cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94–7.62 (m, 5 H), 6.13 (br, 1 H), 4.42 (d, J = 2.2 Hz, 1 H), 3.04 (dd, 1 H), 0.11 (s, 9 H). Anal. Calcd for $C_{12}H_{17}NO_3SSi$: C, 50.86; H, 6.05; N, 4.95; Si, 11.31; Si, 9.91. Found: C, 50.82; H, 5.97; N, 5.20; Si, 11.27; Si, 10.06.

(3*S*,4*R*)-3-(Trimethylsilyl)-4-phenoxy-2-azetidinone (18) was prepared from 11 and sodium phenolate in water. The semicrystalline product was purified in a manner identical with that described for 11 to afford 51% of 18: white crystals, mp 99–100 °C (cyclohexane), $[\alpha]^{20}_D$ +62.0° ($CHCl_3$); IR (KBr) 3200, 1758, 1723, 1603, 1596, 1501, 1230, 1158, 1050, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–6.88 (m, 5 H), 6.41 (br, 1 H), 5.46 (d, J = 1.5 Hz, 1 H), 2.96 (d, 1 H), 0.20 (s, 9 H). Anal. Calcd for $C_{12}H_{17}NO_2Si$: C, 61.24; H, 7.28; N, 5.95; Si, 11.94. Found: C, 61.28; H, 7.41; N, 6.02; Si, 12.15.

Effect of A-Strain on a Diastereoselective Synthesis of 6-Hydroxy-4a-aryldecahydroisoquinolines. Revised Structures of *N*-Acyliminium Ion-Polyene Cyclization Products

Shinzo Kano,* Tsutomu Yokomatsu, Hajime Nemoto, and Shiroshi Shibuya

Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

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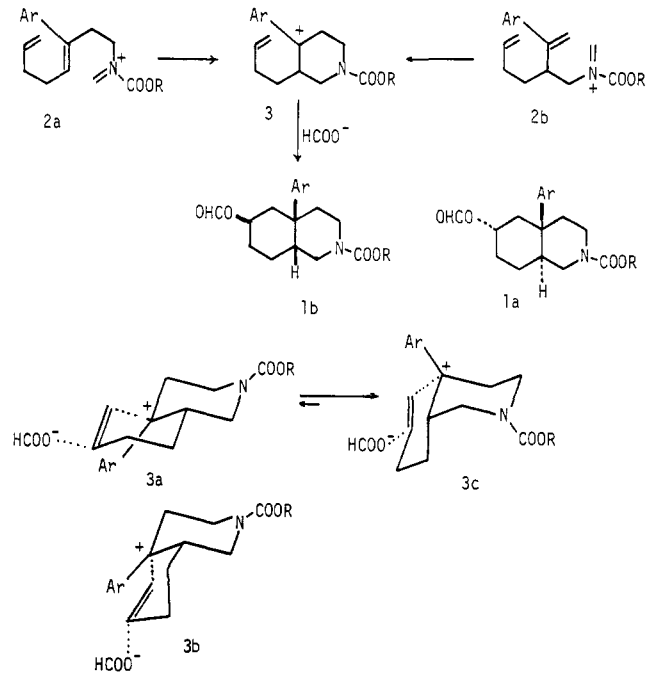
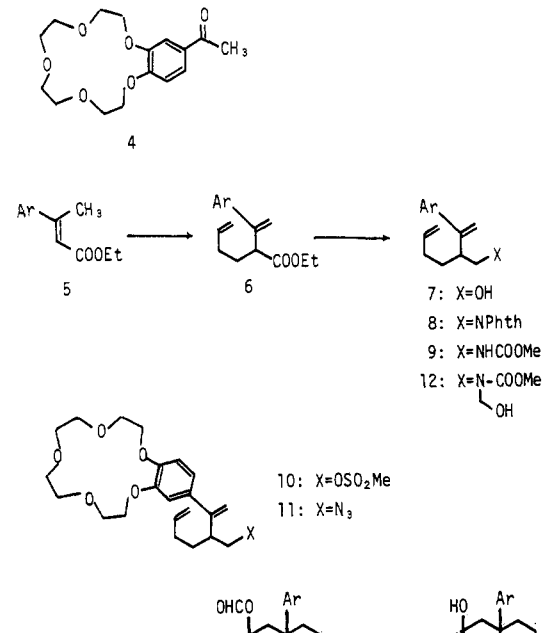
Biomimetic polyene cyclizations have been applied to the synthesis of multicyclic compounds with excellent stereocontrol.[1,2] Allyl alcohols, epoxides, acetals, or sulfonates have been used as suitable cationic initiators for successful polyene cyclizations. The use of *N*-acyliminium ions as cationic initiating center for olefin cyclizations has been well established.[3] The development of *N*-acyliminium ion–polyene cyclizations had led to a versatile route to N-polycyclic compounds in remarkably stereocontrolled manner.[4] Of special interest to us from pharmacological point of view is the development of a facile procedure for a synthesis of 6-hydroxy-4a-aryldecahydroisoquinolines.[5] Previously, we reported an efficient diastereoselective synthesis of 6-oxygenated 4a-aryldecahydroisoquinolines[6,7] by cyclization of **2a** and **2b**.

