Synthesis of Homoallylamines by the Addition of Allylic Indium Reagents to Azomethines and Nitriles

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Triallyldiindium trihalides and allylindate(1-)s reacted with *N*-benzylideneamines regioselectively at the C-3 carbon on the allyl group to give high yields of homoallylic secondary amines. Primary amines were obtained by the action of an excess of allylic indates on aromatic nitriles.

The addition of allylic organometallics to azomethines and nitriles is an important synthetic method for the preparation of homoallylic amines. Earlier methods mostly suffer from low yields and low regioselectivity.[1] Much attention was recently focused on the regio- and stereocontrol of this reaction, which have been constantly improved over the years by changing the metal in allylmetallics from magnesium over lithium, zinc, aluminum to boron and tin.[2]

We reported on the addition of triallyldiindium trihalides (allylindium sesquihalides) to aldehydes,[3a] ketones,[3a] acid anhydrides,[3b] imides,[3c] and quinones.[3d] Recently allylic indate(1-)s, which can be readily derived from allylic indium sesquihalides, were found to have enhanced reactivity to couple with allylic halides regio- and stereospecifically giving high yields of head-to-tail 1,5-dienes.[4] This paper describes the reaction of these allylic indium reagents with azomethines, which affords homoallylic amines in good yields. The reaction of allylic indate(1-)s with nitriles is also described.

Results and Discussion

1. Reactions of Triallyldiindium Trihalides. Triallyldiindium tribromides (allylindium sesquibromide), prepared from indium powder and allyl bromide, was allowed to react with *N*-benzylideneaniline in dioxane at room temperature for 24 h. Chromatographic separation yielded *N*-(1-phenyl-3-butenyl)aniline (**1**) in 84% yield. A small amount (6%) of the starting *N*-benzylideneaniline was recovered. Results for other allylic indium sesquihalides and azomethines are summarized in Table 1. Both indium sesquibromide and sesquiiodide afforded high yields (Entries 1 and 2). 2-Butenyl- and 2-pentenylindium sesquibromides reacted selectively at the C-3 carbon on the allyl group giving mixtures of two diastereomers (Scheme 1). The assignment of the *erythro*/*threo* isomers was made based on the ^{1}H NMR analysis.[2b] Unfortunately, the diastereoselectivity was only modest. The allylation of *N*-benzylideneaniline in DMF and in dioxane gave the same secondary amine **1** (Entries 1 and 3). However, allylation of *N*-benzylidenemethylamine in DMF and in dioxane gave different products. When the reaction was carried out in dioxane, expected homoallylamine **4** was obtained (Entry 6), whereas in DMF corresponding formamide **5** was formed exclusively (Entry 7). The allylation of *N*-benzylidenemethylamine in DMF also gave formamide **6** (Entry 8). The formation of these formamides **5** and **6** could be rationalized by Scheme 2. Indium *N*-alkylhomoallylamides **A**, formed by the allylation of *N*-benzylidenealkylamines react further with DMF to give **5** and **6**. The intermediate from *N*-benzylideneaniline, i.e., indium *N*-phenylhomoallylamide, is less nucleophilic than *N*-alkylhomoallylamides **A** so that amine was the product for Entries 1—5. An excess allylindium sesquibromide reacted with ethyl *N*-phenylformimidate to give *N*-(1-allyl-3-butenyl)aniline (**7**) in 74% yield (Entry 9).

2. Reactions of Allylindate(1-)s. Reaction of *N*-benzylideneaniline with allylindate(1-) in dioxane at room temperature for 2 h gave *N*-(1-phenyl-3-butenyl)-aniline (**1**) in 91% yield. Results for other allylic indates and azomethines are summarized in Table 2. Both *N*-benzylidenemethylamine and *N*-benzylideneaniline reacted smoothly to afford the corresponding homoallylic secondary amines in good yields. Substituted allylic indates added to azomethines regioselectively at the C-3 carbon on the allyl group, but the diastereoselectivities were again not good (Entries 2, 3, and 4). With a catalytic amount of CuI, the *erythro*: *threo* ratio was slightly improved (Entry 5).

