was combined in entry 8, where 2 was almost exclusively obtained in CD_3CN at −20 °C. Formation of the products may be explained via an electron-transfer (ET) mechanism between DDQ and the silyl enol ether involving a geminate radical ion pair (Scheme I).[5] However, the large solvent–temperature effects on the 2 to 3 product ratio points toward two distinctly different mechanistic pathways for their formation. A nucleophilic attack of the silyl enol ether on DDQ to form the carbon–carbon adducts cannot be ruled out. Formation of regiospecific adducts from 8 and 10 rules out the possibility of a proton abstraction after ET (in the geminate radical ion pair stage) followed by collapse of the resulting radical pair.

We have demonstrated that the intermediacy of quinone–substrate adducts in the DDQ oxidation (which is traditionally believed[6,7] to proceed via hydride transfer) is more general than hitherto believed. Formation of similar intermediates has also been observed with other electron acceptors and derivatives of ketones and lactams. Details of this work will be the subject of a future publication.

Experimental Section

General Procedures. All the trimethylsilyl enol ethers were prepared by literature procedures.[8,9] The deuterated solvents were purchased from Merck Isotopes, Inc., and Aldrich Chemical Co. and used without purification. NMR analyses were performed using a Bruker WM-250 spectrometer at 0.4 M concentration in deuterated solvents using equimolar amounts of substrate and DDQ at temperatures ranging from −40 °C to 22 °C. Proton and carbon-13 data were obtained at 250.13 and 62.9 MHz, respectively. A spectral width of 3205 Hz, pulse width of 4 μs (42 °C), repetition rate of 2.6 s, and a 16 K data size were used to acquire ^1H NMR spectra. Carbon-13 data used a spectral width of 15000 Hz, pulse width of 4 μs (30 °C) and a repetition rate of 1.0 s and 32 K data size to acquire spectra. Carbon multiplicities were determined by the attached proton test (APT) method[10] and/or heteronuclear gated decoupling, which also provides carbon-hydrogen coupling data. The 2D COSY45 NMR experiments[11] used a 1 K × 512 data matrix and a digital resolution of 3.91 Hz per point in each dimension. In the heteronuclear shift-correlated (HETCOR) 2D NMR experiment,[12] a 2 K × 64 data matrix and digital resolution of 4.88 and 17.2 Hz per point in the f2 and f1 dimensions were used respectively. All chemical shifts are reported in ppm from tetramethylsilane and referenced to the deuterated solvent used.

4,5-Dichloro-3-hydroxy-6-[(2′-oxocyclohexyl)oxy]-1,2-benzenedicarbonitrile (unsilylated 3) was prepared by the reaction of DDQ (250 mg, 1.1 mmol) and 1 (170 mg, 1 mmol) in THF at 22 °C (0.5 h), removal of THF followed by preparative TLC on silica gel with ethyl acetate (66 mg, 20%). The ^1H NMR spectrum shows a diagnostic dd at 5.11 ppm (J = 10.7, 5.9 Hz) for H-1′. Exact mass calculated for $C_{14}H_{10}N_2O_3Cl_2$ is 324.0067, found 324.0031.

4,5-Dichloro-3-hydroxy-6-[(3′-methyl-2′-oxocyclohexyl)-oxy]-1,2-benzenedicarbonitrile (unsilylated 12) was prepared (20%) in the same fashion as 3 from DDQ and 10. The ^1H NMR spectrum shows an overlapping triplet at 4.38 ppm (J = 3.5 Hz) for H-1′ and establishes an axial stereochemistry for the DDQ moiety. Irradiation of 7′-Me in a homonuclear decoupling experiment reveals a dd (J = 11.8, 5.5 Hz) for H-3′. The large vicinal coupling (11.8 Hz) determines its axial orientation. The mass spectrum [m/e 338/340/342 (dichloro) and 228.2000 for the DDQ-derived substituent] is appropriate for unsilylated 12.

4,5-Dichloro-3-hydroxy-6-[(1′-methyl-2′-oxocyclohexyl)-oxy]-1,2-benzenedicarbonitrile (unsilylated 9) was prepared in the same fashion as 3 from DDQ and 8 (80%). The ^1H NMR spectrum shows a diagnostic singlet at 1.16 ppm for the 7′-Me and an oxygen bearing C-1′ carbon observed at 91.3 ppm in the ^{13}C NMR spectrum. The mass spectrum [m/e 338/340/342 (dichloro), and 228.2000 for the DDQ derived substituent] is appropriate for unsilylated 9.

