or a Perkin-Elmer 8320 capillary gas chromatograph with a 30 m × 0.25 mm bonded FSOT 20% SE-30 capillary column. Spectra were recorded on the following instruments: IR: Perkin-Elmer 283 spectrometer or Nicolet 6000 series FT-IR (TF = thin film). MS: Hewlett-Packard 5995 GC/MS (70 eV) (For both series d and e, only ^{74}Ge peaks are reported). NMR: GE Models QE and GN 300-MHz NMR spectrometers (^{1}H and ^{13}C (Me$_4$Si: $\delta = 0.00$ ppm), ^{11}B (BF$_3$–OEt$_2$: δ 0.0 ppm)). All solvents and reagents were purified prior to use by standard methods (cf. ref 4b).

1,1-Dimethyl-4-methoxy-1-sila-4-borinane (3a). To a mixture of 9-BBN (63.6 g, 0.52 mol) in dry hexanes (625 mL) was added divinyldimethylsilane (29.1 g, 0.26 mol). The stirred mixture was heated at reflux temperature for 2 h. After the mixture was cooled to room temperature, BMS (27.5 mL, 9.45 M; 0.26 mol) was added, followed by heating at reflux for 2 h. After the reaction mixture was cooled to room temperature, MeOH (62.5 mL) was added dropwise (H$_2$ evolution). The solvents were removed by distillation under a nitrogen atmosphere. Vacuum distillation of the residue provided 30.7 g (76%) of **3a** (bp 21–3 °C, 0.15 Torr) and 71.3 g (90%) of **4** (bp 32–3 °C, 0.15 Torr). For **3a**, the physical and spectroscopic properties were identical with previous values.[4b]

1,1-Diethyl-4-methoxy-1-sila-4-borinane (3c). From 9-BBN (5.0 g, 41 mmol) in dry hexanes (50 mL) and divinyldiethylsilane (2.87 g, 20.5 mmol), as for **3a** [BMS (2.05 mL, 9.98 M; 20.5 mmol); MeOH (4 mL)], distillation afforded 5.13 g (80%) of **4** and 2.95 g (78%) of pure **3c** (bp 47–9 °C, 0.2 Torr). ^{11}B NMR (CDCl$_3$): δ 52.3 ppm. ^{13}C NMR (CDCl$_3$): δ 3.8 ($C\mathrm{H_2CH_3}$), 4.5 ($\mathrm{Si}C\mathrm{H_2CH_2}$), 7.3 ($\mathrm{CH_2}C\mathrm{H_3}$), 12.9 (b, $\mathrm{CH_2}C\mathrm{H_2B}$), 52.8 ($\mathrm{O}C\mathrm{H_3}$) ppm. ^{1}H NMR δ 0.51 (q, 4 H, $J = 8$ Hz), 0.61 (ct, 4 H), 0.93 (t, 6 H), $J = 8$ Hz), 0.97 (ct, 4 H), 3.63 (s, 3 H) ppm. MS: m/z 184 (M$^+$, 53), 170 (22), 156 (51), 155 (100), 141 (39), 127 (45), 113 (55); 111 (35); 85 (56); 59 (42); 57 (22).

1,1-Diethyl-4-methoxy-1-germa-4-borinane (3d). From 9-BBN (73.3 g, 0.600 mol) in dry hexanes (700 mL) and divinyldiethylgermane (55.4 g, 0.300 mol), as for **3a** [BMS (33.1 mL, 9.04 M; 0.300 mol); MeOH (37 mL)], distillation provided 80 g (85%) of **4** (bp 47–9 °C, 1.5 Torr) and 50.2 g (73%) of pure **3d** (bp 68–70 °C, 1.2 Torr). ^{11}B NMR (CDCl$_3$): δ 55.6 ppm. ^{13}C NMR (CDCl$_3$): δ 4.0 ($C\mathrm{H_2CH_3}$), 5.3 ($\mathrm{Ge}C\mathrm{H_2CH_2}$), 8.9 ($\mathrm{CH_2}C\mathrm{H_3}$), 14.6 (b, $\mathrm{CH_2}C\mathrm{H_2B}$), 52.8 ($\mathrm{O}C\mathrm{H_3}$) ppm. ^{1}H NMR δ 0.73 (q, 4 H, $J = 8$ Hz), 0.83 (t, 4 H), $J = 7.2$ Hz), 1.03 (t, 6 H, $J = 8$ Hz), 1.06 (t, 4 H), $J = 7.2$ Hz), 3.61 (s, 3 H) ppm. MS: m/z 230 (M$^+$ (Ge – 74), 11), 201 (M – Et, 100), 173 (36), 157 (41), 145 (38), 131 (31), 103 (84), 75 (36).

