OCH_3), 4.8 (1 H, m, olefin), 7.2–8 (5 H, m, arom.); mass spectrum, *m/e* 240 (M^+, 100), 238 (35). Precise mass determination: calcd for $C_{16}H_{18}O$ 240.115022; found 240.1150. Anal. Calcd for $C_{16}H_{18}O$: C, 79.97; H, 6.71; O, 13.32. Found: C, 79.59; H, 6.70; O, 13.63.

1,4-Dihydro-1,8-dimethylphenanthrene (3d): mp 33–34 °C; NMR ($CDCl_3$) δ 1.38 (3 H, m, CH_3), 2.65 (3 H, m, CH_3), 3.65 (3 H, m, CH_2), 5.9 (2 H, m, olefin), 7.5 (5 H, m, arom.); mass spectrum *m/e* 208 (M^+, 100), 206 (70). Precise mass determination: calcd for $C_{16}H_{16}$ 208.125194; found 208.1251. Anal. Calcd for $C_{16}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.68.

Photolysis of 2-Vinylbiphenyl (7). A solution of compound **7** (10^{-2} M) in propylamine was purged with nitrogen and irradiated with Rul 3000-Å lamps for 8 h. After the amine was removed under reduced pressure, the crude photoreaction product was analyzed by NMR and purified by column chromatography on alumina.

From 180 mg of **7**, 125 mg of **6a** (70%) and 15 mg of **9** (8%) were obtained. The structures of these compounds were established by comparison with authentic samples.

2-Ethylbiphenyl (**9**) was prepared by reduction of the starting material in the usual manner.

Acknowledgments. The authors thank Dr. B. M. Carden for linguistic criticism of the manuscript.

Registry No.—**1a,** 103-30-0; **1b,** 18869-29-9; **1c,** 15638-14-9; **1d,** 36888-18-3; **2a,** 645-49-8; **2b,** 2510-76-1; **2c,** 2510-75-0; **2d,** 20657-42-5; **3a,** 20244-28-4; **3b,** 69795-78-4; **3c,** 69795-79-5; **3d,** 69795-80-8; **4a,** 85-01-8; **4b,** 1576-67-6; **4c,** 15638-08-1; **4d,** 7372-87-4; **5a,** 103-29-7; **5b,** 538-39-6; **5c,** 1657-55-2; **5d,** 952-80-7; **6a,** 776-35-2; **6b,** 69795-81-9; **6c,** 69832-49-1; **6d,** 69795-82-0; **7,** 1587-22-0; **9,** 1812-51-7; *p,p'*-dimethylbenzoin, 1218-89-9; *o,o'*-dimethylbenzoin, 4389-39-3; *p*-tolualdehyde, 104-87-0; *o*-tolualdehyde, 529-20-4; 2-iodobiphenyl, 2113-51-1; acetaldehyde, 75-07-0; 1-biphenylethanol, 16927-84-7.

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Electrolytic Decarboxylation Reactions. 4. Electrosyntheses of 3-Alkyl-2-cycloalken-1-ol Acetates from 1-Alkyl-2-cycloalkene-1-carboxylic Acids. Preparation of *dl*-Muscone from Cyclopentadecanone

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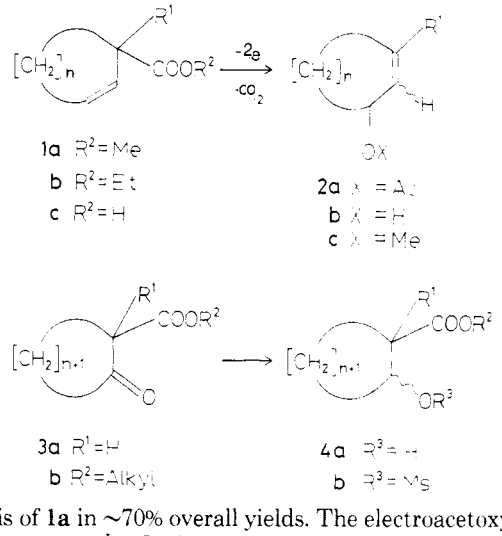
Based on stimulating results on the electrolytic acetoxylation of aliphatic carboxylic acids,[1] we have developed an electrosynthetic procedure for 3-alkyl-2-cycloalken-1-ol acetates (**2a**) from 1-alkyl-2-cycloalkene-1-carboxylic acids (**1c**) prepared from alicyclic 2-oxoalkanoates (**3a**). Synthetic application of such non-Kolbe type reactions on 3-alkenoates has been paid little attention.[2] The present 3-alkyl-2-alken-1-ol synthesis involves a regiospecific acetoxylation at the γ position of the acids **1c**, which serves as an introducing method for a methyl group at the β position of cyclopentadecanone,[3] leading to *dl*-muscone.