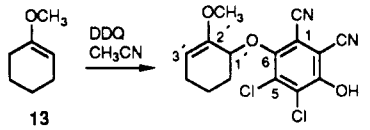
Acknowledgment. We thank Dr. A. W. Douglas and R. A. Reamer for their helpful discussions and support throughout this investigation. We also thank J. L. Smith for the mass spectral studies.

Registry No. 1, 6651-36-1; 2, 123674-90-8; 3, 123674-91-9; (unsilylated 3), 123674-92-0; 4, 19980-43-9; 5, 123674-93-1; 6, 22081-48-7; 7, 123674-94-2; 8, 19980-35-9; 9, 123674-95-3; (unsilylated 9), 123674-96-4; 10, 19980-33-7; 11, 123674-97-5; 12, 123674-98-6; (unsilylated 12), 123674-99-7; DDQ, 84-58-2.

Supplementary Material Available: Spectral data for compounds 2–5, 7, 9, 11, 12, and 14[6] (2 pages). Ordering information is given on any current masthead page.

(5) The dramatic solvent effects on the product ratio (Table I) in competitive single electron transfer (ET) processes was also observed by Kochi [Masnovi, J. M.; Levine, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4356–4358] and Miyashi [Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1986**, *108*, 2755–2757] and can be attributed to a cage–uncage phenomena.

(6) The use of a trialkylsilyl derivative of the ketone is not a necessity for the adduct formation. Thus 14 was formed exclusively by the reaction between 13 and DDQ in CH_3CN at 22 °C.



13 14

The proton and carbon-13 NMR of 14 shows diagnostic resonances for C-1′, (δ_H = 4.66, δ_C = 80.5) and C-3′ (δ_H = 4.91, δ_C = 100.2). The exact mass calculated for $C_{15}H_{12}N_2O_3Cl_2$ is 338.0198, found 338.0031.

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Efficient Preparation of Ketones from *N*-(Ethoxymethylene)aniline and Organometallic Reagents

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A synthesis of aldehydes, based on the addition reaction of Grignard reagents with readily available[2] *N*-(ethoxymethylene)aniline (1), was described at the beginning of this century.[3] We have reinvestigated these reports and

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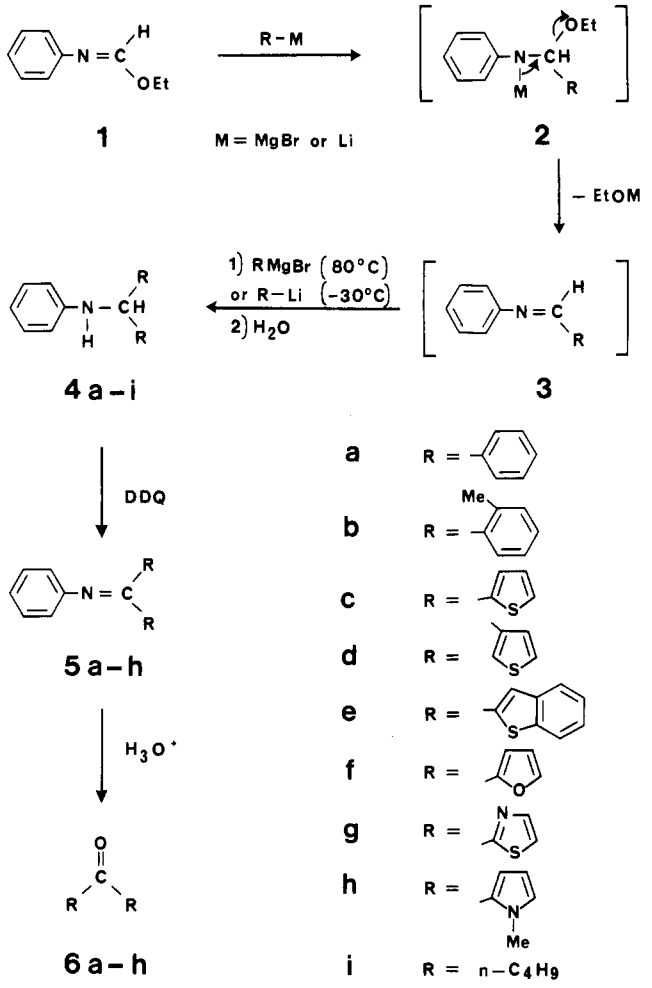
(3) (a) Monier-Williams, G. W. *J. Chem. Soc.* **1906**, *89*, 273. (b) Smith, L. I.; Nichols, J. *J. Org. Chem.* **1941**, *6*, 489.