Scheme I



Scheme II



a: Ar=4-(OCH_3)-C_6H_4- ; b: Ar=3,4-$(OCH_3)_2$-C_6H_3-;
c: Ar=3,4-crowned(15-crown-5)-C_6H_3-

In the previous papers,[6,7] the relative configuration of the cyclization products was assigned to **1a**. The cyclizations were found to proceed via the common benzyl cationic intermediates **3**. We now wish to report that the relative configuration previously assigned by us to these products needs to be revised to **1b**, i.e., 4a,6-cis, 4a,8a-cis as the result of our successful conversion of **1b** (Ar = C_6H_5) to *cis*-4a-phenyl-2-methyldecahydroisoquinoline by an unambigous method.[8] Cis-ring fusion of **1b** can be accounted for by the effect of A-strain[9] on the monocyclization intermedi-

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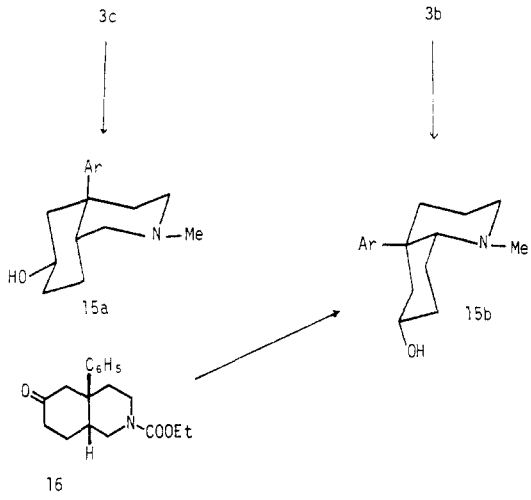
Scheme III



ates **3**. Of the three possible intermediates **3a–c**, **3c** should be predominate, since the phenyl group and butenyl side chain interfere with each other in **3a,b**, which have equatorial substituents (Scheme I).

An efficient approach to the carbamates used in the cyclization reaction started from cinnamates **5**. Wittig reaction of 3,4-crown-(15-crown-5-)–acetophenone **4**[11] with ethyl (diethoxyphosphinyl)acetate gave the ester **5c**, which was also obtained by condensation of **4** with ethyl (trimethylsilyl)acetate[12] as a mixture of *E*/*Z* isomer (2:1). α-Butenylation of **5a–c** (LDA, 1-iodo-3-butene) afforded the corresponding esters **6a–c**, respectively, reduction of which with $LiAlH_4$ gave the alcohols **7a–c** (Scheme II). Condensation of **7a,b** with phthalimide by Mitsunobu's method[13] gave the corresponding N-substituted phthalimides **8a,b**. Treatment of **8a,b** with hydrazine hydrate, followed by methoxycarbonylation with methyl chloroformate yielded the carbamates **9a,b**. Since conversion of **7c** to the corresponding amine leading to **9c** by the above method was not successful, methanesulfonate **10**, derived from **7c**, was treated with sodium azide to give the azide **11**. Reduction of **11** with $LiAlH_4$, followed by methoxycarbonylation gave **9c**.[7]

The next stage of the synthesis involved hydroxymethylation of **9**. Treatment of **8a,b** with paraformaldehyde in the presence of Cs_2CO_3[14] gave **12a,b**, respectively. Hydroxymethylation of **8c** was carried out with 37% formalin in the presence of NaOH in dimethoxyethane to give **12c**.[15]

