Ring-Fused Cyclopropanone *N,O*-Acetals. Electrochemical Preparation and Their Reactivities under Acidic Conditions

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Introduction

Recently, we reported that the indirect electrooxidation of enamines (**1**) in a KI−NaCN−MeOH system induces their intramolecular cyclization and simultaneous cyanation to give ring-fused cyclopropane aminonitriles (**3**).[1] Subsequently, we found that the analogous electrolysis of **1** in KI−NaOMe−MeOH produces the corresponding bicyclo[*n*.1.0]alkanone *N*,*O*-acetals **2**. *N*,*O*-Acetals such as **2** can serve as precursors of bicyclic iminium cations (**4**) which can be trapped by various nucleophiles,[2] and a series of studies on such compounds has been made by Vilsmaier and co-workers, who examined their stereochemistry[3] and synthetic applications.[4] According to their reports, cyclopropanone *N*,*O*-acetals **2** can be obtained by reacting chloroenamines or enaminosulfonium salts with alcoholate,[5] or by alcoholysis of cyclopropanone aminals,[2b] which can be obtained from 2-chlorocycloalkanones and secondary amines.[6]

In this report, we present an alternative method for preparing **2** using an electrochemical technique and several transformations of the resulting products under acidic conditions.

Results and Discussion

Electrolysis of Enamines. Preparative electrolyses were carried out in a divided cell using a platinum anode. In all cases, enamines **1** were electrolyzed under a constant current until 2F/mol of charge had passed through the cell. Cyclopropanation accompanied by methoxylation occurred stereoselectively and resulted in the exclusive formation of *exo*-methoxylated **2**. As shown in Table 1, the corresponding *N*,*O*-acetals **2** were obtained from various **1** in yields of 63−74%.

The transformation of **1** into **2** occurred with somewhat lower yields even if the amounts of KI and sodium methoxide were decreased to 0.2 mol % for the enamine. However, replacement of KI with another halogen ion source, such as KBr or KCl, gave no bicyclic compounds, and instead methoxyenamine[7] was formed in low yield.

The structures of **2** were established by comparison of spectral data with those reported in the literature. In the ^{1}H NMR spectra of **2e** and **2g**, the methylene signals of the morpholino moiety showed an ABXY pattern, which supports the notion that the morpholine ring is in an *endo* position.[3a,b] The stereochemical configuration of **2g** was also determined by an X-ray crystallographic analysis, in which the methoxy group took an *exo* position and the six-membered ring fused to a three-membered ring adopted a half-chair form.

Reactivities of 2 under Acidic Conditions. The resulting *N*,*O*-acetals **2** were highly susceptible to acidic aqueous conditions, and different reactivities between the bicyclohexane and bicycloheptane derivatives were observed in acid-catalyzed hydrolysis and alcoholysis, as has been reported in the case of aminals.[6] For example, treatment of bicyclohexanone *N*,*O*-acetal **2e** with dilute H_2SO_4 at room temperature gave 2-hydroxycyclohexanone (**5**) in 84% yield (Scheme 1), which was isolated as its dimer (**6**), whereas with concentrated HCl, the predominant product was 2-chlorocyclohexanone (**7**). In contrast, similar treatment of bicycloheptanone *N*,*O*-acetal **2g** with dilute H_2SO_4 resulted in the formation of the *N*,*O*-semiacetal (**8**).[6]

On the other hand, the reaction of **2e** with excess methanol in the presence of a catalytic amount of H_2SO_4 at room temperature for 1 h gave the allylic methoxyenamine (**9**) in 78% yield,[5b] presumably via the cycloallylic carbonium ion (**14**). Upon heating at 90 °C or above, the enamine **9** underwent thermal isomerization to give a mixture of **9** and the vinylic methoxyenamine (**10**) in a ratio of 7:3. Likewise, the reaction with ethanol gave the allylic ethoxyenamine (**11**) in a comparable yield.