0022-3263/89/1954-6120$01.50/0

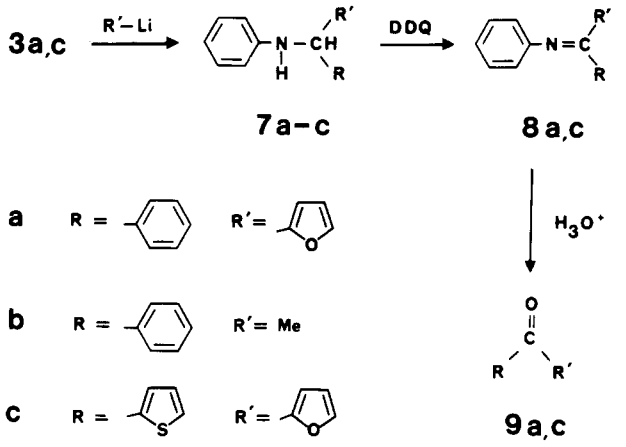
Scheme I



found that the addition reactions with **1** serve as the basis for highly efficient preparations of either aldehydes or ketones (Scheme I).

Phenylmagnesium bromide was reacted with compound **1** in ether to give *N*-(phenylmethylene)aniline (**3a**), which could be hydrolyzed to benzaldehyde.[4] Quantitative yields of **3a** were obtained for the reactions conducted with either 1 equiv or a large excess of the Grignard reagent. The latter result can be explained assuming that (i) the initial adduct **2a** does not decompose to Schiff's base **3a** before quenching the mixture or (ii) the adduct **2a** undergoes elimination of ethoxide ion and the resultant product **3a** is inert toward the reagent PhMgBr under the reaction conditions. The second alternative implies a complete selectivity of the reaction of PhMgBr with **1** in the mixture with **3a**. To test this hypothesis, the product **3a** was treated with an excess of freshly prepared phenylmagnesium bromide, and the mixture was allowed to stand at 23 °C for 12 h, a 24-fold longer period of time than that required to complete the addition reaction of PhMgBr with **1** under the same conditions. After the mixture was quenched with water the starting compound **3a** was recovered quantitatively. However, a prolonged heating of either **1** or **3a** with PhMgBr in benzene at 80 °C produced the adduct **4a**.[5] Similar addition reactions of (2-thienyl)magnesium bromide with **1** furnished Schiff's base **3c** at 23 °C and amine **4c** at 80 °C. We have thus shown that, depending on the conditions, either Schiff's bases **3** or amines **4** can be prepared from readily available compound **1**. The Schiff's bases **3** can be hydrolyzed to aldehydes, as already discussed, while the amines **4** are precursors for ketones **6**, as shown below.

Scheme II



Substitution of lithium reagents for the Grignard reagents[5] in the reaction with **1** provides a practical route to amines **4**. The more reactive lithium derivatives (2 equiv) undergo the double addition under mild conditions to give compounds **4a–i** shown in Scheme I in virtually quantitative yields. In the preparation of ketones **6a–h** the corresponding intermediate benzylic amines **4a–h** are easily dehydrogenated upon treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), and the resultant Schiff's bases **5a–h** are hydrolyzed. The symmetricaly substituted aromatic ketones **6a–h** are thus produced in high overall yields based on the starting compound **1**. Ketones with two different aromatic groups are obtained from the corresponding Schiff's bases **3** in a similar way, as exemplified in Scheme II for the synthesis of **9a** and **9c**. Aliphatic ketones cannot be prepared because the corresponding intermediate amines, such as **4i** (Scheme I) and **7b** (Scheme II) are stable in the presence of DDQ.[7,8]

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(5) A clean addition reaction to **3a** and a double-addition reaction to **1** to give a quantitative yield of **4a** was also observed at 23 °C with old refrigerated solutions of PhMgBr from which magnesium salts had precipitated. Such solutions contain mainly a more reactive $(Ph)_2Mg$ reagent.

