(s, ester carbonyl), 146.55 (s, C-5), 146.22 (s, C-2), 144.38 (s, C-4), 141.48 (d, C-β), 134.61 (d, C-α), 125.71 (d, C-6), 125.27 (s, C-1), 122.15 (d, C-3), 20.78 (q, ester CH_3).

5,6-Diacetoxyindole (7). Compound **6** (3.1 g, 10 mmol) and 0.31 g of 5% Pt/C were dispersed in 60 mL of CH_3CO_2H and hydrogenated on a Parr apparatus at 15 psi for 5 h. Thirty milliliters of acetic anhydride was added, and the reaction was warmed to 30 °C as the solvent was removed at reduced pressure. HPLC purification gave 1.63 g (70%) of **7**: mp 134–136 °C (lit.[3] mp 134–136 °C); ^{1}H NMR (Me_2SO-d_6) δ 11.24 (br s, 1 H), 7.41 (d, J = 2.68 Hz, 1 H), 7.36 (s, 1 H), 7.27 (s, 1 H), 6.45 (d, J = 2.59 Hz, 1 H), 2.27 (s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 169.47 (s, ester carbonyl), 137.84 (s, C-8), 136.28 (s, C-6), 133.52 (s, C-5), 127.55 (d, C-2), 125.59 (s, C-9), 113.75 (d, C-4), 106.12 (d, C-7), 101.56 (d, C-3), 21.00 (q, ester CH_3).

Acknowledgment. I thank Drs. Keith C. Brown and Thomas M. Schultz (Clairol, Inc.) for helpful discussions of this paper and Dr. Joseph Virgilio and Steven Magennis (Givaudan Corp.) for their discussion of nitration procedures.

Registry No. 1, 120-57-0; 2, 712-97-0; 3, 73635-75-3; 4, 15794-35-1; 5, 99459-13-9; 6, 99459-14-0; 7, 15069-79-1; 5-(chloromethoxy)-4-hydroxy-2-nitrobenzaldehyde, 73635-74-2.

Indirect Electrochemical Radical Cyclization of Bromo Acetals by Cobaloxime(I) as an Electron-Transfer Catalyst

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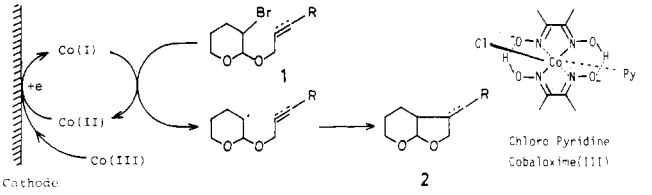
Received July 9, 1985

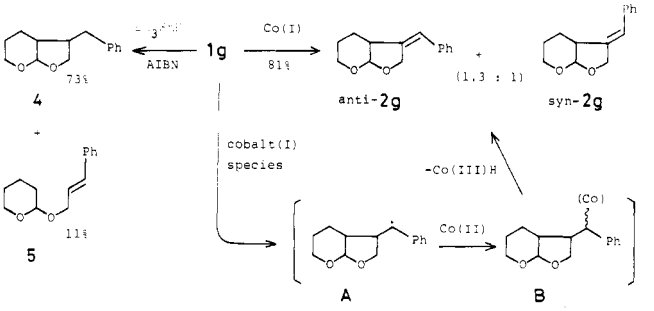
Cyclization by trapping of a free radical with an internal π-bond system is a promising strategy for the construction of carbo- and heteroring molecules under mild conditions.[1] Reported methods utilizing trialkylstannane or -distannane as a radical generator are troublesome in the purification of the products from trialkyltin halide,[2] although a partial solution to this problem has been devised by using polymer-supported organotin compounds.[3] In this paper we disclose a facile procedure for the radical cyclization according to Scheme I, in which electrochemically regenerated cobaloxime(I) (Co(I)) from cobaloxime(III)[4] has been exploited as a mediator for the reductive cleavage of C–Br bonds of brominated olefins and acetylenes **1** to **2**.[5]

Although cobaloxime(I) generated by the reduction of cobaloxime(III), the most simple model compound of vitamin B_{12}, with $NaBH_4$ has been shown to catalyze the reduction of alkyl halides and tosylates to produce alkyl radical and/or organocobaloxime species through an electron-transfer process,[6] no effective electrochemical