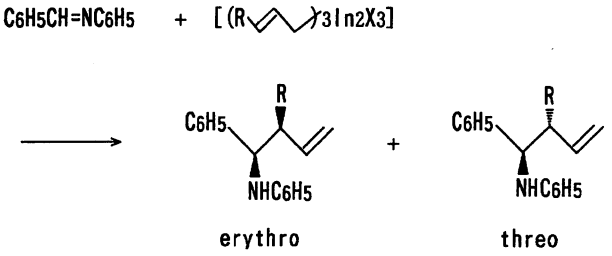
Primary amines were obtained by the action of allylic indates on aromatic nitriles (Scheme 3). However, when aliphatic nitriles such as octanenitrile were used no allylation products were obtained, but the starting aliphatic nitriles were recovered. Octanenitrile-2-*d* was obtained in 83% yield upon quenching a reaction mixture of allylindate and octanenitrile with D_2O (Scheme 4). The basicity of allylindate is strong enough to abstract an α-hydrogen of the octanenitrile to give the corresponding carbanion.

Attempted alkylation of azomethines and nitriles by tetraalkylindate(1-)s,[4] prepared by the addition of alkyllithium to trialkyl- or triphenylindium, was unsuccessful owing to the low reactivity of tetraalkylindate-(1-)s. The reaction of allylic indium sesquihalides with azomethines required longer reaction time (20—40 h) than the reaction of allylic indates. The enhanced utility of allylic indates was also demonstrated by the fact

Table 1. Addition of Allylic Indium Sesquihailides to Azomethines

Entry	Indium sesquilhalide	Solvent	Azomethine	Product	Yield[a]/%
1	$(\text{allyl})_3In_2Br_3$	DMF	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH(CH_2CH{=}CH_2)-NH-C_6H_5$ (**1**)	84
2	$(\text{allyl})_3In_2I_3$	DMF	$C_6H_5CH{=}NC_6H_5$	**1**	82
3	$(\text{allyl})_3In_2Br_3$	Dioxane	$C_6H_5CH{=}NC_6H_5$	**1**	79
4	$(\text{crotyl})_3In_2Br_3$	DMF	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH(CH_3CH{=}CH_2)-NH-C_6H_5$ (**2**)	69[b]
5	$(\text{2-butenyl})_3In_2Br_3$	DMF	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH(CH_3CH_2CH{=}CH_2)-NH-C_6H_5$ (**3**)	78[c]
6	$(\text{allyl})_3In_2Br_3$	Dioxane	$C_6H_5CH{=}N-CH_3$	$C_6H_5CH(CH_2CH{=}CH_2)-NH-CH_3$ (**4**)	94
7	$(\text{allyl})_3In_2Br_3$	DMF	$C_6H_5CH{=}N-CH_3$	$C_6H_5CH(CH_2CH{=}CH_2)-N(CHO)-CH_3$ (**5**)	98
8	$(\text{allyl})_3In_2Br_3$	DMF	$C_6H_5CH{=}N-CH_2C_6H_5$	$C_6H_5CH(CH_2CH{=}CH_2)-N(CHO)-CH_2C_6H_5$ (**6**)	97
9	$(\text{allyl})_3In_2Br_3$	DMF	$C_2H_5O-CH{=}N-C_6H_5$	$(CH_2{=}CH-CH_2)_2CH-NH-C_6H_5$ (**7**)	74

a) Isolated yield based on azomethine. b) *erythro*: *threo* = 55 : 45 (determined by ^{1}H NMR). c) *erythro*: *threo* = 65 : 35 (determined by ^{1}H NMR).



Scheme 1.

that allylic indium sesquihalides did not react with nitriles, in contrast to the smooth reaction of allylindates.

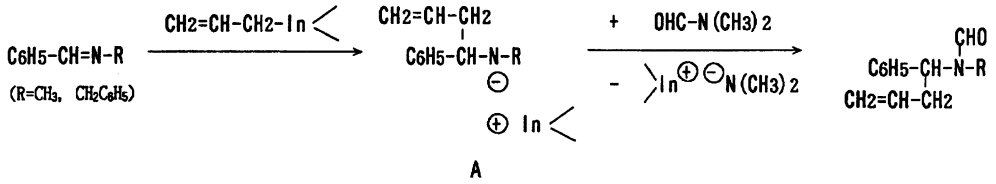
In conclusion, the reactions of allylic indium reagents with azomethines and nitriles gave good yields of homoallylic amines with high γ-regioselectivity. Though the stereoselectivity is not high, easy accessibility to the allylic indium reagents, the high yields, and the mild reaction conditions make the present reactions convenient and useful for the synthesis of homoallylic amines.