Cyclization of **12a–c** with formic acid afforded the corresponding 4a-aryldecahydroisoquinoline 6-formates **13a–c**, as single diastereomers. The equatorial configuration of 6-formate was deduced from the magnitude of the coupling constant for H-6, which was clearly visible in the ^1H NMR spectra as a multiplet ($W_{1/2} \sim 30$ Hz) due to the large diaxial coupling.[16] Reduction of **13a–c** with $LiAlH_4$ gave the corresponding 4a-aryl-2-methylisoquinolin-6-ols **14a–c**, respectively. Formation of **13** can be accounted for by antiperiplanar addition of the benzylic cation and formate in the monocyclization intermediate **3a** as depicted in Scheme I. Of the two possible cis-fused equatorial 6-ols **15a** and **15b**,[17] the products were assigned to type **15a** from the NCH_3 signal (δ 2.07–2.10) (Scheme III).[8,18] The other diastereomer **15b**, formed via **3b**, is ruled out since **15b** (Ar = C_6H_5) was obtained by reduction of **16** with $LiAlH_4$.[8]

As mentioned above, the stereochemistry of the cyclization products reported in the earlier publications[6,7] were thus found to be error and have been revised to those depicted in the products.

Experimental Section

Melting points were recorded on a Yanagimoto micro hot stage and are uncorrected. Infrared (IR) spectra were recorded on a JASCO IRA-1 spectrometer, and mass spectra (MS) were determined on a Hitachi RMU-7L instrument. ^1H NMR spectra of $CDCl_3$ solution with Me_4Si as an internal standard (δ 0) were taken on a Varian EM 390 spectrometer. THF was distilled from sodium benzophenone before use. All air-sensitive reactions were run in flame-dried glassware under N_2. Reagents were added via dry syringes through septa.

Cinnamate 5c. (**a**) To a stirred suspension of NaH (1.8 g of 60% dispersion of oil, used after washed with petroleum ether) in DMF (50 mL) was added a mixture of ethyl (diethoxyphosphinyl)acetate (10.08 g, 45 mmol) and **4** (9.3 g, 30 mmol) in DMF (100 mL) at 25 °C. After the stirring had been continued for 12 h at 60 °C, the mixture was poured onto water and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated to give **5c** (5.81 g, 51.8%): mp 63–65 °C (ether–hexane); IR ($CHCl_3$) 1710 cm^{-1}; MS, *m*/*z* 380 (M^+); ^1H NMR δ 1.29 (3 H, t, *J* = 7 Hz), 2.53 (3 H, d, *J* = 1 Hz), 3.73 (8 H, s), 3.80–3.97 (4 H, m), 4.04–4.23 (4 H, m), 4.18 (2 H, q, *J* = 7 Hz), 6.07 (1 H, br s), 6.83 (1 H, d, *J* = 8 Hz), 7.01 (1 H, d, *J* = 2 Hz), 7.05 (1 H, dd, *J* = 2, 8 Hz). Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.16; H, 7.41.

(**b**) To a stirred solution of LDA (prepared from 2.4 g, 37.5 mmol, of *n*-BuLi, 23.4 mL of 1.6 M hexane solution, and 3.78 g, 37.5 mmol, of diisopropylamine in 40 mL of THF as usual) was added a solution of ethyl (trimethylsilyl)acetate (6.0 g, 37.5 mmol) in THF (15 mL) at −78 °C. After 15 min, to this solution was added **4** (7.75 g, 25 mmol) in THF (40 mL) at the same temperature. After the stirring had been continued for 15 min, the mixture was warmed to room temperature, and after 12 h, the mixture was poured onto cold saturated NH_4Cl and then extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. Excess ethyl (trimethylsilyl)acetate was removed in vacuo on a Kugelrohr oven to yield **5c** (7.94 g, 83.6%) as a mixture of *E*/*Z* (2:1) isomers: ^1H NMR δ 1.11 (1 H, t, *J* = 7 Hz), 1.29 (2 H, t, *J* = 7 Hz), 2.15 (1 H, d, *J* = 1 Hz), 2.53 (2 H, d, *J* = 1 Hz), 5.87 (0.33 H, br s), 6.07 (0.66 H, br s).

General Procedure for a Synthesis of 6a–c. To a stirred solution of LDA (prepared from 1.41 g, 22 mmol, of *n*-BuLi, 13.8 mL of 1.6 M hexane solution, and 2.2 g, 22 mol, of diisopropylamine in THF) was added a solution of **5** (20 mmol) in THF (30 mL) at −78 °C. After 0.5 h, to this solution was added a solution of 1-iodo-3-butene (3.64 g, 20 mmol) in THF (10 mL) at the same temperature. The mixture was gradually warmed to room temperature. After the stirring had been continued for 1 h, the mixture was poured onto water and extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4) and evaporated to yield **6** as an oil.