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Several methods for the preparation of aromatic and heteroaromatic ketones[6] have been reported. In contrast to a vast majority of these reactions the present approach involves the use of one common reagent. Other major advantages of this method are its exceptionally high efficiency, short reaction time, ease of handling of reagents, and the possibility of working on large scales.

Experimental Section

All air-sensitive reactions were conducted under an atmosphere of high-purity nitrogen. THF and ether were distilled from sodium benzophenone ketyl immediately before use. Unless stated otherwise, ^{1}H NMR spectra were recorded on a Varian EM360 (60 MHz) spectrometer in a $CDCl_3$ solution with Me_4Si as an internal standard. FT IR spectra (neat) were obtained on a Bomem Michelson-100 instrument. Melting points (Pyrex capillary) are uncorrected. Yields reported below correspond to analytically pure products.

***N*-(Ethoxymethylene)aniline (1).** Compound 1 was prepared by condensation of aniline with triethyl orthoformate in the presence of *p*-toluenesulfonic acid using a general procedure.[2] Crude 1 was distilled on a Kugelrohr apparatus and then fractionated on a 15-cm Vigreux column, collecting the fraction at bp 87–88 °C (10 mmHg). It is essential that this purification procedure is followed in order to obtain compound 1 that is indefinitely stable when stored refrigerated over dry nitrogen.

Lithium Reagents. Phenyllithium (1.8 M in cyclohexane/ether) and *n*-butyllithium (2.6 M in hexanes) were obtained from Aldrich. In the preparation of (2-methylphenyl)lithium in ether (50 mL) a solution of 2-bromotoluene (3.0 mL, 25 mmol) and *n*-butyllithium (10 mL, 26 mmol) in the ether was kept at 0 °C for 1 h. (Lower temperature results in incomplete bromine–lithium exchange.) Similar bromine–lithium exchange reactions for 3-bromothiophene and 2-bromothiazole to generate 3-thienyllithium and 2-thiazolyllithium, respectively, were completed after 10 min at −40 °C. 2-Thienyllithium and (2-benzo[*b*]thienyl)lithium in ether were generated from thiophene (3.6 mL, 45 mmol) and benzo[*b*]thiophene (6.05 g, 45 mmol), respectively, by treatment with *n*-butyllithium (10 mL, 26 mmol) at 0 °C for 15 min. Similar lithiation reactions of furan and 1-methylpyrrole to give 2-furanyllithium and (1-methylpyrrol-2-yl)lithium, respectively, were completely successful only when conducted in concentrated solutions of THF/ether (1:1) at −10 °C for 2 h and using a 20-fold excess of the heterocycle.

Schiff's Bases 3a and 3c. In the preparation of *N*-(phenylmethylene)aniline (**3a**) a freshly prepared solution of phenylmagnesium bromide (2.1 mmol) in ether (15 mL) or a homogeneous commercial reagent (from which magnesium salts had not precipitated) was added to a solution of **1** (0.30 g, 2.0 mmol) in ether (10 mL), and the mixture was allowed to stand at 23 °C for 1 h. Then the mixture was quenched with an aqueous solution of NH_4Cl, and the ether was dried over Na_2SO_4 and concentrated. Kugelrohr distillation at 0.1 mmHg gave 0.35 g (97%) of **3a** as an oil. The same result was obtained for the reaction conducted with 4.0 mmol of the Grignard reagent. Similar reactions of **1** with 2-thienylmagnesium bromide furnished *N*-(2-thienylmethylene)aniline (**3c**): yield 96%, an oil. Compounds **3a** and **3c** gave ^{1}H NMR spectra identical with those for the corresponding Schiff's bases obtained by condensation of aniline with benzaldehyde and 2-thiophenecarboxaldehyde in the presence of molecular sieves.[7]

General Procedure for the Preparation of Amines 4a–i. A lithium reagent (26 mmol) in ether was treated dropwise at −30 °C with a solution of **1** (1.9 g, 12 mmol) in ether (25 mL). The mixture was stirred at −30 °C for 30 min and then at 0 °C for 30 min and quenched with 1 mL of water. The ether was dried over Na_2SO_4 and concentrated. Solid amines **4a–c,e,g** were crystallized from hexanes or hexanes/ethanol while the oily samples **4d,f,h,i** were purified by flash chromatography on silica gel, eluting with triethylamine/hexanes (1:9). A similar preparation of **4a** and **4c** from **1** and the respective Grignard reagent RMgBr required heating of the mixture in benzene at 80 °C for 4 h.