Scheme I



Scheme II



versions of these reactions have been explored in spite of intensive and intriguing results on indirect electrochemical reduction of C–halogen bonds[7] assisted by vitamin B_{12} derivatives and its model compounds.[8]

The radical cyclization by electrochemically regenerated cobaloxime(I) has been carried out in methanol containing Et_4NOTs as a supporting electrolyte in a divided cell under argon. Thus, the bromo acetal **1d** was electrolyzed in the presence of about 50 mol % of chloropyridinecobaloxime(III) and a small amount of 40% NaOH under a constant current density of 13.3 mA/cm^2 (terminal voltage 9–11 V) at 50–60 °C. After passage of 2 faraday/mol of electricity, the mixture was subjected to the usual extractive workup followed by purification on column chromatography (SiO_2) to give the desired **2d** in 70% yield. No cyclization was observed in the absence of the cobalt catalyst.

An interesting feature of the present radical cyclization is that the reaction can be carried out in methanol, contrary to the trialkyltin hydride promoted radical reaction in aprotic nonpolar solvents. The formation of **2d** from **1d** by this electrochemical method in polar aprotic solvents such as DMF and MeCN decreased to 30% and 18%, respectively. The electrochemical cyclization can be carried out by using less than 20 mol % of cobaloxime(III), though the reaction becomes sluggish. It is noted that the reactivity of the catalyst can be enhanced by addition of 40% NaOH to the medium: the electrolysis of **1d** in the absence of 40% NaOH afforded **2d** in 57% yield by passage of 4.9 faraday/mol of electricity.

As shown in Table I, various brominated olefins and acetylenes derived from cyclic enol ethers and enamine could be converted into the corresponding tetrahydrofuran derivatives. Thus, the reaction proceeded through a closure in the exo mode to only a five-membered ring. However, similar treatment of **3**, bearing a C=C double

(1) (a) Ueno, Y. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 1121. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (c) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(2) (a) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (b) Padwa, A.; Nimmesgermn, H.; Worg, G. S. K. *Tetrahedron Lett.* **1985**, *26*, 957 and references cited therein.

(3) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564.

(4) The reduction of chloropyridine[bis(dimethylglyoximato)]cobalt(III) (cobaloxime(III)) to cobaloxime(I) is known to occur at −1.45 V (vs. Ag/$AgNO_3$): Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 65.

(5) Direct electroreductive cyclization of halogenated alkynes: (a) Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4945. (b) Willett, B. C.; Moore, W. M.; Peters, D. G. *Ibid.* **1979**, *101*, 1162.

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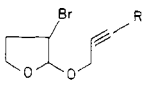
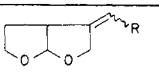
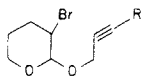
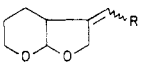
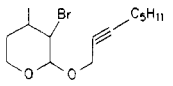
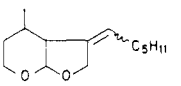
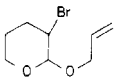
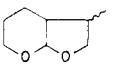
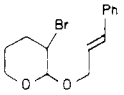
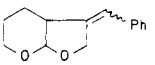
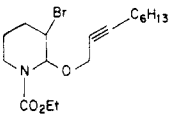
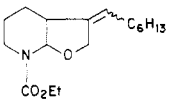
(8) (a) Sheffold, R.; Amble, E. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 629. (b) Scheffold, R.; Dike, M.; Dike, S.; Herold, T.; Walder, L. *J. Am. Chem. Soc.* **1980**, *102*, 3642.

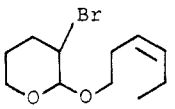
0022-3263/85/1950-5875$01.50/0

Table I. Radical Cyclizations of 1 with Electrogenerated Cobaloxime(I)[a]

entry	substrate 1		elec,[b] faradays/mol	yield,[c] %	product 2
a		R = C_2H_5	2.4	87	
b		R = C_5H_{11}	3.0	84	
c		R = H	3.2	35	
d		R = C_5H_{11}	2.0	70	
e			2.3	82	
f			5.5	44	
g			2.0	81	
h			2.0	75	

[a] Carried out in a similar manner as described in the text. [b] Electricity consumed for the complete conversion of the starting substrate 1. [c] Based on the isolated product after column chromatography.

bond at the C(6)–C(7) position from the brominated carbon atom, with electrogenerated Co(I) species, resulted in no desired cyclized product.