1,1-Dipropyl-4-methoxy-1-germa-4-borinane (3e). From 9-BBN (5.47 g, 44.9 mmol) in dry hexanes (50 mL) and divinyldipropylgermane (4.77 g, 22.4 mmol), as for **3a** [BMS (2.5 mL, 9.00 M; 22.4 mmol); MeOH (4 mL)], distillation provided 5.9 g (84%) of **4** and 4.30 g (76%) of pure **3e** (bp 95–7 °C, 0.2 Torr). ^{11}B NMR (CDCl$_3$): δ 52.5 ppm. ^{13}C NMR (CDCl$_3$): δ 5.2 ($\mathrm{Ge}C\mathrm{H_2CH_2B}$), 14.7 (b, $\mathrm{CH_2}C\mathrm{H_2B}$), 16.6 ($C\mathrm{H_2Et}$), 18.0 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 18.9 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 52.8 ($\mathrm{O}C\mathrm{H_3}$) ppm. ^{1}H NMR δ 0.74 (m, 4 H), 0.82 (ct, 4 H), 0.94 (t, 6 H), $J = 7.2$ Hz), 1.05 (ct, 4 H), 1.43 (m, 4 H), 3.62 (s, 3 H) ppm. MS: m/z (51), 147 (100), 105 (76).

1,1-Dimethyl-1-silacyclohexan-4-one (1a). To a stirred solution of **3a** (6.5 g, 42 mmol) and dichloromethyl methyl ether (DCME) (5.02 g, 42 mmol) in THF (250 mL) at 0 °C was added, via a double-ended needle, lithium *tert*-butoxide solution (from 81 mL, 2.58 M Li(n-Bu) and *tert*-butyl alcohol (20 mL, 208 mmol)). After 10 min, the mixture was allowed to warm to room temperature and after 30 min, ethanol (35 mL 95%), water (10 mL), and NaOH pellets (5.0 g, 125 mg-atom) were added followed by the dropwise addition of 35% hydrogen peroxide (14 mL). After the addition was complete, the mixture was heated at reflux temperature for 1.5 h, allowed to cool to room temperature, and extracted with saturated brine (80 mL). The organic layer was dried (K$_2$CO$_3$), concentrated at reduced pressure, and distilled at 59 Torr to give 5.2 g (88%) of **1a** (bp 118–120 °C). For **1a**, the physical and spectroscopic properties were identical with previous values.[1a,4b,7]

1,1-Diethyl-1-silacyclohexan-4-one (1c). From **3c** (2.66 g, 14.4 mmol), DCME (1.66 g, 14.4 mmol) in THF (90 mL) and LiO(t-Bu) solution (from 40 mL, 1.82 M Li(t-Bu) and t-BuOH (3.8 mL, 72 mmol)), as for **1a** [ethanol (12 mL, 95%), water (3 mL), NaOH pellets (2.0 g, 50 mg-atom), 35% hydrogen peroxide (5.0 mL), saturated brine (35 mL)], distillation gave 1.85 g (75%) of **1c** (bp 67–70 °C, 0.4 Torr). Anal. Calcd for C$_9$H$_{18}$SiO: C, 63.47; H, 10.65. Found: C, 63.21; H, 10.64. ^{13}C NMR (CDCl$_3$): δ 3.9 ($C\mathrm{H_2CH_3}$), 6.6 ($\mathrm{Si}C\mathrm{H_2CH_2}$), 7.3 ($\mathrm{CH_2}C\mathrm{H_3}$), 37.8 ($\mathrm{SiCH_2}C\mathrm{H_2}$), 214.9 ($C{=}\mathrm{O}$) ppm. ^{1}H NMR δ 0.66 (q, 4 H, $J = 7.8$ Hz), 0.93 (ct, 4 H), 1.00 (t, 6 H, $J = 7.8$ Hz), 2.50 (ct, 4 H) ppm. IR (TF): 1708 cm^{-1}. MS: m/z 170 (M$^+$, 19, 142 (M – C$_2$H$_4$, 40), 141 (M – Et, 57), 114 (142 – CO, 55), 113 (141 – C$_2$H$_4$, 100, 87 (22), 86 (72), 85 (53), 75 (31), 59 (22), 58 (70), 57 (89), 56 (37), 55 (59), 53 (21).

