130666-28-3; $Fe(C{\equiv}CCH_2OCH_3)(CO)_2(\eta\text{-}C_5H_5)$, 138813-83-9; $Fe(C{\equiv}CCO_2Et)(dppm)(\eta\text{-}C_5H_5)$, 138813-84-0; $Fe(C{\equiv}CCH_2OCH_3)(dppm)(\eta\text{-}C_5H_5)$, 138813-85-1; $Fe(C{\equiv}CCH_2OCH_3)(dmpm)(\eta\text{-}C_5H_5)$, 138834-37-4; $Fe(C{\equiv}C^tBu)(dmpm)(\eta\text{-}C_5H_5)$, 138834-38-5; $Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)$, 134148-19-9; $Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)$, 134148-20-2; $Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)$, 134148-17-7; $Fe(C{\equiv}C^tBu)(dppm)(\eta\text{-}C_5H_5)$, 134148-18-8; $Fe(C{\equiv}CSiMe_3)(dppm)(\eta\text{-}C_5H_5)$, 134148-16-6; $[Fe\{{=}C{=}C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)][Tf]$, 138813-87-3.

Supplementary Material Available: Hydrogen atom coordinates and isotropic thermal parameters (Table S1) and anisotropic thermal parameters for the non-hydrogen atoms (Table S2) (2 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Bismuth(III) Chloride–Aluminum-Promoted Alkylations of Immonium Cations to Amines in Aqueous Media: Unstabilized Carbanion Equivalents for Use in the Presence of Water

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In the presence of bismuth(III) chloride–metallic aluminum, allyl, propargyl, benzyl, and methyl halides react with a large range of 1-(aminoalkyl)benzotriazoles at room temperature in THF–water to give the corresponding homoalkylated amines in high yields. 1-(Amidoalkyl)benzotriazoles derived from benzaldehyde are also successfully converted under these conditions into N-substituted amides.

Introduction

The Barbier reaction has recently received interest as a one-step alternative to the Grignard reaction, owing to the development of several modifications which expand its synthetic potential. The use of metals alternative to magnesium, such as lithium,[1] zinc,[2] bismuth,[3] and lead,[4] has been investigated and ultrasound irradiation has been found to improve yields.[5] Generally, intermolecular Barbier reactions are between allyl or benzyl halides and aldehydes or ketones, but the use of other alkyl halides has been reported.[2] Recently, electroreductive Barbier-type allylations of carbonyl compounds have been achieved in metal-redox systems such as Sn(IV)/Sn(0)[6] and Bi(III)/Bi(0).[7] Torii and co-workers have achieved the Barbier allylation of imines using either a $TiCl_4$/Al bimetal system[8a] or alternatively an electroreductive allylation procedure employing a combination of a Pb(II)/Pb(0) redox system and an aluminum anode.[8b]

One of the more intriguing developments concerns the allylation of carbonyl compounds in the presence of water utilizing organometallics derived from allyl halides and zinc or tin. Such carbon–carbon bond-forming processes involving unstabilized carbanions in aqueous solution are extremely rare. Allylations of aldehydes were carried out in a variety of two-phase solvent systems. For example, organozinc allylations were performed using aqueous ammonium chloride with either solvent THF[9] or a solid (C-18 silica gel)[10] as coorganic phase, whereas those of tin were carried out in water–ether or water–THF mixtures and required promotion by sonication,[9a,b] traces of acid,[11] or aluminum metal.[11] It is likely that the aluminum has two functions; it both generates Sn(0) by reduction of Sn(II) and Sn(IV) from tin(II) chloride and activates the oxidative addition of allyl bromide to the tin.[12,13] Recent developments in aqueous alkylations include organotin alkylations

Scheme I

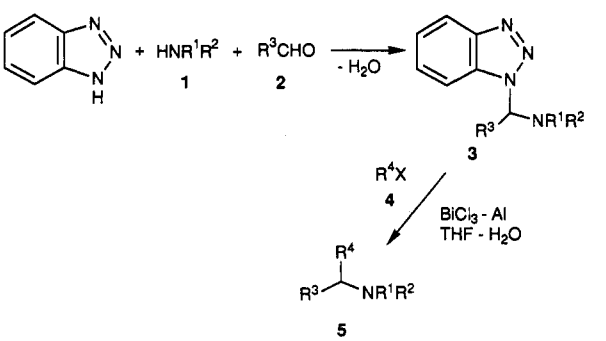

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Table I. Preparation of Amines 5 via Aqueous Alkylation of N-(Alkylamino)benzotriazoles 3