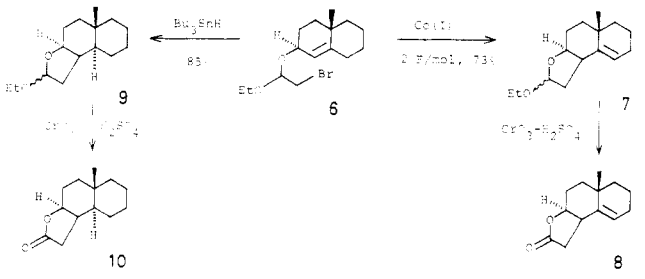


3

Of interest to note is that Co(I)-mediated radical cyclization of **1g** produced a mixture of stereoisomers *anti*-**2g** and *syn*-**2g** (ca. 1.3:1)[9] in 81% yield, whereas the treatment of the same substrate with tri-*n*-butyltin hydride–AIBN in benzene at 80 °C afforded the normal radical cyclization product **4** in 73% yield in addition to the noncyclized **5** (11%). Thus, the cyclization of **1g** with tributyltin hydride is in part prevented in the presence of the very good hydrogen donor. Strikingly different outcomes of Co(I)-mediated cyclization of **1g** from that of aliphatic bromo olefin **1f** should be attributed to the stability of intermediary radical at the benzylic position.[10] The formation of **2g** can be explained by postulating that the initially formed radical **A** combines with a cobalt(II) species to produce the unstable alkylcobalt complex **B**, which in turn undergoes elimination of $Co^{III}H$ species to furnish the olefinic products[11] (Scheme II).

Similar radical cyclization accompanied by the formation of a C–C double bond was encountered in the reaction of the bicyclic derivative **6**. Thus, Co(I)-mediated reduction of **6** as described above resulted in the formation of **7** in 70% yield, whereas treatment of **6** with tri-*n*-butyltin hydride produced **9**, predominantly. The identification of **7** was made by its conversion to γ-lactone **8**[12] by the

Scheme III



oxidation with Jones reagent as reported by Stork et al. in the oxidation of **9** to γ-lactone **10**[2a] (Scheme III).

This electrochemical procedure provides a useful method of radical cyclizations, since the reaction can be conducted with a small amount of relatively inexpensive cobalt complex with ease of product purification. Interestingly, depending on the structure and stability of the radical intermediate, two reaction modes, namely normal hydrogen abstraction or concomitant addition and elimination of cobalt complex, are available. The application of this reaction to carbocyclic systems important in the natural product synthesis is in progress in our laboratory.

Experimental Section

Boiling points are indicated by an air bath temperature without correction, and melting points are uncorrected. IR spectra were obtained with a Jasco IRA-1 grating spectrometer. ^1H NMR spectra were recorded on either a Hitachi R-24 (60-MHz) or a JEOL FX-100 (100-MHz) spectrometer. ^{13}C NMR spectra were obtained with a JEOL FX-100 (25.05-MHz) spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shifts are expressed in δ values relative to Me_4Si as an internal standard. Elemental analyses were performed in our laboratory.

(9) The structure of *anti*-**2g** and *syn*-**2g** are elucidated by comparison with two pairs of signals of ^{13}C NMR at δ 121.5 (d) and 141.8 (s) and at δ 120.4 (d) and 139.9 (s).

(10) Crandall, J. K.; Keyton, D. J. *Tetrahedron Lett.* **1969**, 1655.

(11) (a) Müller, P.; Rètey, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1342. (b) Ladlow, M.; Pattendon, G. *Tetrahedron Lett.* **1984**, *25*, 4317.

(12) The chemical shift values of **8** due to the methyl protons and vinylic proton are comparable with those of reported data of structurally related 3β-acetoxy-17α-methoxypregon-5-en-20-one.[13]

(13) Glazer, E. R. *J. Org. Chem.* **1962**, *27*, 4397.

Materials. Chloropyridine[bis(dimethylglyoximato)]cobalt(III) (cobaloxime(III)) was prepared from $CoCl_2 \cdot 6H_2O$, dimethylglyoxime, and pyridine.[4] According to the method reported,[3] alcohols bearing a unsaturation at the C(2)–C(3) position and cyclic enol ethers (dihydrofuran and dihydropyrans, 1.5–3 equiv) were treated with *N*-bromosuccinimide (1.1–1.5 equiv) at 0–5 °C for 1.5 h and at room temperature for 1 h to give the starting bromo acetals **1**, **3**, and **6** in 85–90% yields.