1,1-Diethyl-1-germacyclohexan-4-one (1d). From **3d** (50.2 g, 218 mmol), DCME (25.0 g, 218 mmol) in THF (1.3 L), and LiO(t-Bu) solution (from 570 mL, 1.80 M Li(t-Bu) and t-BuOH (97 mL, 1.03 mol)), as for **1a** [ethanol (175 mL 95), water (46 mL), and NaOH pellets (27 g, 0.68 g-atom), 35% hydrogen peroxide (72 mL), saturated brine (500 mL)], distillation at 0.4 Torr gave 42.6 g (91%) of **1d** [bp 72–4 °C (lit.[2b] bp 84–5 °C, 1.5 Torr)]. Anal. Calcd for C$_9$H$_{18}$GeO: C, 50.32; H, 8.44. Found: C, 50.39; H, 8.47. ^{13}C NMR (CDCl$_3$): δ 4.5 ($C\mathrm{H_2CH_3}$), 6.4 ($\mathrm{Ge}C\mathrm{H_2CH_2}$), 8.3 ($\mathrm{CH_2}C\mathrm{H_3}$), 38.2 ($\mathrm{GeCH_2}C\mathrm{H_2}$), 213.4 ($C{=}\mathrm{O}$) ppm. ^{1}H NMR δ 0.62 (cq, 4 H, $J = 8$ Hz (calcd), 0.82 (t, 6 H, $J = 8$ Hz (calcd), 0.85 (ct, 4 H), 2.29 (ct, 4 H) ppm. IR (TF): 1705 cm^{-1}, MS: m/z 216 (M$^+$, 32, 187 (M – Et, 55), 159 (187 – C$_2$H$_4$, 37), 131 (159 – CO, 51), 103 (GeC$_2$H$_5$, 100).

1,1-Dipropyl-1-germacyclohexan-4-one (1e). From **3e** (1.96 g, 7.6 mmol), DCME (0.89 g, 7.6 mmol) in THF (45 mL), and LiO(t-Bu) solution (from 20.9 mL 1.82 M Li(t-Bu) and t-BuOH (3.6 mL, 38.1 mol)), as for **1a** [ethanol (6 mL 95%), water (2 mL), and NaOH pellets (0.9 g, 22.5 mg-atoms), 30% hydrogen peroxide (4.2 mL), saturated brine (50 mL)], distillation at 0.9 Torr gave 1.62 g (88%) of **1e** (bp 97–9 °C). Anal. Calcd for C$_{11}$H$_{22}$GeO: C, 54.39; H, 9.13. Found: C, 54.47; H, 9.18. ^{13}C NMR (CDCl$_3$): δ 7.9 ($\mathrm{Ge}C\mathrm{H_2CH_2C{=}O}$), 16.0 ($C\mathrm{H_2Et}$), 17.7 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 18.6 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 38.7 (b, $\mathrm{CH_2}C\mathrm{H_2C{=}O}$), 214.7 ($C{=}\mathrm{O}$) ppm. ^{1}H NMR δ 0.84 (m, 4 H), 0.93 (t, 6 H, $J = 7.2$ Hz), 1.05 (ct, 4 H), 1.43 (m, 4 H), 2.51 (ct, 4 H) ppm. IR (TF): 1706 cm^{-1}. MS: m/z 244 (M + (Ge – 74), 201 (M – Pr, 35), 159 (201 – C$_3$H$_6$, 100).

Acknowledgment. We are indebeted to the NIH-RCMI Program (RR03641) for the funds to purchase the GE 300-MHz NMR spectrometers (QE-300 and GN-300), which made this study possible. The support of the NSF-EPSCoR and NIH-MBRS Programs (RR08102) is gratefully acknowledged.

Registry No. **1a**, 18276-42-1; **1c**, 119996-87-1; **1d**, 41992-17-0; **1e**, 119996-88-2; **3a**, 89555-71-5; **3c**, 119996-84-8; **3d**, 119996-85-9; **3e**, 119996-86-0; **4**, 38050-71-4; divinyldimethylsilane, 10519-87-6; divinyldiethylsilane, 18270-16-1; divinyldiethylgermane, 22773-67-7; divinyldipropylgermane, 119996-89-3.

A Route to Sterically Crowded Benzophenone *N*-Aryl Imines

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Received December 8, 1988

While the direct condensation of an aromatic aldehyde with an aniline produces a Schiff's base with high efficiency,[1] the success of an analogous reaction with a diaryl ketone is strongly dependent on steric hindrance in both the carbonyl and amine reactants. For example, attempted reactions of benzophenone with 2,6-dimethylaniline,[2a]

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[1] Shuman, R. F.; Amstutz, E. D. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 441.

