amount used) of TMSOTf was added to a solution of 6-*O*-(*tert*-butyldiphenylsilyl) derivative **2**, and the first portion (one-third of the total amount used) of trimethylsilyl glycoside **1** dissolved in the appropriate solvent (see Table I for details). The reaction was followed by TLC, and subsequent portions of glycoside **1** and TMS triflate were added periodically. When the reaction was complete, the reaction mixture was neutralized with triethylamine, diluted with dichloromethane, washed with water, aqueous sodium bicarbonate, and water again, and dried. Concentration, followed by column chromatography yielded products **3a–e** listed below.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-acetyl-β-D-galactopyranoside (3a): prepared from methyl 2,3,4-tri-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside[2] (**2a**; 0.056 g, 0.1 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[10] (**1a**; 0.055 g, 0.13 mmol); TLC, solvent A (7:2). Column chromatography [solvent B (4:1)] gave **3a**: 0.046 g (70%); mp 121–122 °C (lit.[16] mp 122 °C); ^{1}H NMR δ 5.37 (br d, 1 H, $J_{3,4}$ = 3.2 Hz, H-4), 4.94–5.21 (m, 5 H, H-2,2′,3,3′,4′), 4.58 (d, 1 H, $J_{1',2'}$ = 8.1 Hz, H-1′), 4.38 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 4.13–4.31 (m, 2 H, H-6,6a′), 3.65–3.97 (m, 4 H, H-5,5′,6,6a), 3.53 (s, 3 H, OCH_3).

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3b): obtained from methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside[2] (**2b**; 0.37 g, 0.5 mmol) and **1a** (0.27 g, 0.65 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3b**: 0.31 g (74%); $[\alpha]_D$ + 92.3° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 5.69 (br d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4), 5.58 (dd, 1 H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.4 Hz, H-2), 5.38 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.4 Hz, H-3), 4.81–5.04 (m, 3 H, H-2′,3′,4′), 4.52 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1′), 3.48–4.04 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.43 (s, 3 H, OCH_3); ^{13}C NMR δ 102.4 (C-1), 100.7 (C-1′), 73.2, 73.8 (C-5,3′), 71.9, 71.8, 71.2 (C-3,2′,5′), 69.7 (C-2), 68.6, 68.3, 68.1 (C-4,6,4′), 61.8 (C-6′), 57.2 (OCH_3). Anal. Calcd for $C_{42}H_{44}O_{18}$: C, 60.28; H, 5.3. Found: C, 59.99; H, 5.27.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3c): (a) prepared from **2b** (0.3 g, 0.4 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[10] (**1c**, 0.18 g, 0.43 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3c**: 0.26 g (76%); mp 214–215 °C (lit.[17] mp 215–216 °C); ^{1}H NMR and ^{13}C NMR spectral data are in agreement with the literature,[17] except for the joint assignment of carbon signals at 70.8 and 70.9 to C-3′,5′, which were misprinted as assigned to C-5,3′. (b) Obtained from **2b** (0.224 g, 0.3 mmol) and trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (**1c-α**, 0.16 g, 0.38 mmol); TLC, solvent A (7:1). Column chromatography [solvent A (10:1)] gave **3c**: 0.12 g (47%).