However, during the ethanolysis of **2g**, replacement of the methoxy by an ethoxy group took place without causing ring-opening, to give the ethoxynorcarane (**13**) in 78% yield. The alcoholyses of **2** were markedly facilitated by a catalytic amount of acid, in contrast to being inhibited by alkaline. Upon adding a few drops of concentrated H_2SO_4 to the alcohol solution of **2**, alcoholysis was completed within 2 h at room temperature in all cases. In the absence of acid catalyst, a reaction time of 2 weeks may be required to complete the ethanolysis of **2f**.[2b] Analogously, treatment of **2e** with acetic acid at room temperature yielded acetoxyenamine (**12**) in 88% yield.

The above reactions appear to proceed through the iminium cation **4**. The different reactivities of the bicyclohexanone and bicycloheptanone *N*,*O*-acetals (**2e**, **2g**) may be due to the strain in the bicyclic system. The cyclopropane ring fused to a five-membered ring seems

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Scheme 1

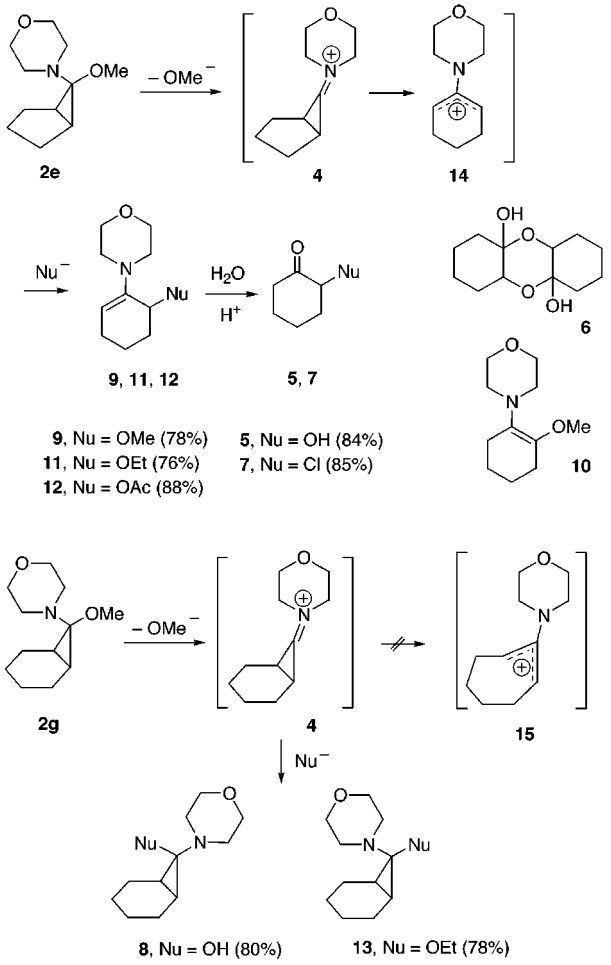
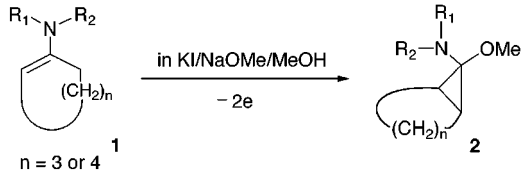


Table 1. Electrochemical Preparation of *N,O*-Acetals 2 from Enamines 1[a]



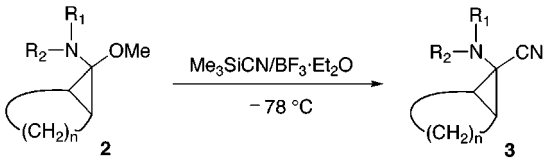
	enamine 1			cyclopropanone *N,O*-acetal **2** (yield, %)[b]
	R_1	R_2	*n*	
1a[c]	Et	Et	3	**2a** (67)
1b[d]	Me	Ph	3	**2b** (69)
1c[c]	$-(CH_2)_4-$		3	**2c** (63)
1d[c]	$-(CH_2)_5-$		3	**2d** (71)
1e[d]	$-(CH_2)_2O(CH_2)_2-$		3	**2e** (74)
1f[d]	$-(CH_2)_4-$		4	**2f** (63)
1g[d]	$-(CH_2)_2O(CH_2)_2-$		4	**2g** (66)

[a] Anolyte: enamine **1** (30 mmol) and KI (30 mmol) in 1 M NaOMe–MeOH (80 mL). Strength of constant current: 0.5 A. Current passed: 2 F/mol. [b] Isolated yield. [c] At rt. [d] At 40 °C.

to favor the ring-opening reaction to give the monocyclic system (**14**), due to the release of strain, whereas the cyclopropane ring fused to a six-membered ring does not rearrange into the strained cycloheptenyl cation (**15**).