Experimental

General Infrared (IR) spectra were recorded on a JASCO A-102 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a Varian XL-200 (200 MHz) spectrometer with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Varian XL-200 (50 MHz) spectrometer. Mass spectra (MS) were recorded on a Hitachi M-2000 instrument with electron impact ionization at 70 eV using a direct inlet system. DMF was distilled from CaH_2 under vacuum and stored over CaH_2. Dioxane was distilled from Na. All reactions were conducted under argon.

Allylation of Azomethines with Allylic Indium Sesquihalides. The following allylation of *N*-benzylideneaniline represents the typical procedure. To a stirred solution of allylindium sesquibromide, prepared from indium powder (230 mg, 2 mmol) and allyl bromide (363 mg, 3 mmol) in dioxane (2 ml) at room temperature for 40 min, was added *N*-benzylideneaniline (290 mg, 1.6 mmol). The mixture was stirred at room temperature for 24 h. Water was added and the product was extracted with ether. The extracts were washed with water and brine, and dried (Na_2SO_4). Evaporation of the solvent and column chromatography on silica gel (hexane : CH_2Cl_2 = 1 : 1) afforded *N*-(1-phenyl-3-butenyl)aniline (**1**) (300 mg, 84%) along with recovered *N*-benzylideneaniline (18 mg, 6%).

***N*-(1-Phenyl-3-butenyl)aniline**[5] **(1).** Colorless oil; IR (neat) 3415, 3085, 3050, 3035, 2920, 2850, 1638, 1600, 1505, 1374, 1318, 1179, 1025, 993, 870, 748, and 690 cm^{-1}; ^{1}H NMR δ = 2.40—2.70 (2H, m, CH_2), 4.10—4.24 (1H, m, NH), 4.35—4.46 (1H, m, CH), 5.12—5.28 (2H, m, olefinic), 5.67—5.91 (1H, m, olefinic), 6.51 (2H, d, J = 8 Hz, Ph), 6.66 (1H, t, J = 8 Hz, Ph), 7.11 (2H, t, J = 8 Hz, Ph), and 7.20—7.40 (5H, m, Ph); ^{13}C NMR δ = 43.2 (t), 57.0 (d), 113.3 (t), 117.2 (d), 118.2 (d), 126.1 (d), 126.8 (d), 128.4 (d), 128.9 (d), 134.5 (d), 143.4 (s), and 147.2 (s); MS (70 eV) m/z (rel



Scheme 2.

Table 2. Addition of Allylic Indates to Azomethines

	Entry Indate	Azomethine	Product	*erythro* : *threo* ratio[a]	Yield[b]/%
1	$[(\text{allyl})_n\text{Me}_{4-n}\text{In}]^-\text{Li}^+$ (n=1,2)	$C_6H_5CH{=}N{-}C_6H_5$	**1**	—	91
2	$[(\text{crotyl})_n\text{Me}_{4-n}\text{In}]^-\text{Li}^+$ (n=1,2)	$C_6H_5CH{=}N{-}C_6H_5$	**2**	40 : 60	84
3	$[(\text{crotyl})_n\text{Me}_{4-n}\text{In}]^-\text{Li}^+$ (n=1,2)	$C_6H_5CH{=}N{-}CH_3$	$C_6H_5CH(CH_3{-}CH{-}CH{=}CH_2){-}NH{-}CH_3$ (**8**)	50 : 50	82
4	$[(\text{prenyl})_n\text{Me}_{4-n}\text{In}]^-\text{Li}^+$ (n=1,2)	$C_6H_5CH{=}N{-}CH_3$	$C_6H_5CH(CH_3CH_2{-}CH{-}CH{=}CH_2){-}NH{-}CH_3$ (**9**)	55 : 45	81
5[c]	$[(\text{prenyl})_n\text{Me}_{4-n}\text{In}]^-\text{Li}^+$ (n=1,2)	$C_6H_5CH{=}N{-}CH_3$	**9**	70 : 30	74

a) Determined by ^{1}H NMR. b) Isolated yield based on azomethine. c) With 10 mol% of CuI.

intensity) 223 (M^+ ; 12) and 182 (100).

