in a number of reports.[1,2,25,26] Similar replacement of the benzotriazole group may be accomplished for a number of the bis[1-(benzotriazol-1-yl)alkyl]amines **2** (Table 4) but, in general, is not useful for adducts **3**.

The reaction of **2b** with benzylmagnesium bromide, and of **2f** with methylmagnesium iodide, results in the substitution of a single benzotriazolate by the Grignard reagent, and the elimination of one molecule of benzotriazole, to furnish high yields of the 1-substituted *N*-alkylidenealkylamines **5b** and **5f** respectively. The reac-

Table 3. ^{1}H- and ^{13}C-NMR Data for Compounds **2–4**

Product	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ
2a/3a[a]	0.98 (m, 9H), 1.12 (m, 9H), 5.71 (s, 0.6H), 7.40 (m, 4H), 7.71 (s, 1H), 8.08 (m, 4H)	25.97, 26.06, 26.37 and 26.69 (CH_3), 93.53 (CH), 114.55, 117.56, 119.25, 123.69, 125.66, 126.62, 146.25 (C_{Bt}), 175.75 (C–N)
2b[b]	0.56 (d, 6H, J = 6.6), 1.30 (d, 6H, J = 6.6), 2.53 (m, 2H), 3.50 (1H, J = 10.6), 5.30 (t, 2H, J = 9.7), 7.02–7.08 (m, 4H), 7.13–7.18 (m, 2H), 7.50 (d, 2H, J = 8.2)	18.60 (CH_3) 19.96 (CH_3), 34.54 (CH[CH_3]$_2$), 79.76 (CHN), 108.89, 119.08, 123.44, 126.71 (CH_{Bt}), 130.91, 145.21 (C_{Bt})
2f[c]	0.70–2.44 (m, 22H), 3.45 (m, 1H), 4.78 (m, 1H), 5.38 (m, 1H), 7.03–7.56 (m, 6H), 7.92 (m, 1H), 8.12 (m, 1H)	23.94, 24.01, 24.12, 24.21, 24.31, 24.45, 24.61, 24.68, 27.23, 27.39, 27.74, 27.99, 28.47, 40.37, 40.52, 41.86 (CH_{alkyl}), 75.28, 88.00 (CH_{Bt}), 108.95, 110.01, 111.17, 118.14, 118.37, 122.73, 122.85, 125.95 (CH_{Bt})
2g	[d]	[d]
3a	1.07 (s, 9H), 1.11 (s, 9H), 5.69 (s, 1H), 7.27–7.43 (m, 2H), 7.70 (s, 1H), 8.00–8.09 (m, 2H)	26.34 (CH_3), 26.63 (CH_3), 37.03, 38.08 (CMe$_3$), 93.42 (CH), 114.46, 119.27, 123.53, 126.50 (CH_{Bt}), 133.08, 146.23 (C_{Bt}), 175.63 (CH=)
3c	7.26–7.50 (m, 11H), 7.57 (s, 1H), 7.85 (dd, 2H, J = 8.1, 1.8), 8.06 (m, 1H), 8.37 (s, 1H)	83.74 (CH_{Bt}), 112.09, 119.87, 124.00, 126.91, 127.31, 128.75, 128.77, 128.92, 128.98, 131.97, (C_{arom}), 134.87, 137.63, 146.65 (C_{arom}), 163.99 (C=N)
3d	7.39 (m, 9H), 7.54 (s, 1H), 7.76 (d, 2H, J = 8.5), 8.09 (m, 1H), 8.33 (s, 1H)	82.86 (CH_{Bt}), 111.74, 119.83, 124.44, 127.73, 128.27, 128.73, 128.89, 129.02, 129.09, 129.18, 129.38, 130.14, 133.00, 135.76 (C_{arom}), 163.21 (C=N)
3e	2.32 (s, 3H), 2.37 (s, 3H), 7.30 (m, 9H), 7.54 (s, 1H), 7.76 (m, 2H), 8.08 (m, 1H), 8.35 (s, 1H)	21.08 (CH_3), 21.53 (CH_3), 84.06 (CH_{Bt}), 112.30, 119.54, 124.18, 126.76, 127.33, 128.92, 129.40, 129.57, 129.65, 129.82, 132.23, 134.70, 138.79, 142.52 (C_{arom}), 163.92 (C=N)
3h	3.63 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 6.40 (dd, 2H), J = 5.2, 2.3), 6.52 (m, 2H), 7.30 (m, 2H), 7.50 (d, 1H, J = 7.9), 7.64 (s, 1H), 7.71 (d, 1H, J = 8.5), 8.02 (m, 1H), 8.07 (d, 1H, J = 8.7), 8.76 (s, 1H, C=N)	55.35, 55.42 (OMe), 79.26 (CH_{Bt}), 97.79, 98.49, 104.16, 105.60, 111.73, 119.63, 123.40, 126.68, 129.07, 129.40 (CH_{arom}), 117.05, 118.94, 132.41, 146.35, 158.14, 160.79, 161.40, 163.89 (C_{arom}), 160.79 (C=N)
4a	0.89 (s, 18H), 2.33 (s, 4H)	27.81 (CH_3), 31.98 (C), 69.53 (CH_2)
4b	0.89 (d, 12H, J = 6.6), 1.75 (sept, 2H, J = 6.6), 2.39 (d, 4H, J = 6.6)	20.64 (CH_3), 28.18 (CH), 58.14 (CH_2)
4c	3.77 (s, 4H), 7.30 (m, 10H)	53.05 (CH_2), 126.82, 128.03, 128.28 (CH_{arom}), 140.23 (C_{arom})
4d	3.72 (s, 4H), 7.27 (m, 8H)	52.23 (CH_2), 128.45, 129.37 (CH_{arom}), 132.60, 138.51 (C_{arom})
4e	2.31 (s, 6H), 3.70 (s, 4H), 7.10 (d, 4H, J = 8.0), 7.18 (d, 4H, J = 8.0)	20.97 (CH_3), 52.60 (CH_2), 128.01, 128.94 (CH_{arom}), 136.31, 137.04 (C_{arom})
4f	0.90 (m, 4H), 1.21 (m, 6H), 1.46 (m, 2H), 1.70 (m, 10H), 2.40 (d, 4H, J = 6.6)	26.04 (CH_2), 26.67 (CH_2), 31.44 (CH_2), 37.87 (CH), 56.97 (CH_2N)
4g[b]	1.17 (d, 6H, J = 6.8), 2.64–2.92 (m, 6H), 7.08–7.26 (m, 10H)	19.71 (CH_3), 39.70 (CH), 56.93 (CH_2), 126.16, 126.94, 128.36 (CH_{arom}), 145.18 (C_{arom})
4h	3.71 (s, 4H), 3.78 (s, 12H), 6.42 (m, 4H), 7.16 (d, 2H, J = 8.5)	48.05 (CH_2), 55.10, 55.21 (Me), 98.31, 103.47, 130.19 (CH_{arom}), 121.14, 158.52, 159.79 (C_{arom})