The 3-alkenoic acids **1c** were all prepared by (i) alkylation of **3a**, (ii) reduction of **3b** with sodium borohydride or lithium tri-*tert*-butoxyaluminum hydride, (iii) dehydration of the alcohol **4a** via the corresponding mesylate **4b**, and (iv) hydrolysis of **1a** in ~70% overall yields. The electroacetoxylation of **1c** (n = 12, R^1 = Me) was carried out in AcOH–*t*-BuOH–Et_3N using platinum electrodes at a constant applied voltage of ~30 V (36–54 mA/cm², 153 F/mol) at 19–22 °C for 4 h. The electrolysis conditions and results of the related compounds **1c** are shown in Table I.



Electrolytic decarboxylation of the acids **1c** by loss of two electrons on the anode would provide the tertiary carbonium ion a and subsequent three-carbon anionotropic rearrangement[4] of the cation a into the secondary carbonium ion b. The results (Table I) reveal that electrodecarboxylation of **1c** in

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Table I. Conditions [a] and Results of Electrolytic Acetoxylation of 1-Alkyl-2-cycloalkene-1-carboxylic Acids 1c

substrate 1c			current density,	electricity,		yield of **2a**,[d]
n	R^1	mmol	mA/cm^2	F/mol	time, h	%
12	Me	0.098	36–54[b]	153	3	79
9	Me	0.067	27–38[c]	180	3.5	93
4	$CH_3(CH_2)_4$	0.067	26–37[c]	190	4	86
3	$CH_3(CH_2)_4$	0.100	32–49[c]	160	4	93
2	$CH_3(CH_2)_5$	0.306	19–58[c]	70	5	84

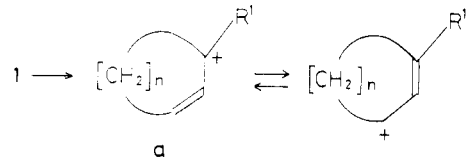
[a] Electrolyzed at 19–22 °C, Pt (3 cm^2), in a mixed solution of AcOH (1.5 mL), AcOEt (3.5 mL), and t-BuOH (0.19 mL) using Et_3N (0.6 mL) as an additive. [b] Adjusted at 30 V (applied voltage). [c] Adjusted at 20 V (applied voltage). [d] Based on isolated product.

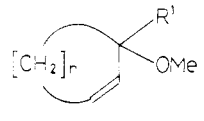
Table II. Conditions [a] and Results of Electrolytic Methoxylation of 1-Alkyl-2-cycloalkene-1-carboxylic Acids 1c

substrate 1c			current density,[b]	electricity,	Time,	yield of **2c** + **5**,[c]
n	R^1	mmol	mA/cm^2	F/mol	h	% (ratio)
12	Me	0.104	41–44	124	3	83 (1:2)[d]
9	Me	0.104	37–44	115	3	83 (1:2)[e]
3	$CH_3(CH_2)_4$	0.392	30–46	35	3.5	57 (7:3)[f]

[a] The electrolyses were carried out at 16–26 °C, Pt anode (3 cm^2) and SUS-27 stainless steel cathode (11 cm^2), in MeOH (15 mL) with Et_3N (210 mg) as an additive. [b] Applied voltage was adjusted at 20 V. [c] Based on isolated products. [d] Estimated by comparison with ^{1}H NMR signals at δ 3.16 and 3.22 (s, OCH_3). [e] Estimated by comparison with ^{1}H NMR signals at δ 3.19 and 3.26 (s, OCH_3). [f] Estimated by VPC (silicon GE-30 10, 4 m × 4 mm, H_2 flow rate 35 mL/min): R_t (min) **5** (8.5) and **2c** (10.2).