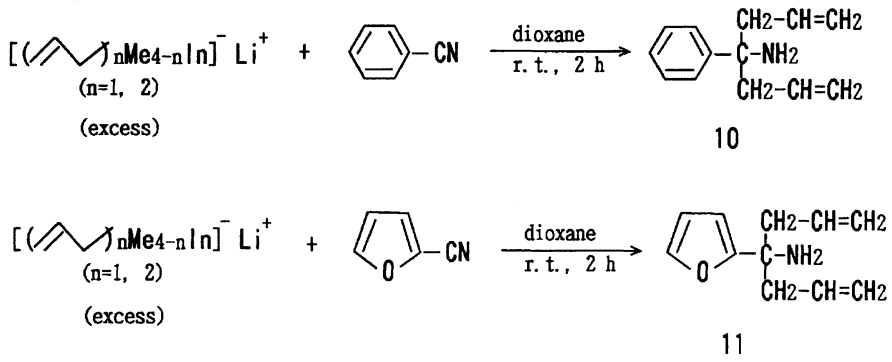
***N*-(2-Methyl-1-phenyl-3-butenyl)aniline**[2b] **(2).** Colorless oil; IR (neat) 3420, 3110, 3030, 2970, 2930, 2880, 1635, 1600, 1582, 1502, 1445, 1355, 1315, 1136, 1005, 992, 875, 750, 703 and 695 cm^{-1}; ^{1}H NMR δ=1.01 and 1.05 (3H, d, J=7 Hz, CH_3), 2.50—2.82 (1H, m, CH), 4.12 (*threo*) and 4.39 (*erythro*) [1H, d, J=7 Hz (*threo*) and J=4 Hz (*erythro*), CH], 4.22—4.32 (1H, m, NH), 5.14—5.32 (2H, m, olefinic), 5.70—5.94 (1H, m, olefinic), 6.52 (2H, d, J=8 Hz, Ph), 6.66 (1H, t, J=8 Hz, Ph), 7.06—7.18 (2H, m, Ph), and 7.22—7.50 (5H, m, Ph); ^{13}C NMR δ=15.2 (q), 17.2 (q), 43.7 (d), 45.2 (d), 61.2 (d), 62.2 (d), 113.2 (d), 113.3 (d), 115.8 (t), 116.1 (t), 117.0 (d), 126.8 (d), 126.9 (d), 127.1 (d), 127.2 (d), 127.4 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.9 (d), 140.2 (d), 140.4 (d), 140.9 (s), 142.5 (s), 147.1 (s), and 147.5 (s); MS (70 eV) m/z (rel intensity) 237 (M^+, 9) and 182 (100).

***N*-(2-Ethyl-1-phenyl-3-butenyl)aniline**[1c] **(3).** Colorless oil; IR (neat) 3420, 3060, 3030, 2970, 2930, 2880, 2860, 1630, 1600, 1582, 1502, 1450, 1353, 1317, 1138, 1008, 869, 745, 705, and 690 cm^{-1}; ^{1}H NMR δ=0.85 (3H, t, J=7 Hz, CH_3), 1.17—1.28 (2H, m, CH_2), 2.14—2.46 (1H, m, CH), 4.10 (*threo*) and 4.41 (*erythro*) [1H, d, J=8 Hz (*threo*) and J=4 Hz, (*erythro*), CH], 4.28—4.42 (1H, m, NH), 5.12—5.30 (2H, m, olefinic), 5.40—5.72 (1H, m, olefinic), 6.48 (2H, d, J=8 Hz, Ph), 6.60 (1H, t, J=8 Hz, Ph), 7.60 (2H, t, J=8 Hz, Ph), and 7.18—7.40 (5H, m, Ph); ^{13}C NMR δ=12.0 (q), 15.2 (q), 23.9 (t), 29.6 (t), 52.2 (d), 53.3 (d), 60.1 (d), 60.8 (d), 113.1 (d), 113.3 (d), 116.9 (d), 117.0 (d), 117.7 (t), 117.8 (t), 126.8 (d), 127.2 (d), 127.6 (d), 127.7 (d), 127.9 (d), 128.2 (d), 128.8 (d), 128.9 (d), 138.1 (d), 139.0 (d), 140.6 (s), 142.9 (s), 146.8 (s), and 147.5 (s); MS (70 eV) m/z (rel intensity) 251 (M^+, 32), 220 (4), and 182 (100).