[a] Mixture of diastereoisomers. NMR analysis is consistant with a mixture of **2a** and **3a**.
[b] Mixture of diastereoisomers (1 : 1).
[c] $CDCl_3$/DMSO-d_6 solvent. Mixture of diastereoisomers/conformers. Highly complex ^{13}C-NMR spectrum; only most intense resonances are recorded.
[d] Insoluble in normal NMR solvents. Product decomposes in CF_3CO_2D.

tion of **2a** with benzylmagnesium bromide also resulted in a high yield of **5a**. In each of these cases, however, small quantities of radical dimer products from the Grignard reagent were also observed, together with small quantities of other products. Attempts to remove these impurities by chromatography resulted in decomposition of imines **5**. However, chromatography did allow the isolation of small quantities of the disubstituted products **6a** and **6b** from the reactions of **2a** and **2b**. These products result from the addition of a second molecule of the Grignard reagent to the imine. Increasing the temperature of the reaction did not result in higher yields of 1,1'-disubstituted products. Similar reaction of **3c** with benzylmagnesium bromide and **3e** with phenylmagnesium bromide resulted in the formation of complex mixtures from which only low yields of the 1,1'-disubstituted alkylamines **6c** and **6e**, respectively, were isolated.

The reactions of adducts **2** with alkyl organolithium reagents resulted in the formation of complex mixtures. However, some reactions of **2** with phenyllithium were found to furnish high yields of symmetrical 1,1'-diphenyldialkylamines **7**. Thus, the reaction of **2b** and **2f** with phenyllithium resulted in the formation of **7b** and **7f**, respectively.