Electrolysis Apparatus. A modified H-type cell (40-mL volume) was used. The cathode compartment, fitted with a thermometer, a magnetic stirrer bar, and a bubbling argon inlet glass tube, was separated from the anode by 1.3-cm diameter glass frits (No. 5G). Two platinum foil electrodes (1.5 cm^2) were placed parallel to each other 2.5 cm apart. The vessel was immersed in a bath warmed to 50–60 °C. Regulated dc power was supplied by a Metronix Model 543B instrument.

General Procedure for Electrolysis of Bromo Acetal 1: Preparation of 7-(1-Hexylidene)-2,9-dioxabicyclo[4.3.0]nonane (2d). Into the cathode compartment was added **1d** (289 mg, 1.0 mmol) and chloropyridinecobaloxime(III) (200 mg, 0.49 mmol); then into the both compartments was added a two solution of 40% NaOH (0.1 mL) and Et_4NOTs (100 mg) in MeOH (8 mL), respectively. The entire mixture was electrolyzed under a constant current of 20 mA (terminal voltage 9–11 V) at 50–60 °C. During the electrolysis, a stream of argon was passed through the cathode chamber. After 2 faradays/mol of electricity was passed, the mixture was poured into cold water and the products were taken up in hexane–ether (1:1). The extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified on column chromatography (SiO_2, hexane–AcOEt, 20:1) to give 147 mg (70%) of **2d** as an oil: bp 120–125 °C (15 mm); IR (neat) 1447, 1400, 1342, 1242, 1220, 1150, 1068, 1037, 958, 910 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.90 (m, 3, CH_3), 1.30 (m, 8, CH_2), 1.70–2.20 (m, 4, CH_2), 2.40–2.90 (m, 1, CHC=C), 3.15–4.08 (m, 2, CH_2O), 4.50 (br s, 2, OCH_2C=C), 5.05–5.45 (m, 1, CH=C), 5.11 (d, J = 4 Hz, 1, OCHO). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.41; H, 10.27.

Spectral data of electrolysis products **2** listed in Table I and the compound **7** are as follows:

4-(1-Propylidene)-2,8-dioxabicyclo[3.3.0]octane (2a): bp 106–108 °C (16 mm); IR (neat) 1448, 1377, 1353, 1300, 1244, 1120, 1063, 974, 930 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.99, 1.05 (t, J = 8 Hz, 3, CH_3), 1.64–2.80 (m, 4, CH_2), 3.10–3.50 (m, 1, CHC=C), 3.50–4.10 (m, 2, CH_2O), 4.42 (m, 2, CH_2O), 5.10–5.55 (m, 1, CH=C), 5.73 (d,d, J = 5, 1 Hz, 1, OCHO).

4-(1-Hexylidene)-2,8-dioxabicyclo[3.3.0]octane (2b): bp 113–115 °C (18 mm); IR (neat) 1460, 1358, 1244, 1190, 1090, 1032, 1008, 942, 921 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.90 (m, 3, CH_3), 1.33 (m, 6, CH_2), 1.70–2.50 (m, 4, CH_2), 3.05–3.60 (m, 1, CHC=C), 3.62–4.05 (m, 2, CH_2O), 4.30–4.55 (m, 2, OCH_2C=C), 5.32 (m, 1, CH=C), 5.76 (d,d, J = 6, 1 Hz, 1, OCHO).

7-Methylene-2,9-dioxabicyclo[4.3.0]nonane (2c): bp 92–93 °C (16 mm); IR (neat) 3070, 1670 (C=C), 1463, 1457, 1363, 1358, 1300, 1262, 1242, 1208, 1120, 1078, 1056, 1038, 1008, 982, 968, 944, 892, 872, 796, 773 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10–2.28 (m, 4, CH_2), 2.38–2.85 (m, 1, CH), 3.20–4.40 (m, 4, CH_2O), 4.54 (m, 1, CH_2C=C), 4.86–5.24 (m, 2, CH_2=C, OCHO).