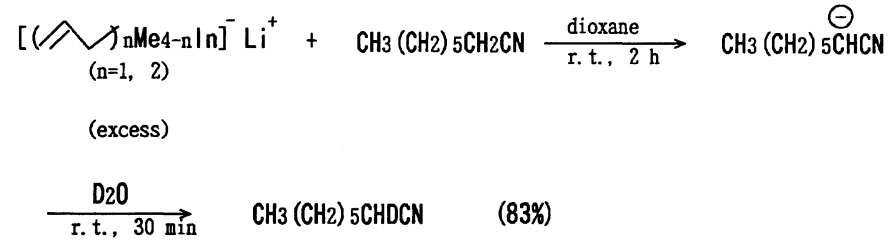
Preparation of *N*,*N*-Disubstituted Formamides. The following reaction of *N*-benzylidenemetylamine represents the typical procedure. To a stirred solution of allylindium sesquibromide, prepared from indium powder (230 mg, 2 mmol) and allyl bromide (363 mg, 2 mmol) in DMF (2 ml) at room temperature for 40 min, was added *N*-benzylidenemethylamine (190 mg, 1.6 mmol). The mixture was stirred at room temperature for 24 h. Water was added and the product was extracted with ether. The extracts were washed with water and brine, and dried (Na_2SO_4). Evaporation of the solvent and vacuum distillation [bp 150 °C/3 Torr (1 Torr=133.322 Pa), bath temperature] gave *N*-methyl-*N*-(1-phenyl-3-butenyl)formamide (**5**) (297 mg, 98%).

***N*-Methyl-*N*-(1-phenyl-3-butenyl)formamide (5).** Colorless oil; IR (neat) 3455, 3085, 3045, 2985, 2935, 2870, 1660, 1495, 1420, 1400, 1385, 1320, 1245, 750, and 733 cm^{-1}; ^{1}H NMR δ=2.65 and 2.68 (3H, s, CH_3), 2.68—2.94 (2H, m, CH_2), 4.62—4.74 and 5.68—5.96 (2H, m, CH and olefinic), 5.08—5.32 (2H, m, olefinic), 7.25—7.56 (5H, m, Ph), 8.17 and 8.37 (1H, s, CHO); ^{13}C NMR δ=25.7 (q), 29.4 (q), 33.3 (t), 34.4 (t), 52.7 (d), 60.9 (d), 117.3 (t), 118.5 (t), 126.9 (d), 127.5 (d), 127.6 (d), 127.8 (d), 128.3 (d), 128.5 (d), 133.3 (d), 134.1 (d), 137.9 (s), 138.0 (s), 162.5 (d), and 162.8 (d); MS (70 eV) m/z (rel intensity) 189 (M^+, 2) and 148 (100). Found: C, 75.91; H, 8.15; N, 7.29%. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40%.

***N*-Benzyl-*N*-(1-phenyl-3-butenyl)formamide (6).** Colorless oil; IR (neat) 3070, 3040, 2925, 2860, 1662, 1495, 1405, 760, 740, and 702 cm^{-1}; ^{1}H NMR δ=2.40—2.80 (2H, m, CH_2), 4.04—4.60 (3H, m, CH–N–CH_2), 4.92—5.15 (2H, m, olefinic), 5.49—5.84 (1H, m, olefinic), 7.04—7.50 (10H, m, Ph), 8.36 and 8.56 (1H, s, CHO); ^{13}C NMR δ=34.9 (t), 37.0 (t), 45.1 (t), 48.5 (t), 55.2 (d), 61.4 (d), 117.3 (t), 118.4 (t), 126.6 (d), 126.9 (d), 127.1 (d), 127.2 (d), 127.6 (d),



Scheme 3.



Scheme 4.

127.7 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.6 (d), 133.4 (d), 134.4 (d), 136.8 (s), 137.0 (s), 138.5 (s), 162.5 (d), and 163.4 (d); MS (70 eV) *m/z* (rel intensity) 265 (M^+, 9), 196 (95), 174 (12), 134 (37), 116 (16), 104 (40), and 91 (100). Found C, 81.27; H, 7.22; N, 5.25%. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28%.