entry no.	3	R^1, R^2	R^3	R^4	5	yield, %
1	3a	Ph, Me	H	$CH_2CH{=}CH_2$	5a	85
2	3b	p-BuC_6H_4, Me	H	$CH_2CH{=}CH_2$	5b	87
3	3c	Ph, Ph	H	$CH_2CH{=}CH_2$	5c	83
4	3d	Bu, Bu	H	$CH_2CH{=}CH_2$	5d	83
5	3e	i-Bu, i-Bu	H	$CH_2CH_2{=}CH_2$	5e	85
6	3f	$-(CH_2)_2O(CH_2)_2-$	H	$CH_2CH{=}CH_2$	5f	80
7	3g	$-(CH_2)_4-$	H	$CH_2CH{=}CH_2$	5g	85
8	3h	$-(CH_2)_5-$	H	$CH_2CH{=}CH_2$	5h	87
9	3i	c-C_6H_{11}, H	H	$CH_2CH{=}CH_2$	5i	80
10	3j	p-MeC_6H_4, H	H	$CH_2CH{=}CH_2$	5j	35[a]
11	3k	Ph(Me)CH, H	i-Pr	$CH_2CH{=}CH_2$	5k	80
12	3l	MeCO, H	Ph	$CH_2CH{=}CH_2$	5l	78
13	3m	$PhCH_2OCO$, H	Ph	$CH_2CH{=}CH_2$	5m	85
14	3c	Ph, Ph	H	$CH_2C{\equiv}CH$	5n	51
	3c	Ph, Ph	H	$CH{=}C{=}CH_2$	5o	41
15	3a	Ph, Me	H	$CH_2C{\equiv}CH$	5p	48[b]
	3a	Ph, Me	H	$CH{=}C{=}CH_2$	5q	36[b]
16	3a	Ph, Me	H	$PhCH_2$	5r	75
17	3c	Ph, Ph	H	$PhCH_2$	5s	79
18	3f	$-(CH_2)_2O(CH_2)_2-$	H	$PhCH_2$	5t	70
19	3e	t-Bu, i-Bu	H	$PhCH_2$	5u	88
20	3a	Ph, Me	H	Ph(Me)CH	5v	75
21	3c	Ph, Ph	H	Me	5w	75
22	3n	i-Pr, i-Pr	H	Me	5x	78
23	3o	Ph, Me	c-C_6H_{11}	Me	5y	60
	3o	Ph, Me	c-C_6H_{11}	H	5z	30

[a] N,N-Bis(3-butenyl)-p-methylaniline (6a) was obtained as a byproduct in 30% yield. [b] NMR yield for inseparable mixture.

of aldehydes with propargyl bromide, giving mixtures of homopropargyl and homoallenyl alcohols,[14] and allylations with bismuth(III) chloride promoted by aluminum in THF–water.[15] To our knowledge, prior to this report, alkylating agents for the aqueous Barbier reaction have been limited to allyl and propargyl halides.

Earlier reports[16] from our laboratory have established a versatile procedure for the two-step alkylation of amines. Initially the amine undergoes a Mannich condensation with benzotriazole and an aldehyde, yielding the 1-(aminoalkyl)benzotriazole 3; this is then alkylated with a Grignard reagent, giving the N-alkylated amine on elimination of benzotriazole. Aqueous Barbier alkylations offer advantages over this procedure in the ability to alkylate substrates not compatible with Grignard reagents such as those containing acidic hydrogens or soluble only in aqueous solutions. Such advantages are exemplified in a recent report[17] outlining the tin-promoted allylation of unprotected sugars in aqueous ethanol. Our initial investigations on aqueous alkylations applied to 1-(aminoalkyl)benzotriazoles 3, reported in an earlier communication,[18] showed that the reaction was successfully promoted by bismuth(III) chloride–aluminum in THF–water. This paper presents the results of a more detailed analysis of the scope of this reaction.