Preparation of Aminonitrile 3 from 2. The addition of Lewis acids to *N,O*-acetals **2** at low temperature was expected to produce iminium cations (**4**), which are stable enough to be trapped in situ by various nucleophiles. The methoxy group of **2** was replaced by a cyano group using

Table 2. Preparation of Aminonitriles 3 from *N,O*-Acetals 2[a]



	N,O-acetal **2**			aminonitrile **3** (yield, %)[b]
	R_1	R_2	*n*	
2a	Et	Et	3	**3a** (84)
2b	Me	Ph	3	**3b** (86)
2c	$-(CH_2)_4-$		3	**3c** (63)
2e	$-(CH_2)_2O(CH_2)_2-$		3	**3e** (54)
2f	$-(CH_2)_4-$		4	**3f** (90)
2g	$-(CH_2)_2O(CH_2)_2-$		4	**3g** (73)

[a] *N,O*-Acetals **2** (20 mmol), Me_3SiCN (30 mmol), $BF_3{\cdot}Et_2O$ (30 mmol) in CH_2Cl_2 (80 mL) at −78 °C for 2 h. [b] Isolated yield.

Me_3SiCN as a carbon nucleophile and BF_3 etherate as the Lewis acid at − 78 °C. As shown in Table 2, not only bicycloheptanone but also bicyclohexanone *N,O*-acetals exclusively provided the corresponding *exo*-nitriles (**3**) in good yields. The pyrrolidinonitriles (**3c**, **3f**) obtained in this way were identical to those prepared by our analogous electrooxidation of **1** in a KI–NaCN–MeOH system.[1] X-ray crystallographic analysis of **3g** indicated that the amino group is in the *endo* configuration.

Experimental Section

Melting and boiling points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 90 and 22.4 MHz, respectively, unless otherwise noted, using $CDCl_3$ as a solvent. Chemical shifts are given in ppm downfield (δ) from TMS as an internal standard. IR spectra were obtained from neat films unless otherwise noted. MS were obtained at an ionization potential of 70 eV.

Enamines **1a**–**g** were prepared as described in the literature.[8,9] **1a**: bp 60 °C (4 mmHg) [lit.[8] bp 64 °C (6 mmHg)]. **1b**: bp 100–112 °C (2 mmHg) [lit.[10] bp 148–153 °C (12 mmHg)]. **1c**: bp 68–70 °C (2 mmHg) [lit.[11] bp 92–93 °C (5 mmHg)]. **1d**: bp 88 °C (3 mmHg)[lit.[12] bp 116–118 °C (16 mmHg)]. **1e**: bp 95–97 °C (4 mmHg) [lit.[10] bp 117–120 °C (10 mmHg)]. **1f**: bp 80–83 °C (2 mmHg) [lit.[11] bp 100–102 °C (5 mmHg)]. **1g**: bp 97–99 °C (3 mmHg) [lit.[10] bp 133–135 °C (17 mmHg)]. Me_3SiCN was prepared according to the reported method.[13] Bp 114 °C (lit.[13] bp 117–118 °C).

Electrolysis of Enamines 1a–g. General Procedure. The apparatus used for electrolysis was similar to that described earlier,[1] except that a porous porcelain cup (23 mm in diameter, 60 mm long, 1.5 mm wall thickness) served as the cathode compartment. A solution of **1** (30 mmol) in 1 M NaOMe–MeOH (80 mL) containing KI (30 mmol) was electrolyzed under a constant current of 0.5 A at room temperature (**1a**, **1c**, **1d**) or at 40 °C (**1b**, **1e**, **1f**, **1g**). After 2 F/mol of electricity had passed through the anolyte, MeOH was removed by evaporation, and water (20 mL) was added to the residue. The oily layer was extracted with Et_2O (20 mL × 3), washed with brine (20 mL), dried (Na_2SO_4), and distilled in vacuo after removal of the drying agent. Product yields are given in Table 1. Analytical samples were obtained by redistillation or recrystallization.