***N*-(Diphenylmethyl)aniline (4a)**: yield 99%; mp 57–59 °C (lit.[9] mp 57.5–59 °C).

***N*-[Bis(2-methylphenyl)methyl]aniline (4b)**: yield 97%; mp 101–103 °C; NMR δ 2.23 (s, 6 H), 3.88 (br d, J = 5 Hz, 1 H), 5.65 (d, J = 5 Hz, 1 H), 6.32 (d, J = 7 Hz, 2 H), 6.40 (t, J = 7 Hz, 1 H), 6.80–7.23 (m, 10 H); IR 3410 cm^{-1}. Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37; N, 4.87. Found: C, 87.66; H, 7.40; N, 4.90.

***N*-[Di(2-thienyl)methyl]aniline (4c)**: yield 98%; mp 73–75 °C; NMR δ 4.28 (br d, J = 5 Hz, 1 H), 5.93 (d, J = 5 Hz, 1 H), 6.55 (d, J = 7 Hz, 2 H), 6.63 (t, J = 7 Hz, 1 H), 6.82–7.25 (m, 6 H); IR 3395 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NS_2$: C, 66.38; H, 4.83; N, 5.16. Found: C, 66.25; H, 4.80; N, 5.08.

***N*-[Di(3-thienyl)methyl]aniline (4d)**: yield 99%; oil; NMR δ 4.15 (br s, 1 H), 5.62 (s, 1 H), 6.48 (d, J = 8, Hz, 2 H), 6.58 (t, J = 8 Hz, 1 H), 6.88–7.33 (m, 8 H); IR 3401 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NS_2$: C, 66.38; H, 4.83; N, 5.16. Found: C, 66.28; H, 4.86; N, 5.10.

***N*-[Di(2-benzo[*b*]thienyl)methyl]aniline (4e)**: yield 97%; mp 109–111 °C; NMR δ 4.48 (br d, J = Hz, 1 H), 6.10 (d, J = 5 Hz, 1 H), 6.57–7.93 (m, 15 H); IR 3391 cm^{-1}. Anal. Calcd for $C_{23}H_{17}NS_2$: C, 74.36; H, 4.59; N, 3.77. Found: C, 74.24; H, 4.51; N, 3.69.

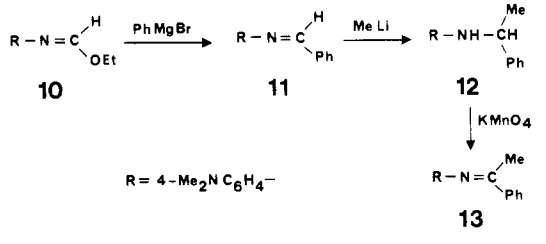
***N*-[Di(2-furanyl)methyl]aniline (4f)**: yield 96%; oil, unstable on air; NMR δ 4.23 (br d, J = 5 Hz, 1 H), 5.62 (d, J = 5 Hz, 1 H), 6.08–6.45 (m, 4 H), 6.78–7.33 (m, 7 H); IR 3387 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.25; H, 5.49; N, 5.71.

***N*-[Di(2-thiazolyl)methyl]aniline (4g)**: yield 99%; mp 98–100 °C; NMR δ 5.75 (br d, J = 4 Hz, 1 H), 6.08 (d, J = 4 Hz, 1 H), 6.57 (d, J = 6 Hz, 2 H), 6.65 (t, J = 6 Hz, 1 H), 7.08 (m, 2 H), 7.13 (d, J = 3 Hz, 2 H), 7.60 (d, J = 3 Hz, 2 H); IR 3366 cm^{-1}. Anal. Calcd for $C_{13}H_{11}N_3S_2$: C, 57.11; H, 4.06; N, 15.37. Found: C, 57.16; H, 4.02; N, 15.42.