Results and Discussion

Allylation of 1-(Aminoalkyl)benzotriazoles. We commenced our investigations using 1-(aminoalkyl)-benzotriazoles 3 derived from reaction of benzotriazole with formaldehyde and a secondary amine. Although both zinc and tin proved ineffective at promoting reaction with allyl bromide under aqueous conditions, reaction with the bismuth system developed by Wada et al.,[15] using bismuth(III) chloride–aluminum at room temperature in THF–water, successfully gave the corresponding allylated amines 5 in high yields (Table I). A series of secondary aromatic amines (entries 1–3) and secondary alkylamines (entries 4–8) were converted by this method into their N-homoallylated derivatives. Interestingly, attempted allylations carried out in THF in the absence of water gave only a complex mixture of products, demonstrating the need for water in the reaction system. Similarly, aqueous allylation of a primary aliphatic amine derivative, (benzotriazol-1-ylmethyl)cyclohexanamine (3i), proceeded smoothly, giving 3-butenylcyclohexylamine (5i) in good yield (entry 9). However, alkylation of a primary aromatic amine derivative, N-(benzotriazol-1-ylmethyl)-p-methylaniline (3j), led to isolation of N-(3-butenyl)-p-methylaniline (5j; 35%), together with a byproduct, N,N-bis(3-butenyl)-p-methylaniline (6a; 30%) (entry 10). The formation of the bis(homoallyl)amine 6a from this reaction is explained by the transfer of a benzotriazolylmethyl group from unchanged 3j to the product 5j giving N-(3-butenyl)-N-(benzotriazol-1-ylmethyl)-p-methylaniline, which then reacts further to form 6a. Allylations were also successful for 1-(aminoalkyl)benzotriazoles derived from aldehydes other than formaldehyde, as shown by entries 11–13 and 23.

Allylation of 1-(Amidoalkyl)benzotriazoles. Previous work[16] has demonstrated the successful Mannich condensation of benzotriazole, an aldehyde, and a primary amide or carbamate to yield 1-(amidoalkyl)benzotriazoles. Allylation under aqueous conditions of 1-(amidoalkyl)-benzotriazoles derived from benzotriazole, benzaldehyde, and either acetamide or benzyl carbamate gave the corresponding homoallyl amide 5l or carbamate 5m in good yield (entries 12 and 13). However, alkylations were unsuccessful for 1-(amidoalkyl)benzotriazoles derived from aliphatic aldehydes or formaldehyde, presumably because dissociation to the reactive immonium cation from such amido derivatives is less favorable than for the aromatic analogues.

Propargylation of 1-(Aminoalkyl)benzotriazoles. Under the same conditions, use of the alkylating agent propargyl bromide gave isomeric mixtures of (propargylmethyl)- and (allenylmethyl)amines with both (benzotriazol-1-ylmethyl)diphenylamine (3c) and N-(benzotriazol-1-ylmethyl)-N-methylaniline (3a) (entries 14 and 15). It is not clear whether the reactive species formed in situ from propargyl bromide and Bi(0) is a dipropargylbismuth bromide or alternatively a diallenylbismuth bromide, as postulated for the tin-promoted aqueous proparylation of aldehydes.[19]

Benzylation of 1-(Aminoalkyl)benzotriazoles. To further expand the synthetic scope of this reaction, we screened a series of alkyl halides for reactivity. The first successful alkylations in aqueous media with benzylic bromides were realized under these conditions. Thus, N-methylaniline, diphenylamine, morpholine, and diisobutylamine, after conversion to their benzotriazole derivatives 3, were smoothly benzylated to give the corresponding (phenylethyl)amines (entries 16–19). Furthermore, alkylation of N-(benzotriazol-1-ylmethyl)-N-methylaniline (3a) with 1-bromo-1-phenylethane gave N-methyl-N-(2-phenylpropyl)aniline (5v) as expected (entry 20). To compare the reactivity of 1-(aminoalkyl)-benzotriazoles with aldehydes, the benzylation of benz-

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aldehyde was attempted under the same conditions, but only a complex mixture resulted. Presumably, 1-(aminoalkyl)benzotriazoles, which undergo alkylation via the more reactive immonium cation intermediates as compared to the case for aldehydes, are more able to react with less activated alkyl halides.

Methylation of 1-(Aminoalkyl)benzotriazoles. 1-(Aminoalkyl)benzotriazoles were also capable of reacting with iodomethane, as demonstrated by the two-step conversion of diphenylamine and diisopropylamine into their *N*-ethyl derivatives (entries 21 and 22). Methylation of *N*-(benzotriazol-1-ylcyclohexylmethyl)-*N*-methylaniline (**3o**) using these conditions gave *N*-(1-cyclohexylethyl)-*N*-methylaniline (**5y**), together with a byproduct, *N*-(cyclohexylmethyl)-*N*-methylaniline (**5z**), corresponding to reduction of the starting material (entry 23). However, other alkyl halides investigated such as ethyl iodide, butyl bromide, and (2-bromoethyl)benzene proved to be unreactive under these conditions.

In conclusion, we have shown that a large variety of amines on conversion to 1-(aminoalkyl)benzotriazole intermediates can be successfully alkylated in water–THF using bismuth(III) chloride–metallic aluminum. Alkylating agents used include benzyl and methyl halides hitherto unknown for the aqueous Barbier reaction.