6-*endo*-Diethylamino-6-*exo*-methoxybicyclo[3.1.0]-hexane (2a): bp 65–66 °C (4 mmHg); IR ν 1097 cm^{-1}; ^1H NMR (400 MHz) δ 1.08 (t, J = 7.2 Hz, 6H), 1.5–1.6 (m, 3H), 1.6–1.8

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(m, 5H), 2.96 (q, J = 7.2 Hz, 4H), 3.27 (s, 3H); ^{13}C NMR (100 MHz) δ 13.9 (CH_3), 45.4 (CH_2), 25.3 (CH_2), 26.7 (CH_2), 33.4 (CH), 55.0 (CH_3), 84.5 (C); MS m/z (relative intensity) 183 (M^+, 49), 168 (100), 152 (50); HR-MS calcd for $C_{11}H_{21}N_1O_1$, 183.1623. Found, 183.1617. Anal. Calcd for $C_{11}H_{21}N_1O_1$: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.04; H, 11.34; N, 7.60.

6-*endo*-Methylphenylamino-6-*exo*-methoxybicyclo[3.1.0]-hexane (2b): bp 120 °C (3 mmHg); IR ν 1101 cm^{-1}; ^{1}H NMR δ 0.7−2.1 (m, 8H), 3.10 (s, 3H), 3.23 (s, 3H), 6.6−7.4 (m, 5H); ^{13}C NMR δ 38.6 (CH_3), 113.3 (CH), 117.7 (CH), 128.7 (CH), 147.2 (C) 23.5 (CH_2), 26.4 (CH_2), 27.0 (CH_2), 30.6 (CH), 34.7 (CH), 53.6 (CH_3), 80.3 (C); MS m/z (relative intensity) 217 (M^+, 59), 184 (100). Anal. Calcd for $C_{14}H_{19}N_1O_1$: C, 77.38; H, 8.81; N, 6.41. Found: C, 77.63; H, 8.97; N, 6.43.

6-*exo*-Methoxy-6-*endo*-pyrrolidinobicyclo[3.1.0]hexane (2c): bp 68−71 °C (4 mmHg); IR ν 1082 cm^{-1}; ^{1}H NMR δ 1.4−2.0 (m, 12H), 2.9−3.2 (m, 4H), 3.30 (s, 3H); ^{13}C NMR δ 25.4 (CH_2), 47.8 (CH_2), 25.8 (CH_2), 26.6 (CH_2), 32.3 (CH), 55.4 (CH_3), 79.4 (C); MS m/z (relative intensity) 181 (M^+, 70), 166 (90), 150 (100). Anal. Calcd for $C_{11}H_{19}N_1O_1$: C, 72.88; H, 10.57; N, 7.73. Found: C, 72.77; H, 10.52; N, 7.79.

6-*exo*-Methoxy-6-*endo*-piperidinobicyclo[3.1.0]hexane (2d): bp 80−82 °C (4 mmHg); IR ν 1080 cm^{-1}; ^{1}H NMR δ 1.2−1.8 (m, 14H), 2.6−3.4 (m, 4H), 3.35 (s, 3H); ^{13}C NMR δ 25.3 (CH_2), 26.6 (CH_2), 51.0 (CH_2), 26.8 (CH_2), 32.9 (CH), 56.3 (CH_3), 83.9 (C); MS m/z (relative intensity) 195 (M^+, 33), 180 (54), 164 (100). Anal. Calcd for $C_{12}H_{21}N_1O_1$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.70; H, 10.84; N, 7.08.

6-*exo*-Methoxy-6-*endo*-morpholinobicyclo[3.1.0]hexane (2e): bp 95−97 °C (4 mmHg) [lit.[5b] bp 77−79 (0.04)]. The IR, ^{1}H NMR, and ^{13}C NMR spectra of **2e** agreed with those reported in the literature.[5b]

7-*exo*-Methoxy-7-*endo*-pyrrolidinobicyclo[4.1.0]heptane (2f): bp 84−87 °C (4 mmHg). The IR and ^{1}H NMR spectra agreed with those reported in the literature.[2b] ^{13}C NMR δ 25.0 (CH_2), 47.8 (CH_2), 19.9 (CH_2), 21.7 (CH_2), 22.1 (CH), 55.7 (CH_3), 79.5 (C); MS m/z (relative intensity) 195 (M^+, 7), 163 (53), 70 (100). Anal. Calcd for $C_{12}H_{21}N_1O_1$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.76; H, 10.87; N, 7.27.