[2] (a) This work. (b) Strekowski, L.; Cegla, M. T.; Harden, D. B.; Mokrosz, J. L.; Mokrosz, M. J. *Tetrahedron Lett.* **1988**, *29*, 4265. (c) Knorr, R. *Chem. Ber.* **1980**, *113*, 2441. (d) Okubo, M.; Ueda, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 281. (e) Okubo, M.; Ueda, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3346.

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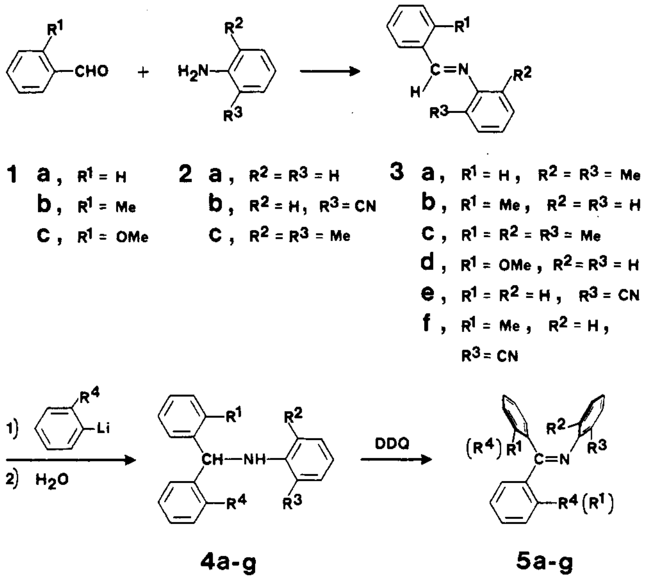
Scheme I



1 a, R^1 = H
b, R^1 = Me
c, R^1 = OMe

2 a, $R^2 = R^3$ = H
b, R^2 = H, R^3 = CN
c, $R^2 = R^3$ = Me

3 a, R^1 = H, $R^2 = R^3$ = Me
b, R^1 = Me, $R^2 = R^3$ = H
c, $R^1 = R^2 = R^3$ = Me
d, R^1 = OMe, $R^2 = R^3$ = H
e, $R^1 = R^2$ = H, R^3 = CN
f, R^1 = Me, R^2 = H, R^3 = CN

4,5	R^1	R^2	R^3	R^4	E/Z ratio for 5
a	H	Me	Me	H	—
b	Me	H	H	H	2 : 98
c	Me	Me	Me	H	29 : 71
d	OMe	H	H	H	3 : 97
e	Me	Me	Me	OMe	19 : 81
f	H	CN	H	H	—
g	Me	CN	H	H	22 : 78

benzophenone with 2-aminobenzonitrile,[2b] 2-methylbenzophenone with aniline,[2c] and 2-methoxybenzophenone with aniline,[2d,e] all failed to produce the corresponding condensation products under a variety of experimental conditions.[3] Several indirect routes to diaryl ketone anils have been developed.[4] As a result, compounds with relatively low steric hindrance, containing only one ortho substituent in the molecule, have been synthesized.[2c,4c–e]

In this paper we report a general method for the preparation of highly sterically crowded benzophenone anils **5** (Scheme I). The approach involves condensation of benzaldehyde **1** with aniline **2** to produce anil **3**, followed by the addition reaction of an aryllithium reagent with **3** and then dehydrogenation of the resultant amine **4** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[5] The method is experimentally simple and highly efficient. The intermediate Schiff's bases **3** are obtained in a nearly quantitative yield in all cases studied. With the exception of the most hindered anil **5e** (33%), the remaining derivatives **5a-d** and **5f-g** are produced in the next two-step transformation in overall yields of 76–96%.

The stereochemistry of **5** was studied by ^{1}H NMR spectroscopy. The spectrum of **5a** with an unsubstituted diphenylmethylene moiety gave a two-proton doublet for ortho protons of one *C*-phenyl group at δ 7.79 and another two-proton doublet for the ortho protons of the second *C*-phenyl group at δ 7.10. The lower field resonance was assigned to the *C*-phenyl approximately coplanar with the central carbon–nitrogen double bond and in anti relationship to the *N*-aryl group.[2c] The remaining *C*-phenyl must be twisted out of the C=N plane in order to minimize steric interaction with the adjacent *N*-aryl group. The *N*-aryl is also twisted, as evidenced by the chemical shift δ 6.79 for the para proton. The observed shielding must be due to conjugation of the sp^2 nitrogen atom with the aryl ring, which reaches a maximium for the ring perpendicular to the C=N bond.[6] This conformation for **5a** was confirmed by NOE experiments. Thus, irradiation of the ortho methyl groups of the *N*-aryl in **5a** gave a strong NOE enhancement to the corresponding ortho protons of the adjacent twisted *C*-phenyl; no magnetization transfer was observed to the coplanar *C*-phenyl group characterized by the low-field resonance for the ortho protons. The same stereochemistry was obtained for **5f**.