7-(1-Hexylidene)-5-methyl-2,9-dioxabicyclo[4.3.0]nonane (2e): bp 129–133 °C (17 mm); IR (neat) 1462, 1378, 1327, 1260, 1192, 1177, 1067, 950, 917 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.38–2.78 (m, 18, CH_3, CH_2, CH), 3.23–3.90 (m, 2, CH_2O), 4.03–4.70 (m, 2, CH_2O), 4.94–5.60 (m, 2, OCHO, CH=C).

7-Methyl-2,9-dioxabicyclo[4.3.0]nonane (2f): bp 93–96 °C (18 mm); IR (neat) 1458, 1438, 1402, 1380, 1250, 1200, 1143, 1117, 1053, 1030, 1020, 998, 960, 922, 888, 868 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.98, 1.00 (d, J = 7 Hz, 3, CH_3), 1.20–2.18 (m, 5, CH_2, CH), 2.18–2.80 (m, 1, CH), 3.48–4.38 (m, 4, CH_2O), 5.02, 5.30 (d, J = 3 Hz, 1, OCHO).

***anti*-7-Benzylidene-2,9-dioxabicyclo[4.3.0]nonane (2g)**: bp 142–144 °C (18 mm); IR (neat) 3040, 3025, 1600, 1498, 1448, 1370, 1264, 1211, 1151, 1118, 1103, 1073, 1040, 1007, 960, 902, 770, 736, 698 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10–2.20 (m, 4, CH_2), 2.55–2.90 (m, 1, CHC=C), 3.25–4.05 (m, 2, CH_2O), 4.81 (m, 2, CH_2O), 5.15 (d, J = 4 Hz, 1, OCHO), 6.24 (m, 1, CH=C), 6.95–7.50 (m, 5, PhH); ^{13}C NMR ($CDCl_3$) δ 20.5 (t), 22.9 (t), 43.5 (d), 64.4 (t), 69.9 (t), 100.4 (d), 120.4 (d), 126.6 (d), 127.8 (d, 2c), 128.5 (d, 2c), 136.9 (s), 139.9 (s). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.97; H, 7.63.

***syn*-7-Benzylidene-2,9-dioxabicyclo[4.3.0]nonane (2g)**: bp 142–145 °C (18 mm); IR (neat) 3040, 3020, 1598, 1496, 1450, 1400, 1276, 1242, 1218, 1158, 1144, 1076, 1036, 987, 960, 904, 898, 872, 778, 697, 658 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10–2.20 (m, 4, CH_2), 2.70–3.10 (m, 1, CHC=C), 3.40–4.10 (m, 2, CH_2O), 4.21–4.82 (m, 2, OCH_2C=C), 5.19 (d, J = 4 Hz, 1, OCHO), 6.23 (m, 1, C=CHPh), 7.22 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 23.2 (t), 38.2 (d), 61.4 (t), 69.8 (t), 101.2 (d), 121.5 (d), 126.8 (d), 127.8 (d, 2c), 128.4 (d, 2c), 136.7 (s), 141.8 (s). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.57.

2-(Ethoxycarbonyl)-7-(1-heptenylidene)-2-aza-9-oxabicyclo[4.3.0]nonane (2h): bp 108–110 °C (2 mm); IR (neat) 1712 (ester C=O), 1470, 1428, 1382, 1347, 1304, 1261, 1252, 1173, 1028, 988 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.88 (m, 3, CH_3), 1.28 (br s, 15, CH_2, CH), 1.30 (t, J = 8 Hz, 3, CH_3), 3.75–4.65 (m, 4, CH_2O), 4.17 (q, J = 8 Hz, 2, CH_2OCO), 5.00–5.50 (m, 1, CH=C), 5.66 (d,d, J = 5, 2 Hz, 1, NCHO).[14]

(2β-Hydroxy-4aβ-methyl-1,2,3,4,4a,5,6,7-octahydro-1β-naphthyl)acetaldehyde Ethyl Acetal (6): bp 118–120 °C (5 mm); IR (neat) 1460, 1375, 1290, 1170, 1070, 960 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10–2.60 (m, 11, CH_2, CH), 1.11 (m, 3, CH_3), 1.18 (t, J = 7 Hz, 3, CH_3), 2.65–3.20 (m, 2, CH_2C=C), 3.20–4.40 (m, 3, CH_2O, CHO), 5.05 (m, 1, OCHO), 5.41 (m, 1, CH=C).[14]