7-*exo*-Methoxy-7-*endo*-morpholinobicyclo[4.1.0]heptane (2g): mp 54−55.5 °C (prisms from *n*-pentane, − 50 °C), bp 103−107 °C (4 mmHg) [lit.[3b] mp 49 °C, bp 57−62 °C (0.007). The IR, ^{1}H NMR, and ^{13}C NMR spectra of **2g** agreed with those reported in the literature.[3b]

Acid Hydrolysis of *N,O*-Acetals 2e and 2g. A heterogeneous mixture of *N,O*-acetal **2e** (1.97 g, 10 mmol) in CH_2Cl_2 (10 mL) and 3 N H_2SO_4 (10 mL) was stirred at room temperature for 5 h. After the reaction was complete, the organic layer was separated, and the water layer was shaken with CH_2Cl_2 (20 mL × 3). The combined CH_2Cl_2 layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was subjected to column chromatography on silica gel with Et_2O to give 2-hydroxycyclohexanone **5** (0.96 g, 84% yield). **5:** bp 83−86 °C (14 mmHg); IR ν 3400, 1710 cm^{-1}. The hydroxy ketone **5** dimerized and solidified upon standing overnight. Dimer of **5** (**6**)**:** mp 110−113 °C (lit.[14] mp 114−118 °C); IR (KBr) ν 3350 cm^{-1}, no (CO). This was identified by direct comparison with an authentic sample.[14]

Similar treatment of **2e** (1.97 g, 10 mmol) with concentrated HCl (10 mL) in CH_2Cl_2 (10 mL) gave 2-chlorocyclohexanone **4** (1.12 g, 85% yield). **4:** bp 85−89 °C (14 mmHg) [lit.[15] bp 90−91 °C (14−15 mmHg)]. This was identified by comparison to an authentic sample prepared as described in the literature.[15]

A solution of *N,O*-acetal **2g** (8.77 g, 45 mmol) in CH_2Cl_2 (50 mL) was occasionally shaken with 3 N H_2SO_4 (40 mL) for 2 h. After the CH_2Cl_2 layer was removed, the aqueous layer was washed with CH_2Cl_2 (20 mL) and added dropwise to 3 N NaOH (60 mL) with stirring at ice-bath temperature. The white solid was collected by filtration and washed with small portions of cold water. Almost pure *N,O*-semiacetal **8** was obtained (6.47 g 80% yield).

7-*endo*-Hydroxy-7-*exo*-morpholinobicyclo[4.1.0]heptane (8): mp 130−132 °C (rodlike crystals from Et_2O) (lit.[3b] mp 128 °C). The IR, ^{1}H NMR, and ^{13}C NMR spectra of **8** agreed with those reported in the literature.[3b]

Acid-Catalyzed Alcoholysis of *N,O*-Acetal 2e and 2g. General Procedure. To a solution of *N,O*-acetal **2** (10 mmol) in absolute alcohol (20 mL) was added a few drop of concentrated H_2SO_4 with stirring at room temperature. After 2 h, a small amount of K_2CO_3 (10 mg) was added to the reaction mixture, and the alcohol was removed by evaporation. The residue was treated with saturated aqueous $NaHCO_3$ (10 mL), and the oily layer was extracted with Et_2O (20 mL × 3), dried (K_2CO_3), and distilled in vacuo.