6a: this compound was obtained in 80% yield; IR (neat) 1725 cm^{-1}; MS, *m*/*z* 274 (M^+); ^1H NMR δ 1.21 (3 H, t, *J* = 7 Hz), 1.70–2.28 (4 H, m), 3.56 (1 H, t, *J* = 7 Hz), 3.84 (3 H, s), 4.17 (2

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H, q, J = 7 Hz), 5.00–5.18 (2 H, m), 5.24 (1 H, s), 5.39 (1 H, s), 5.62–6.05 (1 H, m), 6.92 (2 H, d, J = 8 Hz), 7.41 (2 H, d, J = 8 Hz).

6b: this compound was obtained in 70% yield; MS, m/z 304 (M^+), exact mass m/z 304.1663 (calcd for $C_{18}H_{24}O_4$ m/z 304.1673); IR (neat) 1735 cm^{-1}; ^1H NMR δ 1.21 (3 H, t, J = 7 Hz), 1.60–2.30 (4 H, m), 3.53 (1 H, t, J = 6 Hz), 3.89 (3 H, s), 3.91 (3 H, s), 4.17 (2 H, q, J = 7 Hz), 4.87–5.12 (2 H, m), 5.26 (1 H, s), 5.40 (1 H, s), 5.57–6.13 (1 H, m), 6.90 (1 H, d, J = 9 Hz), 7.01 (1 H, d, J = 2 Hz), 7.07 (1 H, dd, J = 2, 9 Hz).

6c: this compound was obtained in 86% yield; MS, m/z 434 (M^+); exact mass m/z 434.2304 (calcd for $C_{24}H_{34}O_7$ m/z 434.2203); IR ($CHCl_3$) 1725 cm^{-1}; ^1H NMR δ 1.21 (3 H, t, J = 7 Hz), 1.66–2.29 (4 H, m), 3.49 (1 H, br t, J = 6 Hz), 3.77 (8 H, s), 3.86–4.00 (4 H, m), 4.00–4.29 (6 H, m), 4.86–5.16 (2 H, m), 5.26 (1 H, s), 5.35 (1 H, s), 5.52–6.19 (1 H, m), 6.76–7.09 (3 H, m).

Alcohol 7a. To a stirred solution of $LiAlH_4$ (0.74 g, 20 mmol) in ether (50 mL) was added a solution of **6a** (5.48 g, 20 mmol) in ether (50 mL) under ice cooling. After the stirring had been continued at the same temperature for 2 h, the mixture was decomposed with 10% NaOH. After removal of inorganic precipitate, the organic layer was evaporated to give **7a** (3.79 g, 81.6 %) as an oil: MS, m/z 232 (M^+); ^1H NMR δ 1.40–1.82 (2 H, m), 1.97–2.30 (2 H, m), 2.77 (1 H, m), 3.62 (2 H, dd, J = 6, 6 Hz), 3.80 (3 H, s), 4.83–5.13 (2 H, m), 5.07 (1 H, s), 5.34 (1 H, s), 5.57–6.07 (1 H, m), 6.87 (2 H, d, J = 8 Hz), 7.32 (2 H, d, J = 8 Hz).

Alcohol 7b. To a stirred solution of $LiAlH_4$ (0.74 g, 20 mmol) in ether (50 mL) was added a solution of **6b** (6.08 g, 20 mmol) in ether (50 mL) under ice cooling and worked up as above to give **7b** (4.72 g, 90%) as an oil: MS, m/z 262 (M^+); ^1H NMR δ 1.40–1.80 (2 H, m), 1.97–2.30 (2 H, m), 2.81 (1 H, m), 3.80 (2 H, dd, J = 6, 6 Hz), 3.90 (6 H, s), 4.84–5.10 (2 H, m), 5.11 (1 H, s), 5.40 (1 H, s), 5.57–6.10 (1 H, m), 6.80–7.10 (3 H, m).

Alcohol 7c. To a stirred solution of $LiAlH_4$ (1.48 g, 40 mmol) in ether (50 mL) was added a solution of **6c** (8.68 g, 20 mmol) in ether (50 mL) under ice cooling. After the stirring had been continued at room temperature for 2 h, the mixture was decomposed with saturated NH_4Cl. After removal of inorganic precipitate, the organic layer was evaporated to give **7c** (6.39 g, 81.5%) as an oil: IR (neat) 3400 cm^{-1}; MS, m/z 392 (M^+); exact mass m/z 392.2188 (calcd for $C_{22}H_{23}O_6$ m/z 392.2197); ^1H NMR δ 1.32–1.79 (2 H, m), 1.79–2.26 (2 H, m), 2.77 (1 H, m), 3.62 (2 H, br d, J = 7 Hz), 3.76 (8 H, s), 3.79–4.02 (4 H, m), 4.02–4.22 (4 H, m), 4.83–5.07 (2 H, m), 5.04 (1 H, s), 5.32 (1 H, s), 5.52–6.02 (1 H, m), 6.80 (1 H, d, J = 8 Hz), 6.89 (1 H, d, J = 2 Hz), 6.90 (1 H, dd, J = 2, 8 Hz).