A similar analysis including NOE experiments for anils **5b–e** and **5g** with the unsymmetrically substituted diphenylmethylene unit revealed that these compounds are mixtures of *E* and *Z* diastereomers. The *E*/*Z* ratios are given in Scheme I. These are thermodynamic mixtures of diastereomers because attempted heat- and acid-induced isomerization did not change the given ratios. The formation of the equilibrium mixtures of **5** is apparently a result of intrinsic configurational instability of this class of compounds.[7,8]

Experimental Section

Phenyllithium (2 M in cyclohexane/ether) and *n*-butyllithium (1.8 M in hexanes) were obtained from Aldrich. A solution of (2-methoxyphenyl)lithium in ether was generated at −50 °C from 2-bromoanisole and *n*-butyllithium. All reactions with organolithium reagents were conducted in ether distilled from sodium benzophenone ketyl immediately before use and under static pressure of nitrogen. The glassware was dried at 140 °C, assembled hot, and cooled in a stream of nitrogen. The liquids were transferred with syringes. Melting points (Pyrex capillary) are uncorrected. Mass spectra (70 eV) and FT-IR spectra were recorded on a Varian MAT spectrometer and a Bomem Michelson-100 instrument, respectively. Unless stated otherwise, ^{1}H NMR spectra were obtained on a Varian VXR-400 (400 MHz) spectrometer at 25 °C. The spectra were taken in $CDCl_3$ solutions (0.05 M) with Me_4Si as an internal standard. The chemical shift assignments for protons of **5** were obtained by using 1D NOE, 1D decoupling, and 2D COSY experiments.[9] The coupling

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(3) For discussion of the successful condensations of amines with less hindered ketones including 2,6-disubstituted cyclohexanones, see: Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246.

(4) (a) For a review, see: Dayagi, S.; Degani, Y. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; pp 61–147. (b) Feringa, B. L.; Jansen, J. F. G. A. *Tetrahedron Lett.* **1986**, *27*, 507. (c) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Thijs, L.; Veenstra, G. E.; Zwanenburg, B. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1218. (d) Okubo, M.; Hayashi, S.; Matsunaga, M.; Uematsu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2337. (e) Okubo, M.; Uematsu, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1121.

(5) A similar approach failed to be developed previously into a general synthetic method. The use of Grignard reagents in the addition step resulted in single-electron transfer-induced replacement of the methoxy group (ref 2e, 4e) and the addition to the cyano group (ref 2b). Serious problems were encountered in the oxidation step due to the lack of the efficient oxidizing agent (ref 4a). On the other hand, the method described here cannot be extended on the preparation of *C*- or *N*-alkyl-substituted Schiff's bases because the corresponding amines are stable in the presence of DDQ (unpublished results from this laboratory).

(6) The *C*-aryl is coplanar and the *N*-aryl is approximately perpendicular to the C=N plane of (*E*)-**3**, due to conjugation with the C=N bond and the sp^2 nitrogen atom, respectively. (a) van Putten, A.; Pavlik, J. W. *Tetrahedron* **1971**, *27*, 3007. (b) Kobayashi, M.; Yoskida, M.; Minato, H. *Chem. Lett.* **1976**, *185*. (c) Akaba, R. A.; Tokumaru, K.; Kobayashi, T. *J. Chem. Soc. Jpn.* **1980**, *53*, 1993.

(7) Our failure to separate diastereomers of **5** by chromatography is consistent with isomerization of these compounds within the time scale of the separation attempt. For a review of the configurational instability of Schiff's bases, see: McCarty, G. G. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; pp 376–383. For a recent example of the acid-induced isomerization, see: Strekowski, L.; Kong, S. B.; Cegla, M. T.; Harden, D. B. *Heterocycles*, in press.

(8) Note the preferred *Z* configuration with the more sterically demanding *C*-aryl group perpendicular to the central C=N bond and in syn relationship to the *N*-aryl group. In the light of these data the tentative stereochemical assignments for other benzophenone anils given in ref 4e are erroneous.

constants smaller than 1.2 Hz are not reported.