***N*-[Bis(1-methylpyrrol-2-yl)methyl]aniline (4h)**: yield 95%; oil; NMR δ 3.48 (s, 6 H), 3.98 (br d, J = 7 Hz, 1 H), 5.70–6.03 (m, 4 H), 6.38–6.65 (m, 5 H), 6.90–7.22 (m, 2 H); IR 3384 cm^{-1}. Anal. Calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 76.82; H, 7.20; N, 15.72.

***N*-(1-Butylpentyl)aniline (4i)**: yield 99%; oil; NMR δ 0.86 (m, 6 H), 1.37 (m, 12 H), 3.30 (br s, 2 H), 6.42 (d, J = 7 Hz, 2 H), 6.50 (t, J = 7 Hz, 1 H), 7.07 (t, J = 7 Hz, 2 H); IR 3406 cm^{-1}. Anal. Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.38. Found: C, 82.01; H, 11.37; N, 6.26.

(8) Attempted dehydrogenation reactions of **4i** and **7b** with HgO, S, $Pb(OAc)_4$, MnO_2, or $KMnO_4$ also failed to produce the corresponding Schiff's bases. On the other hand, treatment of 4-(dimethylamino)-*N*-(1-phenylethyl)aniline (**12**) with an excess of powdered $KMnO_4$ in anhydrous THF under reflux for 12 h (Misztal, S.; Cegla, M. T. *Synthesis* **1985**, 1134) gave 4-(dimethylamino)-*N*-(1-phenylethylidene)aniline (**13**), albeit in a low yield. The treatment of **12** with other reagents mentioned above, including DDQ, did not produce **13**. Intermediate compounds, namely 4-(dimethylamino)-*N*-(ethoxymethylene)aniline (**10**), *N*-benzylidene-4-(dimethylamino)aniline (**11**), and **12** were prepared using general procedures described in this work.



10 **11** **12** **13**

10 [from $4\text{-}Me_2NC_6H_4NH_2$ and $CH(OEt)_3$]: yield 35%; mp 47–49 °C; NMR δ 1.35 (t, J = 7 Hz, 3 H), 2.90 (s, 6 H), 4.30 (q, J = 7 Hz, 2 H), 6.70 (d, J = 8 Hz, 2 H), 6.85 (d, J = 8 Hz, 2 H), 7.73 (s, 1 H). **11** (from **10** and PhMgBr): yield 96%; (from $4\text{-}Me_2NC_6H_4NH_2$ and PhCHO) yield 89%; mp 95–96 °C (from hexanes); NMR δ 2.93 (s, 6 H), 6.73 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 7.40 (m, 3 H), 7.83 (m, 2 H), 8.47 (s, 1 H). **12** (from **11** and MeLi): yield 95%; oil; NMR δ 1.50 (d, J = 7 Hz, 3 H), 2.76 (s, 6 H), 6.50 (d, J = 8 Hz, 2 H), 6.65 (d, J = 8 Hz, 2 H), 7.32 (m, 5 H). **13**: yield 40%; mp 93–94 °C (from hexanes); NMR (400 MHz) δ 2.29 (s, 3 H), 2.95 (s, 6 H), 6.77 (d, J = 8 Hz, 2 H), 6.79 (d, J = 8 Hz, 2 H), 7.43 (m, 3 H), 7.96 (m, 2 H). Satisfactory microanalyses (C, H) were obtained for **10–13**.

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Preparation of Amines 7a–c. Schiff's base **3a** was reacted with 2-furanyllithium and methyllithium under the conditions given above to furnish anilines **7a** and **7b**, respectively. A similar reaction of **3c** with 2-furanyllithium gave **7c**.

***N*-[α-(2-Furanyl)benzyl]aniline (7a)**: yield 96%; oil; NMR (400 MHz) δ 4.35 (br d, J = 4 Hz, 1 H), 5.58 (d, J = 4 Hz, 1 H), 6.11 (m, 1 H), 6.31 (m, 1 H), 6.60 (d, J = 8 Hz, 2 H), 6.71 (t, J = 8 Hz, 1 H), 7.14 (t, J = 8 Hz, 2 H), 7.26–7.43 (m, 6 H). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.89; H, 6.07. Found: C, 81.75; H, 6.00.