Experimental Section

^{1}H NMR spectra were measured at 300 MHz in $CDCl_3$ unless otherwise stated, with TMS as internal reference. All *J* values are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz and were referenced to the 77.0 ppm resonance of $CDCl_3$. Mass spectra were recorded at 70 eV.

General Procedure for Preparation of 1-(Aminoalkyl)-benzotriazoles 3. Benzotriazole (1.19 g, 10 mmol), the aldehyde (10 mmol), and the amine (10 mmol) were refluxed in toluene (150 mL) for 4–5 h with azeotropic removal of water. (Preformed (hydroxymethyl)benzotriazole (1.49 g, 10 mmol) was used in preference to benzotriazole and formaldehyde.) On completion of the removal of water, the solution was cooled to room temperature and washed successively with aqueous potassium carbonate (100 mL) and water (50 mL). The solution was dried ($MgSO_4$) and the toluene removed by evaporation under reduced pressure to give the 1-(aminoalkyl)benzotriazole, which was used without further purification.

Novel 1-(aminoalkyl)benzotriazoles obtained by this method are detailed below. They exist in solution as equilibrium mixtures of the benzotriazol-1-yl and benzotriazol-2-yl isomers. Their ^{1}H NMR spectra in $CDCl_3$ solution generally show overlapping signals of the two isomers with the benzotriazol-1-yl isomer predominant, but specific assignments were achieved in the ^{13}C NMR spectra, and signals for the minor 2-isomer are given in parentheses.

***N*-(Benzotriazol-1-ylmethyl)-*N*-methyl-*p*-butylaniline (3b)**: 76% yield; mp 59–60 °C (hexane); ^{1}H NMR δ 0.91 (t, *J* = 7.3, 3 H), 1.31 (sext, *J* = 7.5, 2 H), 1.55 (quint, *J* = 7.5, 2 H), 2.52 (t, *J* = 7.5, 2 H), 2.92 (s, 3 H), 6.0 (s, 2 H), 6.9–7.3 (m, 7H), 7.8–8.0 (m, 1 H); ^{13}C NMR δ 13.8, 22.0, 33.6, 34.4, 37.3, 67.1, 110.1, 115.4, 119.4, 123.6, 127.0, 129.1, 132.4, 134.4, 145.6, 145.6 (benzotriazol-2-yl isomer 13.8, 22.1, 33.6, 34.3, 38.6, 72.7, 113.6, 118.1, 126.1, 128.9, 133.2, 144.1, 144.8). Anal. Calcd for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. Found: C, 73.78; H, 7.86; N, 19.23.

(Benzotriazol-1-ylmethyl)diisobutylamine (3e): 80% yield; oil; ^{1}H NMR δ 0.90 (d, *J* = 7, 12 H), 1.95 (nonet, *J* = 7, 2 H), 2.31 (d, *J* = 7, 4 H), 5.46 (s, 2 H), 7.3–7.6 (m, 3 H), 7.8–8.1 (m, 1 H); ^{13}C NMR δ 20.5, 26.1, 61.0, 66.7, 109.6, 119.6, 123.5, 127.1, 133.9, 145.6 (benzotriazol-2-yl isomer 20.4, 26.2, 60.6, 74.4, 118.1, 125.9, 143.9); exact mass $C_{15}H_{23}N_4$ ($M^+ - 1$, CI) requires 259.1923, found 259.1921.

(1-Benzotriazol-1-yl-2-methylpropyl)(1-phenylethyl)amine (3k): 95% yield; mp 95–99 °C (EtOAc); ^{1}H NMR δ 0.65 (d, *J* = 7, 3 H), 1.15 (d, *J* = 6.5, 3 H), 1.25 (d, *J* = 6.5, 3 H), 2.4 (m, 1 H), 3.25 (q, *J* = 7, 1 H), 4.8 (d, *J* = 8.5, 1 H), 7.1–8.1 (m, 10 H); ^{13}C NMR δ 18.6, 19.4, 24.8, 34.4, 54.2, 77.5, 109.6, 119.7, 123.7, 126.8, 127.0, 127.2, 128.3, 133.6, 143.5, 145.4 (benzotriazol-2-yl isomer 18.4, 18.9, 24.9, 34.6, 54.3, 84.8, 118.1, 125.8, 126.2, 127.0, 128.3, 143.6, 143.8). Anal. Calcd for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. Found: C, 73.46; H, 7.53; N, 19.22.