Anils 3a–f. General Procedure. Of the many reported preparations of *N*-benzylidene-2,6-dimethylaniline[6c] (**3a**), *N*-(2-methylbenzylidene)aniline[6a] (**3b**), *N*-(2-methylbenzylidene)-2,6-dimethylaniline[10] (**3c**), *N*-(2-methoxybenzylidene)aniline[11] (**3d**), and 2-(benzylideneamino)benzonitrile[2b] (**3e**) the condensation of **1** (6 mmol) with **2** (5 mmol) in toluene (25 mL) in the presence of molecular sieves 4A[12] for 10 h at 23 °C gave the best results. Removal of the toluene and excess of **1** under reduced pressure gave the corresponding anils **3a–e** (98–99%), which were used without further purification.

2-[(2-Methylbenzylidene)amino]benzonitrile (3f, from 1b and 2b): yield 94% after crystallization from toluene/hexanes; mp 104–106 °C; NMR (60 MHz) δ 2.65 (s, 3 H), 7.15–7.69 (m, 7 H), 8.09 (d, J = 8 Hz, 1 H), 8.75 (s, 1 H). Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.76; H, 5.49. Found: C, 81.84; H, 5.51.

Amines 4a–g. General Procedure. A solution of anil **3** (3.0 mmol) in ether (50 mL) was treated dropwise at −5 °C with an aryllithium reagent (3.2 mmol), and the resultant mixture was stirred at 0 °C for 1 h and then at 20 °C for 1 h. The mixture was quenched with water (0.2 mL), dried over Na_2SO_4, filtered, and concentrated. Crude amines **4a** and **4c–f** were crystallized from hexanes, while products **4b** and **4g** were purified by chromatography on silica gel (hexanes/triethylamine, 9:1).

2,6-Dimethyl-*N*-(diphenylmethyl)aniline (4a, from 3a and PhLi): yield 95%; mp 90–91 °C; IR 3372 cm^{-1}; MS *m/z* (relative intensity) 167 (100), 287 (M^+, 14); NMR δ 1.97 (s, 6 H), 3.47 (br s, 1 H), 5.28 (s, 1 H), 6.78 (t, J = 8 Hz, 1 H), 6.93 (d, J = 8 Hz, 2 H), 7.20–7.40 (m, 10 H). Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37. Found: C, 87.62; H, 7.40.

***N*-(2-Methyl-α-phenylbenzyl)aniline (4b, from 3b and PhLi)**: yield 95%; colorless oil, IR 3407 cm^{-1}; MS *m/z* (relative intensity) 181 (100), 273 (M^+, 22); NMR δ 2.32 (s, 3 H), 4.12 (br d, J = 4 Hz, 1 H), 5.65 (d, J = 4 Hz, 1 H), 6.49 (d, J = 8 Hz, 2 H), 6.68 (t, J = 8 Hz, 1 H), 7.09–7.33 (m, 11 H). Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01. Found: C, 87.69; H, 7.04.

2,6-Dimethyl-*N*-(2-methyl-α-phenylbenzyl)aniline (4c, from 3c and PhLi): yield 98%; mp 93–96 °C; IR 3365 cm^{-1}; MS *m/z* (relative intensity) 181 (100), 301 (M^+, 14); NMR δ 1.95 (s, 6 H), 2.03 (s, 3 H), 3.47 (br d, J = 9 Hz, 1 H), 5.40 (d, J = 9 Hz, 1 H), 6.78 (t, J = 8 Hz, 1 H), 6.93 (d, J = 8 Hz, 2 H), 7.09–7.59 (m, 9 H). Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69. Found: C, 87.51; H, 7.75.

***N*-(2-Methoxy-α-phenylbenzyl)aniline (4d, from 3d and PhLi)**: yield 98%; mp 131–132 °C; IR 3410 cm^{-1}; MS *m/z* (relative intensity) 91 (100), 197 (82), 289 (M^+, 25); NMR δ 3.78 (s, 3 H), 4.28 (br s, 1 H), 5.89 (s, 1 H), 6.54 (d, J = 8 Hz, 2 H), 6.66 (t, J = 8 Hz, 1 H), 6.88 (d, J = 8 Hz, 1 H), 6.92 (t, J = 8 Hz, 1 H), 7.09 (d, J = 8 Hz, 1 H), 7.11 (d, J = 8 Hz, 1 H), 7.20–7.37 (m, 7 H). Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62. Found: C, 82.75; H, 6.68.