Phthalimide 8a. To a mixutre of **7a** (2.32 g, 10 mmol), triphenylphosphine (2.62 g, 10 mmol), and phthalimide (1.47 g, 10 mmol) in THF (30 mL) was added diisopropyl azodicarboxylate (2.02 g, 10 mmol) under ice cooling. After the stirring had been continued for 14 h at room temperature, the solvent was evaporated, and the resulting residue was chromatographed on silica gel. Elution with AcOEt–hexane (1:5, v/v) gave **8a** (2.96 g, 82%): mp 70–71 °C (ether–hexane); IR ($CHCl_3$) 1760, 1700 cm^{-1}; MS, m/z 361 (M^+); ^1H NMR δ 1.50–1.83 (2 H, m), 1.93–2.33 (2 H, m), 3.13–3.50 (1 H, m), 3.74 (3 H, s), 3.73–3.93 (2 H, m), 4.98–5.13 (2 H, m), 5.16 (1 H, s), 5.37 (1 H, s), 5.21–6.03 (1 H, m), 6.79 (2 H, d, J = 9 Hz), 7.30 (2 H, d, J = 9 Hz), 7.60–7.93 (4 H, m). Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.13; H, 6.30; N, 3.73.

Phthalimide 8b. This compound was obtained from **7b** (2.62 g, 10 mmol), triphenylphosphine (2.62 g, 10 mmol), phthalimide (1.47 g, 10 mmol), and diisopropyl azodicarboxylate (2.02 g, 10 mmol) under the same conditions as above in 73% yield (2.85 g): mp 82–83 °C (MeOH–ether); ^1H NMR δ 1.56–1.88 (2 H, m), 1.92–2.32 (2 H, m), 3.09–3.40 (1 H, m), 3.77 (3 H, s), 3.89 (3 H, s), 4.82–5.11 (2 H, m), 5.14 (1 H, s), 5.36 (1 H, s), 5.56–6.06 (1 H, m), 6.72 (1 H, d, J = 9 Hz), 6.86–7.05 (2 H, m), 7.59–7.94 (4 H, m). Anal. Calcd for $C_{24}H_{25}NO_4$: C, 73.63; H, 6.44; N, 3.58. Found: C, 73.63; H, 6.41; N, 3.58.

Carbamate 9a. A mixture of **8a** (3 g, 8.31 mmol), hydrazine hydrate (1.25 g of 80% solution), and EtOH (70 mL) was heated under reflux for 3 h. After removal of the precipitate, the solvent was evaporated. To a stirred mixture of the residual oil, CH_2Cl_2 (10 mL), and Et_3N (1 g, 10 mmol) was added a solution of ClCOOMe (784 mg, 8.3 mmol) in CH_2Cl_2 (2 mL) under ice cooling. After the stirring had been continued for 1 h at room temperature, the mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and evaporated to yield **9a** (1.56 g, 65%) as an oil: IR ($CHCl_3$) 3440, 1720 cm^{-1}; MS, m/z 289 (M^+); exact mass m/z 289.1658 (calcd for $C_{17}H_{23}NO_3$ m/z 289.1676); ^1H NMR δ 1.42–1.80 (2 H, m), 1.96–2.29 (2 H, m), 2.80 (1 H, m), 3.30 (2 H, dd, J = 6, 6 Hz), 3.68 (3 H, s), 3.83 (3 H, s), 4.89–5.18 (2 H, m), 5.03 (1 H, s), 5.37 (1 H, s), 5.58–6.08 (1 H, m), 6.95 (2 H, d, J = 8 Hz), 7.36 (2 H, d, J = 8 Hz).

Carbamate 9b. This compound was obtained by methoxycarbonylation of the amine [obtained from **8b** (3.5 g, 8.95 mmol) and hydrazine hydrate (1.12 g of 80% solution)] with ClCOOMe (846 mg, 8.95 mmol) in CH_2Cl_2 by the same conditions as above in 68% (1.94 g) as an oil: MS, m/z 319 (M^+); ^1H NMR δ 1.43–1.73 (2 H, m), 1.93–2.26 (2 H, m), 2.63–2.93 (1 H, m), 3.26 (2 H, dd, J = 6, 6 Hz), 3.62 (3 H, s), 3.87 (6 H, s), 4.83–5.10 (2 H, m), 5.01 (1 H, s), 5.31 (1 H, s), 5.53–6.03 (1 H, m), 6.85 (3 H, s).