Allylation of Ethyl *N*-Phenylformimidate with Allylindium Sesquibromide. To a stirred solution of allylindium sesquibromide, prepared from indium powder (459 mg, 4 mmol) and allyl bromide (726 mg, 6 mmol) in DMF (2 ml) at room temperature for 40 min, was added ethyl *N*-phenylformimidate (238 mg, 1.6 mmol). The mixture was stirred at room temperature for 2 h. Water was added and the product was extracted with ether. The extracts were washed with water and brine, and dried (Na_2SO_4). Evaporation of the solvent and vacuum distillation (bp 130 °C/10 Torr, bath temperature) gave *N*-(1-allyl-3-butenyl)-aniline (**7**) (220 mg, 1.2 mmol).

***N*-(1-Allyl-3-butenyl)aniline[1c] (7).** Colorless oil; IR (neat) 3405, 3075, 3000, 2975, 2915, 1638, 1600, 1502, 1430, 750, and 690 cm^{-1}; ^1H NMR δ=2.32 (4H, t, J=7 Hz CH_2), 3.25—3.50 (1H, m, NH), 3.44—3.57 (1H, m, CH), 5.15 (2H, d, J=17 Hz, olefinic), 5.16 (2H, d, J=4 Hz, olefinic), 5.76—5.96 (2H, m, olefinic), 6.62 (2H, d, J=7 Hz, Ph), 6.88 (1H, t, J=7 Hz, Ph), and 7.19 (2H, t, J=7 Hz, Ph), ^{13}C NMR δ=38.0 (t), 51.8 (d), 113.2 (d), 117.0 (d), 117.5 (t), 129.2 (d), 134.7 (d), and 147.3 (s); MS (70 eV) *m/z* (rel intensity) 187 (M^+, 39), 186 (28), 146 (100).

Allylation of Azomethines with Allylic Indates. The following reaction of *N*-benzylidenemethylamine and 2-butenylindate represents the typical procedure. To a stirred solution of 2-butenylindium sesquibromide, prepared from indium powder (230 mg, 2 mmol) and 2-butenyl bromide (405 mg, 3 mmol) in dioxane (2 ml) at room temperature for 40 min, was added methyllithium (1.06 M in diethyl ether solution (1M=1 mol dm^{-3}), 4.0 ml, 4.25 mmol) at 0 °C for 10 min, and the mixture was stirred at room temperature for 2 h. To the solution of 2-butenylindate thus prepared was added *N*-benzylidenemethylamine (179 mg, 1.5 mmol) and the whole mixture was stirred at room temperature for 2 h. Water was added and the product was extracted with ether. The extracts were washed with water and brine, and dried (Na_2SO_4). Evaporation of the solvent and vacuum distillation (bp 65 °C/5 Torr, bath temperature) gave *N*, 2-dimethyl-1-phenyl-3-butenylamine (**8**) (216 mg, 82%).

***N*, 2-Dimethyl-1-phenyl-3-butenylamine[1j] (8).** Colorless oil; IR (neat) 3340, 3060, 3030, 2970, 2925, 2900, 2790, 1638, 1600, 1497, 1446, 1376, 1355, 1134, 1000, 970, 840, 762, and 702 cm^{-1}; ^1H NMR δ=0.77 and 0.97 (3H, d, J=6 Hz, CH_3), 1.55—1.74 (1H, m, NH), 2.20 and 2.28 (3H, s, CH_3), 2.28—2.66 (1H, m, CH), 3.16 (*threo*) and 3.49 (*erythro*) [1H, d, J=7 Hz, (*threo*) and J=5 Hz (*erythro*), CH], 4.98—5.31 (2H, m, olefinic), 5.64—5.88 (1H, m, olefinic), and 7.22—7.46 (5H, m, Ph); ^{13}C NMR δ=15.7 (q), 17.9 (q), 34.6 (q), 34.7 (q), 43.6 (d), 45.6 (d), 69.3 (d), 70.1 (d), 114.9 (t), 115.9 (t), 126.8 (d), 126.9 (d), 127.1 (d), 127.2 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.3 (d), 141.4 (s), and 143.8 (s); MS (70 eV) *m/z* (rel intensity) 175 (M^+, 0.2), 167 (4), 149 (13), 136 (7), 129 (7), 123 (7), 109 (7), 97 (8), and 93 (100).