(Benzotriazol-1-ylmethyl)diisopropylamine (3n): 85% yield; an oil which decomposes on standing; peak coalescence broadening is observed in the NMR spectra at room temperature; ^{1}H NMR (DMSO-d_6 at 50 °C) δ 1.05 (d, *J* = 6.6, 12 H), 3.25 (sept, *J* = 6.6, 2 H), 5.63 (s, 2 H), 7.3–7.4 (m, 2 H), 7.9–8.0 (m, 2 H); ^{13}C NMR ($CDCl_3$ at −20 °C) δ 20.4, 46.9, 61.3, 110.7, 118.8, 123.2, 126.3, 132.1, 145.7 (benzotriazol-2-yl isomer 20.5, 48.0, 68.5, 117.5, 125.5, 143.5).

***N*-(Benzotriazol-1-ylcyclohexylmethyl)-*N*-methylaniline (3o)**: 75% yield; mp 93–96 °C (hexane/EtOAc); ^{1}H NMR δ 0.85–2.20 (m, 10 H), 2.83 (s, 3 H), 2.95–3.10 (m, 1 H), 6.04 (d, *J* = 10.5, 1 H), 6.8–7.4 (m, 8 H), 7.8–8.1 (m, 1 H); ^{13}C NMR δ 25.4, 25.8, 26.2, 29.3, 29.9, 31.5, 38.6, 80.1, 109.8, 116.0, 119.0, 119.9, 123.7, 127.0, 129.3, 133.8, 145.5, 149.9 (benzotriazol-2-yl isomer 25.3, 25.6, 26.1, 29.4, 29.9, 32.3, 40.1, 85.0, 114.7, 118.2, 119.5, 126.1, 129.1, 143.5, 149.5). Anal. Calcd for $C_{20}H_{24}N_4$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.92; H, 7.66; N, 17.59.

Alkylation of *N*-(Alkylamino)benzotriazoles: General Procedure. Water (1.0 mL) was added cautiously to an ice-cooled mixture of aluminum powder (0.13 g, 4.8 mmol) and bismuth trichloride (0.756 g, 2.4 mmol) stirred in THF (2.5 mL) under N_2. After the resulting exothermic reaction had subsided, the alkyl bromide or iodide **4** (2.4 mmol) was added to the solution at 0 °C and stirring continued for a further 10 min. The benzotriazole derivative **3** (1.2 mmol) was then added and the reaction mixture stirred overnight. The inorganic byproduct was filtered off and washed with chloroform (4 × 5 mL). The combined chloroform–THF solutions were then washed with aqueous sodium bicarbonate (10 mL) to remove benzotriazole and dried over magnesium sulfate. Evaporation of the solvent gave the homoallylic amine **5** as an oil (see Table I) generally with no further purification necessary as indicated by TLC and NMR methods. When purification was required, or if separation of two products was needed, the crude product was subjected to flash column chromatography over basic alumina eluted with hexane for aliphatic amines and silica gel eluted with hexane–chloroform (9:1) for aromatic amines.

The following amines were confirmed by comparison with their previously reported physical and spectral properties: *N*-(3-butenyl)-*N*-methylaniline (**5a**),[20] (3-butenyl)dibutylamine (**5d**),[21] *N*-(3-butenyl)morpholine (**5f**),[22] *N*-(3-butenyl)piperidine (**5h**),[23] (3-butenyl)cyclohexylamine (**5i**),[24] *N*-methyl-*N*-(2-phenylethyl)-aniline (**5r**),[25] (2-phenylethyl)diphenylamine (**5s**),[26] *N*-(2-phenylethyl)morpholine (**5t**),[27] (2-phenylethyl)diisobutylamine (**5u**),[28] ethyldiphenylamine (**5w**),[29] ethyldiisopropylamine (Huenig's base; **5x**),[30] and *N*-(cyclohexylmethyl)-*N*-methylaniline (**5z**).[31] Novel amines and amides obtained by this method are detailed below.

***N*-(3-Butenyl)-*N*-methyl-4-butylaniline (5b)**: oil; ^{1}H NMR δ 0.94 (t, *J* = 7, 3 H), 1.36 (m, 2 H), 1.56 (m, 2 H), 2.31 (q, *J* = 8, 2 H), 2.50 (t, *J* = 7, 2 H), 2.87 (s, 3 H), 3.33 (t, *J* = 8, 2 H), 5.00–5.10 (m, 2 H), 5.75–5.90 (m, 1 H), 6.61–6.65 (d, *J* = 8.8, 2 H), 7.01–7.04 (d, *J* = 8.8, 2 H); ^{13}C NMR δ 13.9, 22.3, 31.0, 33.9,

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34.5, 38.3, 52.6, 112.4, 116.1, 129.0, 130.5, 136.0, 147.2; exact mass $C_{15}H_{22}N$ ($M^+ - 1$) requires 216.1752, found 216.1751.