Hindered alkyl aldehydes and aryl aldehydes react with benzotriazole and ammonia to form bis[1-(benzotriazol-1-yl)alkyl]amines **2** and 1-(benzotriazol-1-yl)-*N*-alkylidenealkylamines **3**, respectively. Both adducts **2** and **3** are quantitatively reduced with lithium aluminum hydride to symmetrical primary alkyl substituted amines **4**. The reaction of adducts **2** and **3** with organometallic reagents is not general; however, several adducts **2** do undergo reaction with Grignard reagents to furnish 1-substituted

Table 4. Compounds **5**, **6** Prepared

Educt	Organo-metallic	Product	Yield[a] (%)	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS)[b] δ
2a	BnMgBr	**5a**	64	[b]0.84 (s, 9H), 0.94 (s, 9H), 2.57 (d, 1H, J = 10.2), 2.65 (d, 1H, J = 10.2), 2.89 (t, 1H, J = 10.2), 6.75 (s, 1H), 6.98–7.33 (m, 5H)	26.80, 26.85 (CH_3), 33.88, 36.71 ($\underline{C}Me_3$), 65.07 (CH_2), 82.21 (CH), 125.84, 126.89, 127.49, 127.69, 129.88, 128.43 (CH_{arom}), 140.66, 140.83 (C_{arom}), 170.45 (C=N)
2a	BnMgBr	**6a**	4	0.99 (s, 18H), 2.20 (dd, 2H, J = 13.4, J = 11.2), 2.68 (dd, 2H, J = 11.2, 1.7), 2.97 (dd, 2H, J = 13.4, 1.7), 7.20–7.33 (m, 10H)	26.27 (CH_3), 38.71 (CH_2), 62.02 (CH), 126.01, 128.42, 129.12 (CH_{arom}), 140.97 (C_{arom})
2b	BnMgBr	**5b**	70	[b]0.77 (d, 3H, J = 6.8), 0.85 (d, 6H, J = 6.7), 0.96 (d, 3H, J = 6.6), 1.84 (oct, 1H, J = 6.4), 2.27 (oct, 1H, J = 5.8), 2.69 (m, 2H), 2.97 (m, 1H), 6.84 (d, 1H, J = 5.8), 7.03–7.35 (m, 5H)	18.95, 19.18, 19.50, 19.85 (CH_3), 32.51, 33.65 (CH), 39.91 (CH_2), 78.88 (CHN), 125.59, 125.80, 127.82, 128.30, 129.67 (CH_{arom}), 139.93 (C_{arom}), 169.27 (C=N)
2b	BnMgBr	**6b**	3	0.91 (dd, 12H, J = 6.6, 5.6), 1.18 (br s, 2H), 1.66 (m, 1H), 2.36 (m, 1H), 2.82 (m, 2H), 7.26 (m, 10H)	17.44, 19.30 (Me), 32.80 ($\underline{C}HMe_2$), 41.02 (CH_2), 58.20 (CHN), 126.09, 128.40, 129.15 (CH_{arom}), 140.00 (C_{arom})
2b	PhLi	**7b**	91	[c]0.62 (d, J = 6.8), 0.76 (d, J = 6.8), 0.92 (m, 12H), 1.72 (m, 1H), 1.91 (m, 1H), 2.91 (d, 1H, J = 7.6), 3.32 (d, 1H, J = 6.3), 7.06–7.36 (m, 6H), 7.41 (m, 2H), 7.59 (m, 2H)	18.52, 19.72, 19.83, 19.89 (CH_3), 33.15, 34.71 ($\underline{C}HMe_2$), 65.92, 66.37 (CHN), 126.36, 126.45, 127.13, 127.22, 127.55, 127.61, 127.71, 127.82, 127.99, 128.07, 128.71 (C_{arom}), 143.30, 143.58 (C_{arom})
3c	BnMgBr	**6c**	4	2.72 (d, 1H, J = 8.9), 2.76 (d, 1H, J = 8.9), 2.91 (d, 1H, J = 5.2), 2.95 (d, 1H, J = 5.2), 4.1 (dd, 2H, J = 8.9, 5.2), 7.07–7.29 (m, 20H)	46.43 (CH_2), 57.50 (CH), 126.34, 126.39, 127.04, 128.13, 128.37, 129.31 (CH_{arom}), 139.01, 145.55 (C_{arom})
3e	PhMgBr	**6e**	5	2.32 (s, 6H), 5.79 (s, 2H), 7.13 (d, 4H, J = 7.7), 7.25 (d, 4H, J = 7.7), 7.35 (m, 10H)	21.05 (CH_3), 75.98 (CH), 126.40, 126.47, 127.36, 128.39, 129.10 (CH_{arom}), 137.18, 140.91, 143.91 (C_{arom})
2f	MeMgI	**5f**	82	0.75–0.90 (m, 2H), 1.10 (d, 3H, J = 6.4), 1.07–1.38 (m, 9H), 1.64–1.80 (m, 10H), 2.18 (m, 1H), 2.68 (quint, 1H, J = 6.4), 7.37 (d, 1H, J = 5.6)	20.00 (Me), 25.33, 25.36, 25.91, 26.13, 26.30, 26.51, 29.72, 29.81, 29.83, 30.07, 43.20, 43.37 (CH_2), 71.46 (CHN), 166.58 (C=N)
2f	PhLi	**7f**	92	[c]0.66–2.07 (m, 22H), 2.94 (d, 1H, J = 7.8), 3.30 (d, 1H, J = 6.6), 7.02–7.60 (m, 10H)	26.30, 26.40, 26.55, 26.67, 29.20, 30.17, 30.22, 30.56 (CH_2), 43.56, 44.37 (CH), 65.02, 66.28 (CHN), 126.24, 126.39, 127.12, 127.21, 127.56, 127.80, 127.96, 128.11, 128.71 (CH_{arom}), 143.61, 143.72 (C_{arom})