3-Azi-1-methoxybutyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3d): obtained from 3-azi-1-methoxybutyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside (**2d**, 0.067 g, 0.08 mmol) and **1c** (0.047 g, 0.11 mmol); TLC, solvent C (3:1) gave **3d**: 0.04 g (54%); mp 123–125 °C; $[\alpha]_D$ +122.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 5.93–6.03 (m, 2 H, H-2,4 of two isomers), 5.63–5.73 (m, 2 H, H-1,3 of two isomers), 5.37 (br d, 1 H, $J_{3',4'}$ ~ 3.3 Hz, H-4′), 5.19 (dd, 1 H, $J_{1',2'}$ = 7.9 Hz, $J_{2',3'}$ = 10.3 Hz, H-2′), 5.02 (dd, 1 H, $J_{2',3'}$ = 10.3 Hz, $J_{3',4'}$ = 3.3 Hz, H-3′), 4.90–4.94 and 4.54–4.58 (2 m, 1 H, H_α of two isomers), 4.66–4.74 (m, 1 H, H-5 of two isomers), 4.52 (d, 1 H, $J_{1',2'}$ = 7.9 Hz, H-1′), 3.74–4.15 (m, 5 H, H-6,6a,5′,6′,6a′), 3.14 and 3.37 (2 s, 3 H, OCH_3 of two isomers), 1.98, 2.01, 2.09 and 2.16 (4 OAc), 1.57–1.83 (m, 1 H, H_β of two isomers), 1.02 and 1.18 (2 s, 3 H, CH_3 of two isomers); ^{13}C NMR δ 98.1 and 102.3 (C_α of two isomers), 101.1 and 101.3 (C-1′ of two isomers), 92.9 and 93.1 (C-1 of two isomers), 70.8, 70.9, 71.0 (C-3′,5′ of two isomers), 68.2, 68.3, 68.4, 68.6, 68.8, 69.0, 69.4, 69.5 (C-2,3,4,5,6,2′ of two isomers), 67.0 (C-4′), 61.2 (C-6′), 52.1, 55.9 (OCH_3 of two isomers), 38.8, 38.9 (C_β of two isomers), 23.2 (C_γ of two isomers), 20.7 ($COCH_3$), 20.3 (C_γ-CH_3). Anal. Calcd for $C_{46}H_{50}N_2O_{19}$: C, 59.10; H, 5.39; N, 3.00. Found: C, 59.02; H, 5.45; N, 3.21.

(16) Bredereck, H.; Wagner, A.; Geissel, D.; Gross, P.; Hutten, U.; Ott, H. *Ber.* **1962**, *95*, 3056–3063.
(17) Kovac, P. *Carbohydr. Res.* **1986**, *153*, 237–251.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-β-D-galactopyranoside (3e): prepared from methyl *O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranosyl]-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside[2] (**2e**; 0.192 g, 0.1 mmol) and **1a** (0.067 g, 0.16 mmol); TLC, solvent A (10:1) or B (9:2). Column chromatography [solvent A (15:1)] gave **3e**: 0.146 g (72%); mp 163–165 °C; $[\alpha]_D$ +200.0° (*c* 0.6, $CHCl_3$); ^{1}H NMR δ 5.79, 5.87, 5.99 (3 br d, 3 H, $J_{3,4}$ = $J_{3',4'}$ = $J_{3'',4''}$ ~ 3.4 Hz, H-4,4′,4″), 5.43–5.76 (m, 6 H, H-2,3,2′,3′,2″,3″), 4.81–5.14 (m, 3 H, H-2‴,3‴,4‴), 4.83 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.59, 4.62 (2 d, 2 H, $J_{1,2}$ = $J_{1'',2''}$ = 7.9 Hz, H-1,1″), 4.08 (d, 1 H, $J_{1''',2'''}$ = 7.8 Hz, H-1‴), 3.63–4.20 (m, 12 H, H-5,6,6a,5′,6′,6a′,5″,6″,6a″,5‴,6‴,6a‴), 3.30 (s, 3 H, OCH_3), 1.92–2.04 (4 s, 12 H, 4 OAc); ^{13}C NMR δ 102.2 (C-1), 100.4, 100.7, 101.2 C-1′,1″,1‴), 72.3, 72.7, 72.9 (C-5,5′,5″), 71.1, 71.7 (2 C), 71.8 (2 C), (C-3,3′,3″,3‴,5‴), 69.8 (2 C), 70.0 (C-2,2′,2″), 66.2, 67.2, 67.7, 68.0 (2 C), 68.1, 68.6 (C-4,6,4′,6′,4″,6″,2‴,4‴), 61.7 (C-6‴), 56.8 (OCH_3), 20.5, 20.6 ($COCH_3$). Anal. Calcd for $C_{114}H_{100}O_{34}$: C, 67,99; H, 5.00. Found: C, 67.66; H, 5.14.

De-O-acylation of tetrasaccharide **3e** [0.05 g, 0.025 mmol; $NaOCH_3$, methanol–toluene (5:1), pH ~ 9, 60 °C, 24 h] gave, after purification (HPLC: Zorbax-NH_2, 5% CH_3CN/H_2O), methyl *O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-galactopyranosyl-(1→6)-*O*-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (**4e**): 0.017 g (82%); MS (Cf) $[M + Na]^+$ 703.2 (calcd for $C_{25}H_{44}O_{21}$: MS 680.237).