(3-Butenyl)diphenylamine (5c): oil; ^1H NMR δ 2.39 (q, J = 8, 2 H), 3.75 (t, J = 8, 2 H), 5.00–5.09 (m, 2 H), 5.75–5.86 (m, 1 H), 6.90–7.10 (m, 6 H), 7.20–7.30 (m, 4 H); ^{13}C NMR δ 31.6, 51.4, 116.4, 120.8, 121.2, 129.2, 135.4, 147.7; exact mass $C_{16}H_{18}N$ (M^+ + 1, CI) requires 224.1439, found 224.1429.

(3-Butenyl)diisobutylamine (5e): oil; ^1H NMR δ 0.87 (d, J = 7, 12 H), 1.68 (nonet, J = 7, 2 H), 2.07 (d, J = 7, 4 H), 2.12–2.19 (m, 2H), 2.41 (t, J = 7, 2 H), 4.93–5.04 (m, 2 H), 5.77–5.86 (m, 1 H); ^{13}C NMR δ 20.9, 26.7, 31.7, 54.9, 63.9, 115.0, 137.6; exact mass $C_{12}H_{26}N$ (M^+ + 1, CI) requires 184.2065, found 184.2069.

***N*-(3-Butenyl)pyrrolidine (5g)**: oil; ^1H NMR δ 1.75–1.85 (m, 4 H), 2.25–2.35 (m, 2 H), 2.48–2.57 (m, 6 H), 4.95–5.10 (m, 2 H), 5.76–5.90 (m, 1 H); ^{13}C NMR δ 23.3, 33.4, 54.1, 55.9, 115.5, 136.7; exact mass $C_8H_{16}N$ (M^+ + 1, CI) requires 126.1283, found 126.1284.

***N*-(3-Butenyl)-*p*-methylaniline (5j)**: oil, ^1H NMR δ 2.23 (s, 3 H), 2.37 (q, J = 7, 2 H), 3.17 (t, J = 7, 2 H), 3.5 (bs, 1 H), 5.06–5.17 (m, 2 H), 5.77–5.83 (m, 1 H), 6.54 (d, J = 8.5, 2 H), 6.98 (d, J = 8.5, 2 H); ^{13}C NMR δ 20.4, 33.7, 43.2, 113.1, 117.0, 126.6, 129.7, 135.8, 146.0; exact mass $C_{11}H_{15}N$ requires 161.1204, found 161.1201.

5-Methyl-4-((1-phenylethyl)amino)-1-hexene (5k): oil as a mixture of diastereoisomers (1:1); partial separation of the diastereoisomers was achieved by column chromatography; ^1H NMR δ 0.71 (d, J = 7, 3 H), 0.77 (d, J = 7, 3 H), 1.12–1.20 (bs, 1 H), 1.22 (d, J = 6.6, 3 H), 1.45–1.55 (m, 1 H), 2.05–2.20 (m, 3 H), 3.79 (q, J = 6.6, 1 H), 4.91–5.02 (m, 2 H), 5.64–5.78 (m, 1 H), 7.09–7.26 (m, 5 H); ^{13}C NMR δ 18.3, 18.9, 24.9, 30.4, 34.8, 55.4, 59.4, 116.6, 126.6, 126.8, 128.1, 136.2, 146.4 (non-overlapping signals for the second diastereoisomer: 17.0, 24.9, 29.1, 55.1, 58.5, 116.7, 128.2, 137.0, 146.3); exact mass $C_{15}H_{24}N$ (M^+ + 1, CI) requires 218.1909, found 218.1913.

***N*-(1-Phenyl-3-butenyl)acetamide (5l)**: oil; ^1H NMR δ 2.0 (s, 3 H), 2.57 (t, J = 7, 2 H), 5.05–5.17 (m, 3 H), 5.63–5.74 (m, 1 H), 5.78 (bs, 1 H), 7.25–7.38 (m, 5 H); ^{13}C NMR δ 23.3, 40.4, 52.4, 118.1, 126.4, 127.3, 128.5, 133.9, 141.6, 169.2; exact mass $C_{12}H_{16}NO$ (M^+ + 1, CI) requires 190.1232, found 190.1252.