[a] All products were isolated as oils.
[b] Additional aryl resonances ascribed to observation of rotamers.
[c] Mixture of diastereoisomers.

N-alkylidenealkylamines **5**, and with phenyllithium to give 1,1'-diphenyldialkylamines **7**.

Melting points were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian XL300 spectrometer (300 and 75 MHz, respectively), using $CDCl_3$ as solvent (unless otherwise stated) and TMS as an internal reference. High resolution (HRMS) and electron impact source mass spectra were recorded on a Kratos AEI MS 30 with a Data General Nova data system. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR; spectra of solids were recorded as nujol mulls, whereas spectra of oils were recorded neat. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Commercially available reagent grade solvents were thoroughly dried in accord with standard methods prior to use. Preparative chromatography was performed by flash column chromatography with silica gel (silica gel 60, mesh 240–400, Merck).

Bis[1-(benzotriazol-1-yl)-2-methylpropyl]amine (2b); Typical Procedure:
2-Methylpropanal (**1b**; 69 mmol, 5.0 g) and benzotriazole (69 mmol, 8.2 g) are dissolved in anhydr. methanolic NH_3 (34.5 mL, 2 mol^{-1}) and stirred at r.t. for 18 h. The precipitate is filtered from solution, washed with dry EtOH and dried under reduced pressure. Compound **2b** is obtained as a white solid; yield: 9.6 g (76%).

Bis[1-(benzotriazol-1-yl)-2,2-dimethylpropyl]amine (**2a**): Obtained from 2,2-Dimethylpropanal (**1a**; 1.0 g, 10 mmol) and benzotriazole (1.4 g, 10 mmol) as described for **2b** as a white solid; yield: 1.9 g (84%).

α-(Benzotriazol-1-yl)-4-chloro-N-(4-chlorobenzylidene)benzylamine (**3d**): Obtained from 4-Chlorobenzaldehyde (**1d**; 2.0 g, 14 mmol) and benzotriazole (1.7 g, 14 mmol) as described for **2b** in anhydr. ethanolic NH_3 (10 mL; 2 mol dm^{-3}); yield: 4.0 g (90%).

α-(Benzotriazol-1-yl)-4-methyl-N-(4-methylbenzylidene)benzylamine (**3e**): obtained from 4-Methylbenzaldehyde (**1e**; 2.0 g, 17 mmol) and benzotriazole (2.0 g, 17 mmol) as described for **3d** as a yellow oil; yield: 4.1 g (90%).

Bis(2-methylpropyl)amine (4b); Typical Procedure:
To a suspension of $LiAlH_4$ (0.46 g, 12 mmol) in dry THF (30 mL), under N_2, and at r.t., is added a solution of compound **2b** (2.0 g, 5.5 mmol) dissolved in THF (30 mL), in small portions over 30 min. The mixture is stirred at r.t. for a further 30 min, and then poured onto crushed ice (50 mL). The solution is extracted with Et_2O (3 × 30 mL), and the extract is washed with H_2O. After drying ($MgSO_4$), the solvent is removed under reduced pressure to afford **4b**; yield: 0.6 g (90%) (Table 2).