Registry No. **1a**, 19126-95-5; **1c**, 117405-70-6; **1c-α**, 123163-89-3; **2a**, 110319-38-5; **2b**, 110319-39-6; **2d** isomer 1, 123076-15-3; **2d** isomer 2, 123076-20-0; **2d** deprotected deriv isomer 1, 117405-74-0; **2d** deprotected deriv isomer 2, 117405-77-3; **2e**, 110319-60-3; **3a**, 97058-67-8; **3b**, 123076-16-4; **3c**, 108999-02-6; **3d** isomer 1, 123076-17-5; **3d** isomer 2, 123163-90-6; **3e**, 123076-18-6; **4e**, 123076-19-7; 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose, 70191-05-8.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) Oxidation of Silyl Enol Ethers to Enones via DDQ–Substrate Adducts

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Received May 8, 1989

Recently we reported[1] that the reaction of silyl imidates of the 4-aza-3-keto steroids with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) affords Δ^1-lactams via unprecedented adduct formation between the substrate and quinone followed by an electrocyclic reaction to establish the unsaturation. Oxidation of ketones to enones via reaction of their silyl enol ethers with DDQ was believed to involve allylic hydride abstraction to afford an oxygenated allylic cation which furnishes enone on workup.[2] Reinvestigation of this reaction has now established the intermediacy of substrate–quinone adducts.

(1) Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Douglas, A. W.; Grabowski, E. J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3318–3319.
(2) (a) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736–738. (b) Jung, M. E.; Pan, Y.-G.; Rathke, M. W.; Sullivan, D. F.; Woodbury, R. P. *J. Org. Chem.* **1977**, *42*, 3961–3963. (c) Ryv, I.; Murai, S.; Hatayame, Y.; Sonoda, N. *Tetrahedron Lett.* **1978**, 3455–3458. (d) Fevig, T. L.; Elliott, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064–5067.

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Scheme I

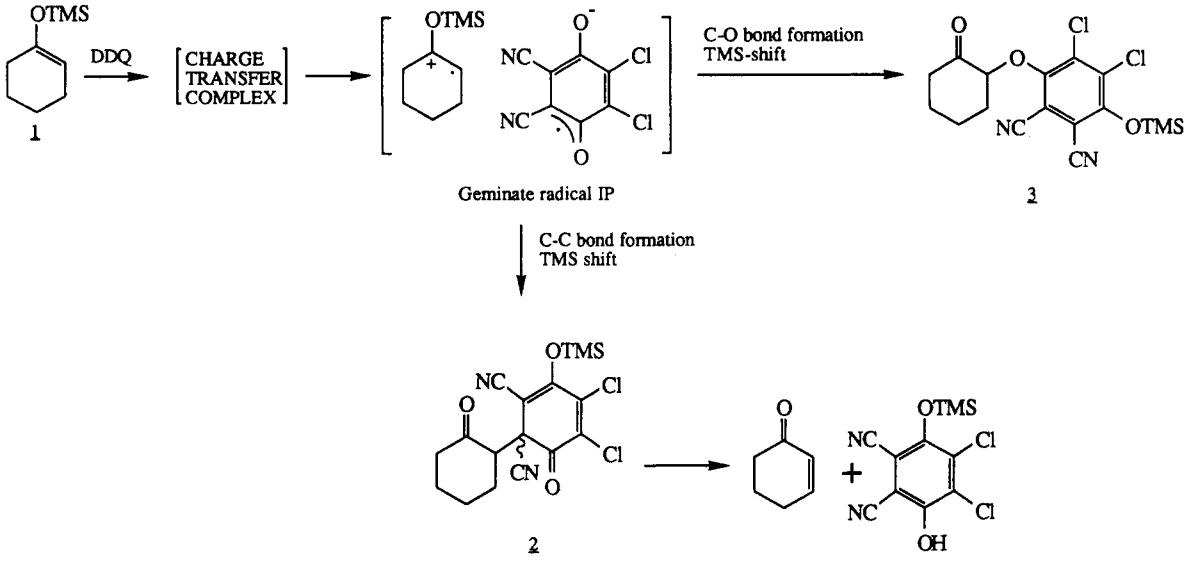
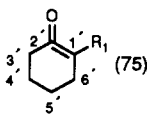
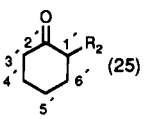
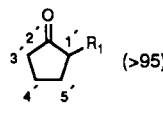
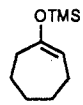
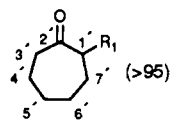
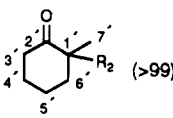
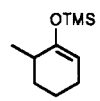
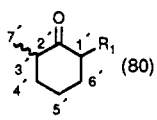
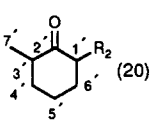
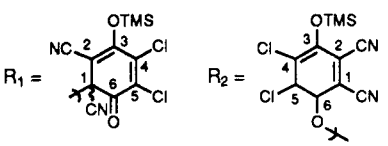