2-Ethyl-*N*-methyl-1-phenyl-3-butenylamine[1c,1i] (9). Colorless oil; IR (neat) 3345, 3075, 3040, 2970, 2935, 2880, 2820, 2790, 1638, 1602, 1497, 1446, 1376, 1355, 1135, 970, 840, 760, and 704 cm^{-1}; ^1H NMR δ=0.68—1.00 (3H, m, CH_3), 1.00—1.28 (2H, m, CH_2), 1.40—1.70 (1H, m, NH), 2.18 and 2.28 (3H, s, CH_3), 1.92—2.40 (1H, m, CH), 3.20 (*threo*) and 3.55 (*erythro*) [1H, d, J=8 Hz, (*threo*) and J=4 Hz (*erythro*), CH], 5.00—5.32 (2H, m, olefinic), 5.35—5.70 (1H, m, olefinic), and 7.18—7.40 (5H, m, Ph); ^{13}C NMR δ=11.6 (q), 11.9 (q), 23.9 (t), 24.1 (t), 34.4 (q), 34.5 (q), 51.9 (d), 53.3 (d), 67.9 (d), 68.8 (d), 116.7 (t), 117.8 (t), 126.8 (d), 127.1 (d), 127.7 (d), 128.0 (d), 128.1 (d), 128.2

(d), 138.6 (d), 140.3 (d), 140.9 (s), and 142.4 (s); MS (70 eV) m/z (rel intensity) 161 (1.2), 149 (0.6), 132 (4), and 120 (100).

Allylation of Nitriles with Allylindate. The following allylation of benzonitrile represents the typical procedure. To a stirred solution of allylindium sesquibromide, prepared from indium powder (459 mg, 4 mmol) and allyl bromide (726 mg, 6 mmol) in dioxane (2 ml) at room temperature for 40 min, was added methyllithium (1.06 M in diethyl ether solution, 8.0 ml, 8.5 mmol) at 0 °C for 10 min, and the mixture was stirred at room temperature for 2 h. To this solution of allylindate was added benzonitrile (165 mg, 1.6 mmol), and the whole mixture was stirred at room temperature for 2 h. Water was added and the product was extracted with ether. The extracts were washed with water and brine, and dried (Na_2SO_4). Evaporation of the solvent and vacuum distillation (bp 105 °C/2 Torr, bath temperature) gave 4-phenyl-1,6-heptadien-4-amine (**10**) (245 mg, 82%).

4-Phenyl-1,6-heptadien-4-amine (10). Colorless oil; IR (neat) 3385, 3075, 3025, 2980, 2915, 1638, 1495, 1441, 765 and 700 cm^{-1}; ^1H NMR δ=1.83 (2H, s, NH_2), 2.43 (2H, dd, J=8 Hz, J=13 Hz, CH_2), 2.69 (2H, dd, J=6 Hz, J=13 Hz, CH_2), 5.01—5.17 (4H, m, olefinic), 5.45—5.66 (2H, m, olefinic), and 7.21—7.50 (5H, m, Ph); ^{13}C NMR δ=48.0 (t), 56.8 (s), 118.5 (t), 125.6 (d), 126.1 (d), 127.9 (d), 133.8 (d), and 146.5 (s); MS (70 eV) m/z (rel intensity) 187 (M^+, 36) and 186 (100). Found C, 83.54; H, 9.40; N, 7.46%. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48%.

4-(2-Furyl)-1,6-heptadien-4-amine (11). Colorless oil; IR (neat) 3375, 3085, 2995, 2925, 1640, 1505, 1438, 1160, 1000, 918, 810, and 738 cm^{-1}; ^1H NMR δ=1.77 (2H, s, NH_2), 2.39 (2H, dd, J=8 Hz, J=13 Hz, CH_2), 2.63 (2H, dd, J=7 Hz, J=14 Hz, CH_2), 5.04—5.10 (4H, m, olefinic), 5.51—5.74 (2H, m, olefinic), 6.12—6.18 (1H, m, furan), 6.30—3.36 (1H, m, furan), and 7.35—7.42 (1H, m, furan); ^{13}C NMR δ=45.1 (t), 54.7 (s), 105.0 (t), 109.7 (d), 118.6 (d), 133.3 (d), 141.2 (d), and 160.0 (s); MS (70 eV) m/z (rel intensity) 177 (M^+, 8), 176 (32), 167 (9), 161 (22), 145 (34), 139 (5), 125 (13), 119 (7), 111 (23), 105 (6), 97 (33), 91 (6), 83 (43), 77 (8), 69 (85), and 57 (100). Found C, 74.75; H, 8.55; N, 7.74%. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90%.

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