***N*-(1-Phenylethyl)aniline (7b)**: yield 91%, oil. The NMR spectrum was virtually identical with that published.[10]

***N*-(2-Furanyl-2-thienylmethyl)aniline (7c)**: yield 92%; oil; NMR δ 4.37 (br d, J = 5 Hz, 1 H), 5.88 (d, J = 5 Hz, 1 H), 6.13–6.37 (m, 2 H), 6.50–7.40 (m, 13 H). Anal. Calcd for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13. Found: C, 70.76; H, 5.20.

Preparation of Schiff's Bases 5a–h, 8a,c. Amines **4a–h** and **7a,c** were dehydrogenated by treatment with DDQ using a general procedure published by us recently[7] and purified by flash chromatography on silica gel (triethylamine/hexanes, 1:9). Solid products **5a–e,g,h** and **8a** were additionally crystallized from hexanes.

***N*-(Diphenylmethylene)aniline (5a)**: yield 99%; mp 106–110 °C (lit.[11] mp 111–112 °C).

***N*-[Bis(2-methylphenyl)methylene]aniline (5b)**: yield 99%; mp 83–85 °C (lit.[12] mp 85.5–86 °C).

***N*-[Di(2-thienyl)methylene]aniline (5c)**: yield 96%; mp 112–114 °C; NMR δ 6.60–7.50 (m); IR 1581 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; N, 5.20. Found: C, 66.68; H, 4.05; N, 5.10.

***N*-[Di(3-thienyl)methylene]aniline (5d)**: yield 88%; mp 93–95 °C; NMR δ 6.60–6.95 (m, 4 H), 6.98–7.43 (m, 5 H), 7.48–7.73 (m, 2 H); IR 1595 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; N, 5.20. Found: C, 66.75; H, 4.16; N, 5.12.

***N*-[Di(2-benzo[*b*]thienyl)methylene]aniline (5e)**: yield 99%, mp 170–172 °C; NMR δ 6.63–7.83 (m); IR 1584 cm^{-1}. Anal. Calcd for $C_{23}H_{15}NS_2$: C, 74.76; H, 4.09; N, 3.79. Found: C, 74.68; H, 4.03; N, 3.68.

***N*-[Di(2-furanyl)methylene]aniline (5f)**: yield 94%; oil, unstable on air; NMR δ 6.07 (m, 2 H), 6.45 (m, 1 H), 6.65 (m, 1 H) 6.78 (m, 1 H), 7.03 (m, 3 H), 7.25 (m, 2 H), 7.53 (m, 1 H); IR 1602 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.00; H, 4.71; N, 5.78.

***N*-[Di(2-thiazolyl)methylene]aniline (5g)**: yield 99%; mp 120–121 °C: NMR δ 6.60–7.25 (m, 5 H), 7.32 (d, J = 3 Hz, 1 H), 7.42 (d, J = 3 Hz, 1 H), 7.73 (d, J = 3 Hz, 1 H), 7.87 (d, J = 3 Hz, 1 H); IR 1606 cm^{-1}. Anal. Calcd for $C_{13}H_9N_3S_2$: C, 57.54; H, 3.34; N, 15.49. Found: C, 57.46; H, 3.25; N, 15.37.

***N*-[Bis(1-methylpyrrol-2-yl)methylene]aniline (5h)**: yield 87%; mp 53–55 °C; NMR δ 3.00 (s, 3 H), 3.92 (s, 3 H), 5.88–7.25 (m, 11 H); IR 1571 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.53; H, 6.51; N, 15.96. Found: C, 77.43; H, 6.43; N, 16.00.

***N*-[α-(2-Furanyl)benzylidene]aniline[13] (8a)**: yield 95%; mp 72–73 °C; NMR δ 6.10–7.90 (m). Anal. Calcd for $C_{17}H_{13}NO$: C, 82.55; H, 5.30. Found: C, 82.53; H, 5.35.

***N*-(2-Furanyl-2-thienylmethylene)aniline (8c)**: yield 96%; oil; NMR δ 6.10–6.55 (m, 2 H), 6.66–7.70 (m, 9 H). Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38. Found: C, 71.20; H, 4.41.