Benzyl *N*-(1-phenyl-3-butenyl)carbamate (5m): oil; ^1H NMR δ 2.45–2.60 (m, 2 H), 4.80 (bs, 1 H), 5.00–5.20 (m, 5 H), 5.60–5.85 (m, 1 H), 7.20–7.45 (m, 10 H); ^{13}C NMR δ 41.0, 54.5, 66.8, 118.4, 128.1, 125.8, 126.2, 127.4, 128.4, 128.5, 128.5, 133.7, 136.4, 156.0; exact mass $C_{18}H_{20}NO_2$ (M^+ + 1, CI) requires 282.1494, found 282.1497.

(3-Butynyl)diphenylamine (5n): oil; ^1H NMR δ 1.99 (t, J = 2.5, 1 H), 2.53 (td, J = 8 and 2.5, 2 H), 3.92 (t, J = 8, 2 H), 6.92–7.01 (m, 6 H), 7.20–7.30 (m, 4 H); ^{13}C NMR δ 17.3, 51.0, 69.9, 81.8, 120.9, 121.6, 129.4, 147.2; exact mass $C_{16}H_{15}N$ requires 221.1204, found 221.1203.

(2,3-Butadienyl)diphenylamine (5o): oil; ^1H NMR δ 4.35 (dt, J = 6 and 3, 2 H), 4.74 (dt, J = 6 and 3, 2 H), 5.22 (quint, J = 6, 1 H), 6.91–7.04 (m, 6 H), 7.20–7.28 (m, 4 H); ^{13}C NMR δ 50.9, 76.4, 87.1, 121.0, 121.4, 129.2, 147.6, 209.0; exact mass $C_{16}H_{15}N$ requires 221.1204, found 221.1209.

***N*-(3-Butynyl)-*N*-methylaniline (5p)**: obtained as an oil in a 4:3 mixture with *N*-(2,3-butadienyl)-*N*-methylaniline (**5q**), which was inseparable by chromatography; all NMR signals were assignable except overlapping aromatic signals in the ^1H NMR spectrum; ^1H NMR δ 1.99 (t, J = 3, 1 H), 2.42 (td, J = 8 and 3, 2 H), 2.96 (s, 3 H), 3.55 (t, J = 8, 2 H), 6.92–7.01 (m, 3 H), 7.20–7.30 (m, 2 H); ^{13}C NMR δ 16.4, 38.4, 51.7, 69.6, 82.1, 112.2, 116.6, 129.2, 148.4; for the mixture of isomers exact mass $C_8H_{13}N$ requires 159.1048, found 159.1045.

***N*-(2,3-Butadienyl)-*N*-methylaniline (5q)**: oil obtained as 3:4 mixture with *N*-(3-butynyl)-*N*-methylaniline (**5p**) inseparable by chromatography; ^1H NMR δ 2.92 (s, 3 H), 3.96 (dt, J = 6 and 3, 2 H), 4.73 (dt, J = 6 and 3, 2 H), 5.13 (quint, J = 6, 1 H), 6.91–7.04 (m, 3 H), 7.20–7.28 (m, 2 H); ^{13}C NMR δ 38.0, 51.5, 75.8, 86.0, 112.9, 116.7, 129.1, 149.0, 209.0.

***N*-(2-Phenylpropyl)-*N*-methylaniline (5v)**: oil; ^1H NMR δ 1.29 (d, J = 7, 3 H), 2.74 (s, 3 H), 3.20 (sext, J = 7, 1 H), 3.37 (dd, J = 7.7 and 14.6, 1 H), 3.48 (dd, J = 7 and 14.6, 1 H), 6.63–6.72 (m, 3 H), 7.18–7.34 (m, 7 H); ^{13}C NMR δ 18.8, 38.3, 39.5, 61.0, 111.7, 115.7, 126.3, 127.2, 128.4, 129.1, 145.1, 149.0; exact mass $C_{16}H_{19}N$ requires 225.1517, found 225.1514.

***N*-(1-Cyclohexylethyl)-*N*-methylaniline (5y)**: obtained as an oil in a 2:1 mixture with *N*-(cyclohexylmethyl)-*N*-methylaniline (**5z**) inseparable by chromatography; NMR signals were assigned by comparison with the NMR spectra of *N*-(cyclohexylmethyl)-*N*-methylaniline (**5z**) obtained by sodium borohydride reduction of *N*-(benzotriazol-1-ylcyclohexylmethyl)-*N*-methylaniline (**3o**); ^1H NMR δ 0.80–1.05 (m, 2 H), 1.09 (d, J = 6.6, 3 H), 1.15–1.83 (m, 9 H), 2.69 (s, 3 H), 3.49–3.57 (m, 1 H), 6.61–6.75 (m 3 H), 7.17–7.23 (m, 2 H); ^{13}C NMR δ 14.8, 26.2, 26.3, 26.4, 30.4, 30.6, 30.8, 41.9, 58.5, 111.6, 115.4, 129.0, 149.5; exact mass $C_{15}H_{23}N$ requires 217.1830, found 217.1831.