Table I. Adduct Distribution of the DDQ Oxidation as a Function of the Substrate (22 °C, THF-d_8)[a]

entry	substrate	adducts (distribution)[b]	
1[c]	 1	 (75) 2	 (25) 3
2	 4	 (>95) 5	
3	 6	 (>95) 7	
4	 8	 (>99) 9	
5[d]	 10	 (80) 11	 (20) 12

[a] Traces of the corresponding enones were produced in each case. [b] These are mole percentages based on ^{1}H NMR integrations. [c] R_1 and R_2 are as follows:



[d] Four stereoisomers for 11 and one stereoisomer for 12 were formed.

Results and Discussion

The reaction of silyl enol ether 1 and DDQ (Table I, entry 1) was examined at intervals using in situ NMR spectroscopy (^{13}C, ^{1}H, and ^{29}Si NMR). At 22 °C the adduct formation in dioxane-d_8 was complete within minutes as was apparent from the immediate color change from deep purple to light yellow.[3] Diastereomeric carbon–carbon adducts 2 and carbon–oxygen adduct 3 were produced. Heating the solution to 100 °C for 24 h completely converted 2 to 2-cyclohexen-1-one, presumably via a concerted six-electron pathway,[4] while 3 remained unchanged. Diagnostic ^{13}C resonances for 2 are the set of substituted C-1′ carbons (δ_C = 63.2, 65.2 ppm) and the quaternary C-1 carbons (δ_C = 49.5, 50.7 ppm). In 3, the key ^{13}C resonance is C-1′ (δ_C = 86.1 ppm). The equatorial disposition of R_1 and R_2 in 2 and 3 was established by ^{1}H–^{1}H vicinal diaxial couplings (12.7 Hz for 2 and 10.7 Hz for 3). Silicon-29 NMR indicated that the adduct formation was concomitant with migration of the silyl group from the silyl enol ether (δ_{Si} = 16.1 ppm) to the DDQ derived substituents in 2 (δ_{Si} = 29.7, 29.9 ppm) and 3 (δ_{Si} = 27.0 ppm). Unsilylated 3 was isolated and characterized by NMR and HRMS; isolation of 2 was unsuccessful due to its inherent reactivity. Tables I and II summarize the results of combined solvent–temperature–substrate studies for this reaction. The adduct distribution is a function of the substrate structure as shown in Table I, although no structural correlation emerges. The results in Table II indicate that formation of 3 was suppressed at lower temperatures and in polar solvents. The dramatic solvent–temperature effect

Table II. Solvent–Temperature Studies of the Reaction between DDQ and 1

entry	solvent (μ)[a]	temperature, °C	adduct ratio (2:3)[b]
1[c]	benzene (0)	22	1:1
2[c]	dioxane (0)	22	2:1
3	CH_2Cl_2 (0.6)	22	1.5:1
4	THF (0.63)	22	3:1
5	THF	−40	19:1
6	CD_3NO_2 (3.46)	22	6.0:1
7	CD_3CN (3.92)	22	9:1
8	CD_3CN	−20	99:1

[a] Dipole moment in Debyes. [b] These are mole ratios based on ^{1}H NMR integrations. [c] A trace of phenylsilyl ether is formed.

(3) Charge-transfer absorption maxima of the colored electron-donor–acceptor (EDA) complex of the enol ethers with DDQ in dry THF was 520 nm for 1, 580 nm for 10, and 600 nm for 8.

(4) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1971; pp 169–173.

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.

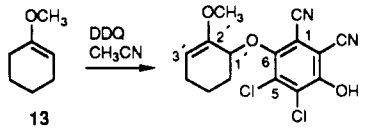
Acknowledgment. We thank Dr. A. W. Douglas and R. A. Reamer for their helpful discussions and support throughout this investigation. We also thank J. L. Smith for the mass spectral studies.

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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Received April 20, 1989

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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