Radical Cyclization with Tributyltin Hydride: Preparation of 7-Benzyl-2,9-dioxabicyclo[4.3.0]nonane (4). A mixture of **1g** (297 mg, 1 mmol), *n*-Bu_3SnH (0.4 mL, 1.5 mmol), and azobis(isobutyronitrile) (AIBN, 10 mg) was dissolved in benzene (3 mL) and then heated to reflux for 2 h. The mixture was concentrated, and the residue was purified by column chromatography (SiO_2, hexane–AcOEt, 20:1) to give 159 mg (73%) of **4** and 24 mg (11%) of the uncyclized **5**.[15] **4**: bp 126–128 °C (25 mm); IR (neat) 1595, 1455, 1375, 1335, 1325, 1240, 1170, 1070, 955, 875 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10–2.00 (m, 6, CH_2, CH), 2.38–2.80 (m, 2, CH_2Ar), 3.24–4.12 (m, 4, CH_2O), 5.20 (d, J = 3 Hz, 1, OCHO), 7.13 (br s, 5, PhH). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.28; H, 8.55.

(2β-Hydroxy-4aβ-methyl-1,2,3,4,4a,5,6,7,8,8aα-decahydro-1β-naphthyl)acetaldehyde Ethyl Acetal (9): bp 120–125 °C (5 mm); IR (neat) 1470, 1372, 1280, 1160, 980 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.80–1.20 (m, 6, CH_3), 1.10–2.20 (m, 16, CH_2, CH), 3.20–4.26 (m, 3, CH_2O, CHO), 5.07 (m, 1, OCHO).[14]

Oxidation of Hemiacetal 7: Preparation of (2β-Hydroxy-4aβ-methyl-1,2,3,4,4a,5,6,7-octahydro-1β-naphthyl)acetic Acid γ-Lactone (8). To a solution of **7** (100 mg, 0.42 mmol) in ether was added a chromium trioxide–H_2SO_4 (5 mL)[16] with vigorous stirring for 1 h under N_2 at 0–5 °C. The mixture was worked up in the usual manner, and the products were purified by column chromatography (SiO_2, hexane–AcOEt, 5:1) to give 59 mg (68%) of **8** as a solid: mp 88–89 °C (from hexane); IR (Nujol) 1790 (lactone C=O), 1370, 1355, 1238, 1162, 1145, 1110, 1018, 1000, 880 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.05–2.10 (m, 10, CH_2), 1.17 (s, 3, CH_3), 2.43–2.62 (m, 2, CH_2CO), 3.00–3.35 (m, 1, CH), 4.40–4.62 (m, 1, CHO), 5.45 (m, 1, CH=C); ^{13}C NMR ($CDCl_3$) δ 18.3 (t), 25.2 (t), 25.7 (t), 26.4 (q), 33.5 (s), 34.8 (t), 36.3 (t), 40.1 (t), 43.3 (d), 80.3 (d), 127.4 (d), 138.0 (s), 176.6 (s); FD mass spectrum,[17] m/z 206 (M^+). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.81; H, 8.95.

(2β-Hydroxy-4aβ-methyl-1,2,3,4,4a,5,6,7,8,8aα-decahydro-1β-naphthyl)acetic Acid γ-Lactone (10): mp 67–68 °C (from hexane); IR (Nujol) 1780 (lactone C=O), 1372, 1288, 1160, 1032, 1010, 914, 832 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.02 (s, 3, CH_3), 1.04–2.40 (m, 14, CH_2, CH), 2.50–2.60 (m, 2, CH_2CO), 4.53 (dt, J = 11, 7 Hz, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 18.2 (q), 21.7 (t), 25.4 (t), 26.9 (t, 2C), 29.8 (t), 33.3 (s), 37.3 (t), 40.2 (d), 43.4 (d), 43.5 (t), 79.8 (d), 177.2 (s); FD mass spectrum,[17] m/z 208 (M^+). Anal. Calcd for $C_{13}H_{20}O_2$: 74.96; H, 9.68. Found: C, 74.99; H, 9.76.

(14) Attempts at further purification for a satisfactory elemental analysis were unsuccessful.

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(17) We are grateful to Kuraray Chemical Co. for measurements of FD mass spectra with a JEOL HX-100 spectrometer.