***N*-[2-Methoxy-α-(2-methylphenyl)benzyl]-2,6-dimethylaniline [4e, from 3c and (2-methoxyphenyl)lithium]**: yield 57%, mp 111–113 °C; IR 3395 cm^{-1}; MS *m/z* (relative intensity) 105 (100), 211 (100), 331 (M^+, 22); NMR δ 1.98 (s, 6 H), 2.05 (s, 3 H), 3.52 (s, 3 H), 3.56 (br s, 1 H), 5.86 (s, 1 H), 6.75 (t, J = 8 Hz, 1 H), 6.80 (d, J = 8 Hz, 1 H), 6.90–6.97 (m, 3 H), 7.07–7.28 (m, 4 H), 7.35 (d, J = 8 Hz, 1 H), 7.51 (d, J = 8 Hz, 1 H). Anal. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60. Found: C, 83.06; H, 7.68.

2-[(Diphenylmethyl)amino]benzonitrile (4f, from 3e and PhLi): yield 90%; mp 115–117 °C (lit.[2b] mp 115–117 °C).

2-[(2-Methyl-α-phenylbenzyl)amino]benzonitrile (4g, from 3f and PhLi): yield 88%; colorless oil; IR 2210, 3360 cm^{-1}; MS *m/z* (relative intensity) 181 (100), 298 (M^+, 10); NMR (60 MHz) δ 2.26 (s, 3 H), 5.00 (br d, J = 4 Hz, 1 H), 5.75 (d, J = 4 Hz, 1 H), 6.42 (d, J = 8 Hz, 1 H), 6.58 (t, J = 8 Hz, 1 H), 6.90–7.60 (m, 11 H). Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.25; H, 6.01.

Anils 5a–g. General Procedure. A mixture of amine **4** (2 mmol), DDQ (0.5 g, 2.2 mmol), and benzene (50 mL) was stirred for 2 h under the following conditions: **4a–d**, 23 °C; **4e–g**, 80 °C. (Note: the use of toluene gives lower yields of **5**.) Then the mixture was cooled and extracted with aqueous solution of NaOH (5%, 3 × 10 mL). The benzene was dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography on silica gel (hexanes/triethylamine, 9:1) gave analytically pure **5**. Solid samples **5b** and **5f** were additionally crystallized from hexanes.

2,6-Dimethyl-*N*-(diphenylmethylene)aniline (5a): yield 96%; yellow oil; IR 1578, 1592, 1621 cm^{-1}; MS *m/z* (relative intensity) 208 (100), 285 (M^+, 71); NMR δ 2.05 (s, CH_3), 6.79 (t, J = 8 Hz, H4 of *N*-Ar), 6.88 (d, J = 8 Hz, H3 and H5 of *N*-Ar), 7.10 (d, J = 8 Hz, H2 and H6 of *C*-Ph syn to *N*-Ar), 7.19–7.28 (m, H3-5 of *C*-Ph syn to *N*-Ar), 7.40–7.50 (m, H3-5 of *C*-Ph anti to *N*-Ar), 7.79 (d, J = 8 Hz, H2 and H6 of *C*-Ph anti to *N*-Ar). Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71. Found: C, 88.30; H, 6.74.

***N*-(2-Methyl-α-phenylbenzylidene)aniline (5b, *E*/*Z* = 2:98)**: yield 92%; mp 102–104 °C (lit. mp 103–105 °C,[2c] 100–103 °C[4c]).

2,6-Dimethyl-*N*-(2-methyl-α-phenylbenzylidene)aniline (5c, *E*/*Z* = 29:71): yield 91%; yellow oil; IR 1579, 1592, 1621 cm^{-1}; MS *m/z* (relative intensity) 208 (24), 222 (24), 284 (49), 298 (100), 299 (M^+, 76); NMR for (*Z*)-**5c** (0 °C) δ 2.02 (s, CH_3 of *N*-Ar), 2.09 (s, CH_3 of *C*-PhMe), 6.79 (t, J = 8 Hz, H4 of *N*-Ar), 6.89 (d, J = 8 Hz, H3 and H5 of *N*-Ar), 6.97 (d, J = 8 Hz, H6 of *C*-PhMe), 7.14 (d, J = 8 Hz, H3 of *C*-PhMe), 7.16–7.26 (m, H4 and H5 of *C*-PhMe), 7.40–7.50 (m, H3–5 of *C*-Ph), 7.72 (d, J = 8 Hz, H2 and H6 of *C*-Ph); NMR for (*E*)-**5c** (0 °C) δ 2.15 (s, CH_3 of *N*-Ar), 2.20 (s, CH_3 of *C*-PhMe), 7.59 (d, J = 8 Hz, H6 of *C*-PhMe). Anal. Calcd for $C_{22}H_{21}N$: C, 88.24; H, 7.07. Found for the *E*/*Z* mixture: C, 88.27; H, 7.11.