Carbamate 9c. To a stirred mixture of **8c** (5.88 g, 15 mmol), pyridine (30 mL) was added CH_3SO_2Cl (2.0 g, 18 mmol) under ice cooling. The mixture was stirred for 12 h and then poured onto water. The mixture was extracted with CH_2Cl_2. The extract was washed with 10% HCl and brine, dried (Na_2SO_4), and evaporated to give **10** (6.77 g, 96%); this was used for the following reaction without purification. A mixture of **10** (4.51 g, 9.6 mmol) and NaN_3 (922 mg, 14.4 mmol) in DMF (30 mL) was heated at 50 °C under stirring for 12 h. The mixture was poured onto water and extracted with ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The remaining residue was chromatographed on silica gel. Elution with $CHCl_3$–ether–EtOAc (5:5:1, v/v) gave **11** (2.78 g, 66.7%) as an oil: IR (neat) 2045 cm^{-1}; MS, m/z 417 (M^+); ^1H NMR δ 1.48–1.81 (2 H, m), 1.81–2.28 (2 H, m), 3.23–3.37 (2 H, m), 3.74 (8 H, s), 3.81–3.98 (4 H, m), 5.29 (1 H, s), 5.54–6.04 (1 H, m), 6.86 (3 H, br s). This was used for the following reaction without further purification. To a stirred solution of $LiAlH_4$ (490 mg, 13.3 mmol) in ether (30 mL) was added a solution of **11** (2.4 g, 5.17 mmol) in ether (50 mL) under ice cooling. After the stirring had been continued at the same temperature for 2 h, the mixture was decomposed with water. After removal of inorganic precipitate by filtration, the organic layer was evaporated. To a mixture of the remaining oil and Et_3N (2.6 g, 26.6 mmol) in CH_2Cl_2 (30 mL) was added a solution of ClCOOMe (489 mg, 5.17 mmol) in CH_2Cl_2 (5 mL) under ice cooling. After the stirring had been continued at room temperature for 2 h, the mixture was poured onto water and extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4), and evaporated. The remaining residue was chromatographed on silica gel (25 g). Elution with ether gave **9c** (1.25 g, 54% from **11**) as an oil: MS, m/z 449 (M^+); exact mass m/z 449.2429 (calcd for $C_{24}H_{35}NO_7$ m/z 449.2411); ^1H NMR δ 1.53–1.79 (2 H, m), 1.96–2.32 (2 H, m), 2.66–2.92 (1 H, m), 3.27 (2 H, dd, J = 7, 7 Hz), 3.66 (3 H, s), 3.77 (8 H, s), 3.86–4.02 (4 H, m), 4.09–4.26 (4 H, m), 4.86–5.16 (2 H, m), 5.04 (1 H, s), 5.33 (1 H, s), 5.59–6.05 (1 H, m), 6.92 (3 H, m).

Hydroxymethylation of 9a. A mixture of powdered paraformaldehyde (114 mg), Cs_2CO_3 (1.125 g, 3.46 mmol), and **9a** (1 g, 3.46 mmol) in THF (30 mL) was stirred at room temperature for 15 h, the mixture was filtered, and the solvent was evaporated. The residual oil was chromatographed on silica gel. Elution with AcOEt–hexane (1:2, v/v) gave **12a** (673 mg, 61%) as an oil: IR ($CHCl_3$) 3630, 3580, 3400, 1690 cm^{-1}; MS, m/z 319 (M^+); ^1H NMR δ 1.43–1.83 (2 H, m), 1.90–2.33 (2 H, m), 2.68–3.16 (1 H, m), 3.44 (2 H, d, J = 7 Hz), 3.71 (3 H, s), 3.81 (3 H, s), 4.82 (2 H; d, J = 7 Hz), 4.91–5.13 (2 H, m), 5.03 (1 H, s), 5.34 (1 H, s), 5.47–6.07 (1 H, m), 6.90 (2 H, d, J = 7 Hz), 7.33 (2 H, d, J = 7 Hz).

Hydroxymethylation of 9b. A mixture of powdered paraformaldehyde (103 mg), Cs_2CO_3 (1.02 g, 3.13 mmol), and **9b** (1 g, 3.13 mmol) in THF (10 mL) was stirred at room temperature for 15 h and worked up as above to give **12b** (613 mg, 56%) as an oil: MS, m/z 349 (M^+).