1-Benzyl-2,2-dimethyl-*N*-(2,2-dimethylpropylidene)propylamine (5a):
To a solution of **2a** (2.0 g, 7.6 mmol) in dry THF (60 mL), under N_2, and at r.t., is added a solution of BnMgBr (46 mmol) in THF (25 mL). The mixture is stirred for 24 h and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil (0.8 g), estimated yield by NMR analysis based on **2a**, 64%.

IR (neat): ν = 1670 cm^{-1} (s, C=N). Flash chromatography using Et_2O/hexane (1:3) gave a yellow oil of bis(1-benzyl-2,2-dimethylpropyl)amine **(6a)** (0.1 g).

1-Benzyl-2-methyl-*N*-(2-methylpropylidene)propylamine (5b):
To a solution of **2b** (3.0 g, 8.2 mmol) in dry THF (60 mL), under N_2, and at r.t., is added a solution of BnMgBr (40 mmol) in THF (20 mL). The mixture is stirred for 24 h and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil (1.8 g), estimated yield by NMR analysis based on **2b**, 70%.

IR (neat): ν = 1666 cm^{-1} (s, C=N). Flash chromatography using Et_2O/hexane (1:3) gave a yellow oil of bis(1-benzyl-2-methylpropyl)amine **(6b)** (0.1 g).

1-Cyclohexyl-*N*-(cyclohexylmethylene)ethylamine (5f):
To a solution of **2f** (2.0 g, 4.5 mmol) in dry THF (60 mL), under N_2, and at r.t., is added a solution of MeMgI (18 mmol) in THF (15 mL). The mixture is stirred for 24 h and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil (0.8 g), estimated yield by NMR analysis based on **2f**, 82%.

IR (neat): ν = 1667 cm^{-1} (s, C=N).

Bis(2-methyl-1-phenylpropyl)amine (7b):
To a solution of **2b** (1.0 g, 2.8 mmol) in dry THF (30 mL), under N_2, and at −78 °C, is added a solution of PhLi (8.3 mmol) in cyclohexane (4.6 mL). The mixture is allowed to warm to r.t., stirred for 24 h, and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressue to give a yellow oil; yield: 0.7 g (91%).

HRMS: *m/z* calc. for $C_{20}H_{27}N$: 238.1596; found: 238.1630 ($M^+ - 43$ [-*i*-Pr]).

MS: *m/z* (%) = 239 (18), 238 ($M^+ - 43$, 86) (19), 154 (100), 153 (41), 152 (29), 133 (51), 106 (43), 92 (86).

Bis(α-benzylbenzyl)amine (6c):
To a solution of **3c** (0.5 g, 1.6 mmol) in dry THF (20 mL), under N_2, and at r.t., is added a solution of BnMgBr (5.0 mmol) in THF (10 mL). The mixture is stirred for 24 h and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil. Flash chromatography using Et_2O/hexane (1:3) gave a clear oil; yield: 0.02 g (4%).

Bis(α-phenyl-4-methylbenzyl)amine (6e):
To a solution of **3e** (1.5 g, 1.4 mmol) in dry THF (20 mL), under N_2, and at r.t., is added a solution of PhMgBr (5.6 mmol) in THF (10 mL). The mixture is stirred for 24 h and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil. Flash chromatography using Et_2O/hexane (1:3) gave a yellow oil; yield: 0.03 g (5%).

Bis(α-cyclohexylbenzyl)amine (7f):
To a solution of **2f** (1.0 g, 2.2 mmol) in dry THF (30 mL), under N_2, and at −78 °C, is added a solution of PhLi (9.5 mmol) in cyclohexane (5.2 mL). The mixture is allowed to warm to r.t., stirred for 24 h, and poured onto crushed ice (20 mL). The aqueous solution is extracted with Et_2O (3 × 20 mL). The organic extract is washed with H_2O (3 × 10 mL) and dried ($MgSO_4$). The solvent is removed under reduced pressure to give a yellow oil; yield: 0.75 g (92%).

HRMS: *m/z* calc. for $C_{20}H_{24}N$: 278.1909; found: 278.1884 ($M^+ - 83$ [-*c*-C_6H_{11}]).

MS: *m/z* (%) = 279 (21), 278 (M-83, 100), 194 (13), 173 (17), 106 (26), 91 (75).

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