General Procedure for the Preparation of Ketones 6a–h and 9a,c. A solution of Schiff's base **5a–h** (1.0 mmol) in methanol (15 mL) was treated with a 5% solution of HCl in aqueous methanol (1:1, 5 mL), and the mixture was stirred at 23 °C for 2 h. Then the mixture was diluted with water (10 mL) and extracted with ether. The ether was washed with an aqueous solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated. Crude ketones **6** were purified by flash chromatography on silica gel (triethylamine/hexanes, 1:1), and the purified samples were crystallized from dry hexanes. **6a**: yield 99%; mp 49–51 °C. **6b**: yield 95%; mp 69–71 °C (lit.[6b] mp 72 °C). **6c**: yield 99%; mp 86–88 °C (lit.[6f] mp 87–88.5 °C). **6d**: yield 95%; mp 75–78 °C (lit.[6h] mp 78–80 °C); NMR δ 7.90 (dd, J = 3 Hz, J = 2 Hz, 2 H), 7.52 (dd, J = 5 Hz, J = 2 Hz, 2H), 7.27 (dd, J = 5 Hz, J = 3 Hz). **6e**: yield 95%; mp 167–169 °C (lit.[6i] mp 167.5 °C); NMR δ 8.07 (s, 2 H), 7.13–7.97 (m, 8 H). **6f**: yield 92%; mp 30–32 °C (lit.[6j] mp 33 °C). **6g**: yield 92%; mp 138–140 °C (lit.[6k] mp 140–141 °C). **6h**: yield 84%; mp 24–26 °C (lit.[6o] mp 25–26 °C). Schiff's bases **8a,c** were hydrolyzed using the same procedure. **9a**: yield 93%; mp 42–44 °C (lit.[6v] mp 43.5–44 °C). **9c**: yield 92%; oil [lit.[6w] bp 140–141 °C (5 mm)]. Ketones **6** and **9** gave NMR spectra virtually identical with those published: **6b**,[6d,e] **6c**,[6x] **6f**,[6y] **6g**,[6k,m] **6h**,[6n–p] **9a**,[6z] **9c**.[6x]

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Registry No. 1, 6780-49-0; **3a**, 538-51-2; **3c**, 5918-68-3; **4a**, 1865-12-9; **4b**, 123209-08-5; **4c**, 123209-09-6; **4d**, 123209-10-9; **4e**, 123239-43-0; **4f**, 123209-11-0; **4g**, 123209-12-1; **4h**, 123209-13-2; **4i**, 29647-68-5; **5a**, 574-45-8; **5b**, 62093-69-0; **5c**, 123209-15-4; **5d**, 123209-16-5; **5e**, 123209-17-6; **5f**, 123209-18-7; **5g**, 123209-19-8; **5h**, 123209-20-1; **6a**, 119-61-9; **6b**, 1018-97-9; **6c**, 704-38-1; **6d**, 26453-81-6; **6e**, 97978-07-9; **6f**, 17920-86-4; **6g**, 55707-55-6; **6h**, 80838-84-2; **7a**, 36749-19-6; **7b**, 779-54-4; **7c**, 123209-14-3; **8a**, 123209-21-2; **8c**, 123209-22-3; **9a**, 2689-59-0; **9c**, 20409-51-2; PhMgBr, 100-58-3; PhLi, 591-51-5; *o*-MeC_6H_4Li, 6699-93-0; BuLi, 109-72-8; 2-thienylmagnesium bromide, 5713-61-1; 2-thienyllithium, 2786-07-4; 3-thienyllithium, 1192-06-9; 2-benzo[*b*]thienyllithium, 50779-55-0; 2-furyllithium, 2786-02-9; 2-thiazolyllithium, 40610-14-8; (*N*-methyl-2-pyrrolyl)lithium, 31785-72-5.

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A Practical, Efficient Large-Scale Synthesis of 1,6-Anhydrohexopyranoses[1]

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1,6-Anhydrohexopyranoses have proven to be valuable synthons for the preparation of biologically important and structurally diverse natural products (e.g. rifamycin S,[3a] indanomycin,[3b] thromboxane B2,[3c] (+)-biotin,[3d] tetrodotoxin,[3e] quinone,[3f] and macrolide[3g] antibiotics, etc.) as well as for modified sugars.[4,5] Their [3.2.1]bicyclic framework elicits high stereo- and regioselectivities, and the fact that the pyranose ring is locked in the $^1C_4$ conformation generates stereocenters which are opposite to those encoun-

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