Hydroxymethylation of 9c. A mixture of 37% formalin (1 mL), 3 M NaOH (1 mL), and **9c** (1 g, 2.23 mmol) in DME (5 mL) was stirred at room temperature for 15 h. After the solvent was evaporated, the mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4), and evaporated. The remaining residue was chromatographed

on silica gel. Elution with $CHCl_3$–ether (1:1 v/v) gave **9c** (430 mg, 43%) and successive elution with the same solvent yielded **12c** (427 mg, 40%, 70.2% based on the recovery of the starting material): ^1H NMR δ 1.43–1.77 (2 H, m), 1.90–2.32 (2 H, m), 3.77 (8 H, s), 3.86–4.02 (4 H, m), 4.09–4.26 (4 H, m), 4.86–5.16 (2 H, m), 5.04 (1 H, s), 5.33 (1 H, s), 5.59–6.05 (1 H, m), 6.92 (3 H, m).

4a,6-*cis*,4a,8a-*cis*-4a-Aryldecahydroisoquinoline 6-Formate 13a. A mixture of **12a** (319 mg, 1 mmol) and formic acid (1 mL) was stirred at room temperature for 2 h. The mixture was made basic with 5% $NaHCO_3$ and extracted with $CHCl_3$. The extract was washed with water, dried (Na_2SO_4), and evaporated, and the remaining residue was chromatographed on silica gel (10 g). Elution with hexane–EtOAc (3:1, v/v) gave **13a** (271 mg, 72%): MS, m/z 347 (M^+); ^1H NMR δ 1.23–2.43 (11 H, m), 2.73 (1 H, d with small splitting, J = 12 Hz), 3.00 (1 H, dd, J = 2, 12 Hz), 3.66 (3 H, s), 3.80 (3 H, s), 5.10 (1 H, m, $W_{1/2}$ = 25 Hz), 6.92 (2 H, d, J = 9 Hz), 7.33 (2 H, d, J = 9 Hz), 7.97 (1 H, s).

4a,6-*cis*,4a,8a-*cis*-4a-Aryldecahydroisoquinoline 6-Formate 13b. A mixture of **12b** (349 mg, 1 mmol) and formic acid (1 mL) was stirred at room temperature for 2 h and worked up as above. The product was chromatographed on silica gel (10 g). Elution with hexane–AcOEt (2:1) gave **13b** (277 mg, 73.6%) as an oil: MS, m/z 377 (M^+); exact mass m/z 377.1807 (calcd for $C_{20}H_{27}NO_6$ m/z 377.1824); ^1H NMR δ 1.14–2.48 (11 H, m), 2.78 (1 H, d with small splitting, J = 12 Hz), 3.04 (1 H, dd, J = 3, 12 Hz), 3.68 (3 H, s), 3.90 (6 H, s), 5.11 (1 H, m, $W_{1/2}$ = 30 Hz), 6.94 (3 H, s), 7.93 (1 H, s).

4a,6-*cis*,4a,8a-*cis*-4a-Aryldecahydroisoquinoline 6-Formate 13c. A mixture of **12c** (479 mg, 1 mmol) and formic acid (1 mL) was stirred and worked up as above. The product was chromatographed on silica gel (10 g). Elution with $CHCl_3$–ether–AcOEt (5:5:1, v/v) gave **13c** (355 mg, 70%): mp 132–134 °C (MeOH–ether); MS, m/z 507 (M^+); ^1H NMR δ 1.20–2.40 (11 H, m), 2.70 (1 H, br d, J = 13 Hz), 2.99 (1 H, dd, J = 2, 13 Hz), 3.59 (3 H, s), 3.70 (8 H, s), 3.78–3.97 (4 H, m), 4.03–4.20 (4 H, m), 5.07 (1 H, m, $W_{1/2}$ = 30 Hz), 6.86 (3 H, br s), 7.91 (1 H, s). Anal. Calcd for $C_{26}H_{37}NO_9$: C, 61.52; H, 7.35; N, 2.76. Found: C, 61.56; H, 7.41; N, 2.74.

General Procedure for a Synthesis of 4a,6-*cis*,4a,8a-*cis*-4a-Aryl-6-hydroxy-2-methyldecahydroisoquinoline 14. To a stirred solution of $LiAlH_4$ (4 mL of 1 M solution in THF) was added a solution of **13** (1 Mmol) in THF (15 mL) under ice cooling. After the stirring had been continued at room temperature for 14 h, the mixture was worked up as usual.