1-Methoxy-6-morpholinocyclohexene (9): yield 78%; bp 63−64 °C (0.05 mmHg) [lit.[5b] bp 62−64 °C (0.04 mmHg)]. The IR, ^{1}H NMR, and ^{13}C NMR spectra of this fraction agreed with those reported in the literature.[5b] Distillation at a higher temperature gave a mixture of allylic and vinylic methoxyenamines (**10**).[7] For example, a fraction at 100−102 °C (3 mmHg) consisted of two regioisomers **9**/**10**, in a ratio of 7:3. Allylic methoxyenamine **9**: ^{13}C NMR δ 48.7 (CH_2), 67.0 (CH_2), 17.5 (CH_2), 24.6 (CH_2), 26.4 (CH_2), 55.3 (CH_3), 71.3 (CH), 104.0 (CH), 145.4 (C). Vinylic methoxy enamine **10**: ^{13}C NMR δ 50.1 (CH_2), 67.7 (CH_2), 23.0 (CH_2), 23.2 (CH_2), 24.4 (CH_2), 26.2 (CH_2), 56.3 (CH_3), 128.1 (C), 143.1 (C).

1-Ethoxy-6-morpholinocyclohexene (11): yield 76%; bp 58−59 °C (0.07 mmHg); IR ν 1647, 1123 cm^{-1}; ^{1}H NMR δ 1.21 (t, J = 7 Hz, 3H), 1.4−2.3 (m, 6H), 2.7−3.0 (m, 4H), 3.6−4.0 (m, 7H), 4.77 (t, J = 4 Hz, 1H); ^{13}C NMR δ 48.6 (CH_2), 67.0 (CH_2), 15.9 (CH_3), 17.6 (CH_2), 24.6 (CH_2), 27.2 (CH_2), 63.2 (CH_2), 72.0 (CH), 103.8 (CH), 145.3 (C). Anal. Calcd for $C_{12}H_{21}N_1O_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 67.87; H, 9.85; N, 6.51.

7-*exo*-Ethoxy-7-*endo*-morpholinobicyclo[4.1.0]heptane (13): yield 78%; bp 100 °C (3 mmHg) (Kugelrohr); mp 57−58 °C (leaflets from *n*-hexane); IR ν 1113 cm^{-1}; ^{1}H NMR δ 1.11 (t, J = 7 Hz, 3H), 1.1−2.1 (m, 10H), 3.63 (q?, 2H), 2.76 (H_A, 2H), 3.06 (H_B, 2H), 3.53 (H_X, 2H), 3.79 (H_Y, 2H) (ABXY system); ^{13}C NMR δ 49.8 (CH_2), 67.6 (CH_2), 16.2 (CH_3), 19.5 (CH_2), 21.5 (CH_2), 21.9 (CH), 64.4 (CH_2), 81.6 (C). Anal. Calcd for $C_{13}H_{23}N_1O_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.31; H, 10.27; N, 6.16.

Acetolysis of *N,O*-Acetal 2e. To a stirred solution of **2e** (1.97 g, 10 mmol) in Et_2O (20 mL) was added AcOH (1.32 g, 22 mmol), and the mixture was allowed to stand overnight at room temperature. Excess AcOH was quenched with $NaHCO_3$ (0.5 g, 6 mmol), and the solid was removed by filtration. Distillation of the filtrate gave 1.87 g of acetoxyenamine **12** in a yield of 88%.

1-Acetoxy-6-morpholinocyclohexene (12): bp 110 °C (3 mmHg) (Kugelrohr); IR ν 1730 cm^{-1}; ^{1}H NMR δ 1.5−2.0 (m, 4H), 2.07 (s, 3H), 2.0−2.3 (m, 2H), 2.5−3.1 (m, 4H), 3.68 (t, J = 4.7 Hz, 4H), 4.94 (t, J = 4.0 Hz, 1H), 5.52 (m, 1H); ^{13}C NMR δ 48.8 (CH_2), 67.0 (CH_2), 17.6 (CH_2), 21.3 (CH_3), 24.4 (CH_2), 29.3 (CH_2), 65.7 (CH), 106.7 (CH), 143.7 (C), 170.4 (CO); MS m/z (relative intensity) 225 (M^+, 34), 166 (83), 165 (100). Anal. Calcd for $C_{12}H_{19}N_1O_3$: C, 63.97; H, 8.50; N, 6.22. Found: C, 64.00; H, 8.54; N, 6.06.