***N*-(2-Methoxy-α-phenylbenzylidene)aniline (5d, *E*/*Z* = 3:97)**: yield 98%; mp 77–79 °C (lit.[4e] mp 78–79 °C).

***N*-[2-Methoxy-α-(2-methylphenyl)benzylidene]-2,6-dimethylaniline (5e, *E*/*Z* = 19:81)**: yield 58%; yellow oil; IR 1250, 1594, 1622 cm^{-1}; MS *m/z* (relative intensity) 238 (38), 298 (100), 314 (80), 328 (37), 329 (M^+, 71); NMR for (*Z*)-**5e** δ 2.07 (s, CH_3 of *N*-PhMe), 2.39 (s, CH_3 of *C*-PhMe), 3.40 (s, *O*-CH_3), 6.70 (d, J = 8 Hz, H3 of *C*-PhOMe), 6.72–6.79 (m, H4 of *N*-Ar and H5 of *C*-PhOMe), 6.87 (d, J = 8 Hz, H3 and H5 of *N*-Ar), 6.91 (d, J = 8 Hz, H6 of *C*-PhOMe), 7.16–7.22 (m, H3 and H5 of *C*-PhMe, H4 of *C*-PhOMe), 7.27 (t, J = 8 Hz, H4 of *C*-PhMe), 7.39 (d, J = 8 Hz, H6 of *C*-PhMe); NMR for (*E*)-**5e** δ 1.97 (s, CH_3 of *C*-PhMe), 2.10 (s, CH_3 of *N*-Ar), 3.62 (s, *O*-CH_3), 7.52 (d, J = 8 Hz, H6 of *C*-PhOMe); HR-MS calcd for $C_{23}H_{23}NO$ 329.1780, found 329.1793.

2-[(Diphenylmethylene)amino]benzonitrile (5f): yield 90%; mp 118–119 °C (lit.[2b] mp 118–119 °C).

2-[(2-Methyl-α-phenylbenzylidene)amino]benzonitrile (5g, *E*/*Z* = 22:78): yield 86%; yellow oil; IR 1620, 2220 cm^{-1}; NMR for (*Z*)-**5g** δ 2.12 (s, CH_3), 6.63 (d, J = 8 Hz, H3 of PhCN), 6.96 (t, J = 8 Hz, H5 of PhCN), 7.10–7.27 (m, H3–6 of *C*-PhMe and H4 of PhCN), 7.41 (t, J = 8 Hz, H3 and H5 of *C*-Ph), 7.46–7.55 (m, H4 of *C*-Ph and H6 of PhCN), 7.80 (d, J = 8 Hz, H2 and H6 of *C*-Ph); NMR for (*E*)-**5g** δ 2.34 (s, CH_3), 7.59 (d, J = 8 Hz, H6 of *C*-PhMe). Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.10; H, 5.44. Found: C, 84.95; H, 5.49.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The Varian VXR-400 NMR spectrometer was obtained with partial support from an award by the NSF Chemical Instrumentation Program (CHEM-8409599).

Registry No. **1a**, 100-52-7; **1b**, 529-20-4; **1c**, 135-02-4; **2a**, 62-53-3; **2b**, 1885-29-6; **2c**, 87-62-7; **3a**, 3096-95-5; **3b**, 10228-77-0; **3c**, 10399-72-1; **3d**, 3369-37-7; **3e**, 64641-82-3; **3f**, 119970-98-8; **4a**, 92917-43-6; **4b**, 119970-99-9; **4c**, 119971-00-5; **4d**, 119971-01-6; **4e**, 119971-02-7; **4f**, 115407-63-1; **4g**, 119971-03-8; **5a**, 119971-04-9; *E*-**5b**, 69052-75-1; *Z*-**5b**, 62093-68-9; *E*-**5c**, 119971-05-0; *Z*-**5c**, 119971-06-1; *E*-**5d**, 119971-07-2; *Z*-**5d**, 119971-08-3; *E*-**5e**, 119971-09-4; *Z*-**5e**, 119971-10-7; **5f**, 119971-11-8; *E*-**5g**, 119971-12-9; *Z*-**5g**, 119971-13-0.

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