14a: 82% yield; mp 74–76 °C (ether–hexan); IR ($CHCl_3$) 3600, 3590 cm^{-1}; MS, m/z 275 (M^+); ^1H NMR δ 2.10 (3 H, s), 3.82 (3 H, s), 3.60–4.12 (1 H, m), 6.93 (2 H, d, J = 9 Hz), 7.35 (2 H, d, J = 9 Hz). Anal. Calcd for $C_{17}H_{25}NO_2 \cdot H_2O$: C, 65.59; H, 9.28; N, 4.77. Found: C, 69.64; H, 9.26; N, 4.78.

14b: 64% yield; mp 104–107 °C (MeOH–ether); IR ($CHCl_3$) 3660, 3600 cm^{-1}; MS, m/z 305 (M^+); ^1H NMR δ 2.09 (3 H, s), 3.57–3.97 (1 H, m), 3.86 (6 H, s), 6.90 (3 H, br s). Anal. Calcd for $C_{18}H_{27}NO_3 \cdot H_2O$: C, 66.84; H, 9.04; N, 4.33. Found: C, 66.63; H, 8.91; N, 4.21.

14c: 94% yield; mp 79–82 °C (ether); MS, m/z 435 (M^+); ^1H NMR δ 2.06 (3 H, s), 3.78 (8 H, s), 3.80–4.00 (4 H, m), 4.00–4.23 (4 H, m), 6.73–7.00 (3 H, m). Anal. Calcd for $C_{24}H_{37}NO_6 \cdot H_2O$: C, 63.55; H, 8.67; N, 3.10. Found: C, 63.89; H, 8.69; N, 3.19.

Registry No. **4**, 41757-95-3; **5a**, 7706-82-3; **5b**, 7706-60-7; (*E*)-**5c**, 99809-84-4; (*Z*)-**5c**, 99828-80-5; **6a**, 97580-22-8; **6b**, 97580-23-9; **6c**, 97580-24-0; **7a**, 97580-26-2; **7b**, 97580-27-3; **7c**, 97580-28-4; **8a**, 97580-30-8; **8b**, 97580-31-9; **8c**, 99809-85-5; **9a**, 97580-35-3; **9b**, 97580-36-4; **9c**, 97580-37-5; **10**, 97580-33-1; **11**, 97580-34-2; **12a**, 97580-38-6; **12b**, 97580-39-7; **12c**, 97579-65-2; **13a**, 99809-86-6; **13b**, 99809-87-7; **13c**, 99809-88-8; **14a**, 99809-89-9; **14b**, 99809-90-2; **14c**, 99809-91-3; $(MeCH_2O)_2P(O)CH_2CO_2CH_2Me$, 867-13-0; $H_2C{=}CH(CH_2)_2I$, 7766-51-0.

Polar Substituent Effects in the Bicyclo[2.2.2]octane Ring System: Polarography of 4-Substituted Bicyclo[2.2.2]oct-1-yl Iodides

William Adcock,* Gaik B. Kok, and V. Sankar Iyer

School of Physical Sciences, The Flinders University of South Australia, Bedford Park, S.A., Australia 5042

Dennis G. Peters* and Kristin M. Lundy

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

William Kitching

Department of Chemistry, University of Queensland, Brisbane, Australia 4067

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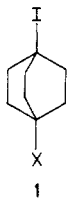
Polarographic half-wave potentials ($E_{1/2}$ values) have been reported recently for reduction of a limited number of 4-substituted bicyclo[2.2.2]oct-1-yl iodides **1**.[1] Unlike



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the effects of substituents monitored by chemical reactivity probes (energy monitors) in this classical saturated model system,[2] the $E_{1/2}$ values were found to correlate poorly against polar field parameters (σ_F).[3] Electroreduction of haloalkanes[4-7] is known to be irreversible, and the overall two-electron process involves a rate-determining dissociative electron transfer in the first step followed by rapid reduction of the radical to form a carbanion (eq 1). The

$$RX \xrightarrow{e} R\cdot + X^- \xrightarrow{e} R^- \xrightarrow{SH} RH \qquad (1)$$

transition state for the process is probably a radical anion ($[RX]^-\cdot$)[8] possessing partial radical character ($[RX]^-\cdot$ is usefully denoted by canonical structures **2** and **3** with the former being considered dominant) which leads to radical stability being manifested in the potential-determining first step.[9] From this viewpoint, destabilization of the transition state as a result of unfavorable substituent-induced structural constraints on bridgehead radical stability was

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(8) (a) It has been shown by ESR spectroscopy in matrices[8b] that electron capture by alkyl halides leads to the formation of alkyl radical–halide ion adducts ($R\cdots X^-$) as intermediates rather than true σ^* radical anions ($[RX]^-\cdot$). (b) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223 and references cited therein.
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