Transformation of *N,O*-Acetals 2 into Aminonitriles 3. General Procedure. To a stirred solution of *N,O*-acetal **2** (10 mmol) and Me_3SiCN (1.44 g, 15 mmol) in CH_2Cl_2 (25 mL) was added dropwise a solution of $BF_3{\cdot}Et_2O$ (2.13 g, 15 mmol) within 10 min at dry ice temperature. Stirring was continued for 2 h, and the mixture was then allowed to stand until it was warmed to 0 °C. The reaction mixture was poured into cold water (30 mL), and the organic layer was washed with water, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. The product **3** was isolated by distillation or column chromatography on silica gel by eluting with a mixture of Et_2O−hexane. Product yields are shown in Table 2.

6-*exo*-Cyano-6-*endo*-diethylaminobicyclo[3.1.0]hexane (3a): IR ν 2214 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.10 (t, J = 7.2 Hz, 6H), 1.5−1.8 (m, 2H), 1.8−2.0 (m, 6H), 2.68 (dq, J = 7.2, 2.8 Hz, 4H); ^{13}C NMR (100 MHz) δ 12.9 (CH_3), 47.4 (CH_2), 24.8 (CH_2), 26.4 (CH_2), 34.1 (CH), 42.3 (C), 120.0 (CN, $^3J_{CH}$ = 4.5 Hz);[16] MS

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m/*z* (relative intensity) 178 (M^+, 28), 163 (70), 121 (100). Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 74.02; H, 10.26; N, 15.59.

6-*exo*-Cyano-6-*endo*-methylphenylaminobicyclo[3.1.0]-hexane (3b): bp 118−121 °C (2 mmHg); IR ν 2220 cm^{-1}; ^1H NMR (400 MHz) δ 1.1−1.3 (m, 1H), 1.5−1.7 (m, 2H), 1.7−1.9 (m, 1H), 1.9−2.2 (m, 3H), 2.3−2.4 (m, 1H), 2.94 (s, 3H), 6.8−6.9 (m, 1H), 6.9−7.0 (m, 2H), 7.2−7.3 (m, 2H); ^{13}C NMR (100 MHz) δ 38.5 (CH_3), 114.3 (CH), 119.2 (CH), 128.8 (CH), 147.6 (C), 23.9 (CH_2), 26.2 (CH_2), 26.6 (CH_2), 34.1 (CH), 36.2 (CH), 38.8 (C), 119.6 (CN, $^3J_{CH} = 4.5 \sim 3.1$ Hz);[16] MS *m*/*z* (relative intensity) 212 (M^+, 83), 169 (100), 77 (75). Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.10; H, 7.83; N, 12.88.

6-*exo*-Cyano-6-*endo*-pyrrolidinobicyclo[3.1.0]hexane (3c): bp 88−92 °C (4 mmHg). This was identical to an authentic sample prepared by our previous electrochemical method.[1]

6-*exo*-Cyano-6-*endo*-morpholinobicyclo[3.1.0]hexane (3e): bp 105−107 °C (2 mmHg); ^{13}C NMR δ 51.1 (CH_2), 66.9 (CH_2), 25.9 (CH_2), 26.2 (CH_2), 33.5 (CH), 42.1 (C), 117.9 (CN); MS *m*/*z* (relative intensity) 192 (M^+, 84), 134 (71), 106 (100). Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.92; H, 8.50; N, 14.39. The IR, ^1H NMR, and ^{13}C NMR spectra agreed with those reported in the literature.[16]

7-*exo*-Cyano-7-*endo*-pyrrolidinobicyclo[4.1.0]heptane (3f): mp 50−51 °C (prisms from cyclohexane, −20 °C), bp 102−107 °C (4 mmHg) [lit.[3b] mp 44 °C, bp 80−85 °C (0.05 mmHg)]. This was identical to an authentic sample prepared by our previous electrochemical method,[1] and the IR, ^1H NMR, and ^{13}C NMR spectra agreed with those reported in the literature.[3b]

7-*exo*-Cyano-7-*endo*-morpholinobicyclo[4.1.0]heptane (3g): mp 103−105 °C (prisms from cyclohexane) (lit.[17] mp 102 °C). The IR, ^1H NMR, and ^{13}C NMR spectra agreed with those reported in the literature.[17]

Supporting Information Available: X-ray characterization data for **2g** and **3g**, including tables of experimental details, ORTEP drawings, selected bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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