***N*-(Cyclohexylmethyl)-*N*-methylaniline (5z).** Sodium borohydride (0.094 g, 2.5 mmol) was added to a stirred solution of *N*-(benzotriazol-1-ylcyclohexylmethyl)-*N*-methylaniline (**3o**; 0.528 g, 1.65 mmol) in dry THF (15 mL) and the reaction mixture stirred at room temperature overnight. The reaction was quenched with ice–water (10 mL), the product extracted with ether (20 mL), and the extract dried ($MgSO_4$) and evaporated under reduced pressure to give *N*-(cyclohexylmethyl)-*N*-methylaniline[31] (0.090 g, 27% yield) as an oil.

***N*,*N*-Bis(3-butenyl)-*p*-methylaniline (6a)**: oil; ^1H NMR δ 2.24 (s, 3 H), 2.32 (q, J = 8, 4 H), 3.33 (t, J = 8, 4 H), 5.02–5.13 (m, 4 H), 5.78–5.88 (m, 2 H), 6.61 (d, J = 8, 2 H), 7.02 (d, J = 8, 2 H); ^{13}C NMR δ 20.1, 31.7, 50.8, 112.4, 116.2, 125.0, 129.8, 136.0, 145.6; exact mass $C_{15}H_{21}N$ requires 215.1669, found 215.1674.

Registry No. **1a**, 100-61-8; **1b**, 137273-36-0; **1c**, 122-39-4; **1d**, 111-92-2; **1e**, 110-96-3; **1f**, 110-91-8; **1g**, 123-75-1; **1h**, 110-89-4; **1i**, 108-91-8; **1j**, 106-49-0; **1k**, 98-84-0; **1l**, 60-35-5; **1m**, 621-84-1; **1n**, 108-18-9; **2a**, 50-00-0; **2k**, 78-84-2; **2l**, 100-52-7; **2o**, 2043-61-0; **3a**, 15497-51-5; **3b**, 137273-37-1; **3b** (2 isomer), 138723-77-0; **3c**, 15497-48-0; **3d**, 15497-45-7; **3e**, 137273-38-2; **3e** (2 isomer), 138723-78-1; **3f**, 5472-71-9; **3g**, 19213-23-1; **3h**, 15622-20-5; **3i**, 126541-65-9; **3j**, 62001-37-0; **3k**, 138723-68-9; **3k** (2 isomer), 138723-74-7; **3l**, 119020-88-1; **3m**, 125453-15-8; **3n**, 138723-69-0; **3n** (2 isomer), 138723-75-8; **3o**, 138723-70-3; **3o** (2 isomer), 138723-76-9; **5a**, 13424-22-1; **5b**, 137273-30-4; **4** (X = Br, R^4 = $CH_2CH{=}CH_2$), 106-95-6; **4** (X = Br, R^4 = $CH_2C{\equiv}CH$), 106-96-7; **4** (X = Br, R^4 = CH_2Ph), 100-39-0; **4** (X = Br, R^4 = CH(Me)Ph), 585-71-7; **4** (X = I, R^4 = Me), 74-88-4; **5c**, 50965-59-8; **5d**, 108144-23-6; **5e**, 137273-31-5; **5f**, 10315-96-5; **5g**, 7255-63-2; **5h**, 4088-34-0; **5i**, 61907-83-3; **5j**, 137273-32-6; (*R**,*R**)-**5k**, 138810-13-6; (*R**,*S**)-**5k**, 138810-14-7; **5l**, 126525-24-4; **5m**, 138723-71-4; **5n**, 137273-34-8; **5o**, 137273-35-9; **5p**, 137273-33-7; **5q**, 131467-47-5; **5r**, 28059-49-6; **5s**, 115419-49-3; **5t**, 46346-12-7; **5u**, 23911-69-5; **5v**, 138723-72-5; **5w**, 606-99-5; **5x**, 7087-68-5; **5y**, 138723-73-6; **5z**, 23824-51-3; Al, 7429-90-5; $BiCl_3$, 7787-60-2; benzotriazole, 95-14-7.