AcOH–t-BuOH–Et_3N affords exclusively the acetates **2a** via the carbonium ion b. In contrast, electromethoxylation of **1c** (n = 12, R^1 = Me) conducted in the more polar solvent MeOH–Et_3N using the same apparatus fitted with a platinum anode and a stainless steel (SUS-27) cathode at a constant applied voltage of ~20 V (41–44 mA/cm^2, 124 F/mol) at 20–26 °C for 3 h gave a mixture of **2c** (n = 12, R^1 = Me; 28% yield) and **5** (n = 12, R^1 = Me; 55% yield). These results (Table II)

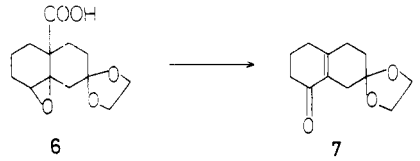




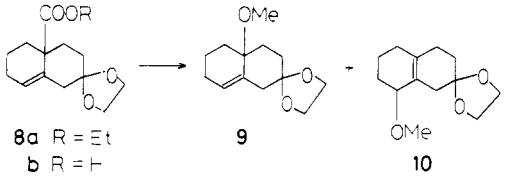
5

suggest that the strong nucleophilicity of methanol, compared to acetic acid, would preferentially lead to combination with the initially produced cation a to give **5**, whereas the carbonium ion b would be stabilized in the weak nucleophilic medium.[5]

On the other hand, electrodecarboxylation of 8,8a-epoxy-2,2-(ethylenedioxy)decalin-4a-carboxylic acid (**6**) in MeOH–Et_3N at 20 V (23–32 mA/cm^2) afforded smoothly the corresponding enone **7** in 84% yield as the sole product. However, under the same reaction conditions electrodecarboxylation of the octalin derivative **8** in MeOH–Et_3N provided the mixed products **9** (28.6%) and **10** (39.7%).

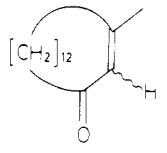


6 7



8a R = Et
b R = H 9 10

Part of our synthetic interest was directed to the conversion of the acetate **2a** (n = 12, R^1 = Me) into *dl*-muscone. After hydrolysis of **2a** (n = 12, R^1 = Me) with potassium hydroxide in aqueous methanol, oxidation of **2b** (n = 12, R^1 = Me) with pyridinium chlorochromate to give **11** and subsequent hydrogenation using palladium on charcoal afforded a 59% overall yield of *dl*-muscone.



11

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^{1}H NMR spectra were determined at 60 MHz with a Hitachi R-24 or at 100 MHz with a JEOL MH-100 spectrometer. ^{13}C NMR spectra were determined at 25.05 MHz with a JEOL pulsed Fourier transform spectrometer, Model FX-100. Samples were dissolved in $CDCl_3$, and the chemical shift values were expressed in δ values (ppm) relative to Me_4Si as an internal standard. Elemental analyses were performed in our laboratory.

Methyl 1-Methyl-2-oxocyclopentadecane-1-carboxylate (3b, n = 12, R^1 = R^2 = Me). A mixture of **3a**[6] (n = 12, R^2 = Me; 425 mg, 1.51 mmol), K_2CO_3 (1.64 g, 11.9 mmol), and MeI (460 mg, 3.29 mmol) in acetone (12 mL) was refluxed for 12 h. The insoluble material was separated by centrifugation, and the organic layer was concentrated. The residue was chromatographed (SiO_2, 7:1 hexane–AcOEt) to give 386 mg (86%) of **3b** (n = 12, R^1 = R^2 = Me) as a waxy oil: bp 104.0–108.0 °C (0.005 mm, Kugelrohr); IR (neat) 1743 (ester C=O), 1711 (C=O) cm^{-1}; ^{1}H NMR (60 MHz) δ 1.30 (s, 3, CH_3), 1.33 (br s, 24, CH_2), 2.40 (m, 2, $COCH_2$), 3.71 (s, 3, OCH_3); ^{13}C NMR δ 18.8 (q, CCH_3), 22.5 (t), 25.8 (t), 26.1 (t), 26.3 (t), 26.8 (t), 27.0 (t), 27.5 (t), 34.9 (t, C-15), 37.5 (t, C-3), 52.2 (q, OCH_3), 59.4 (s, C-1), 174.1 (s, ester C=O), 207.7 (s, C-2). Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88. Found: C, 73.01; H, 10.94.

Methyl 1-methyl-2-oxocyclododecane-1-carboxylate (3b, n = 9, R^1 = R^2 = Me) was prepared in the same manner as described above in 90% yield by treatment of **3a**[7] (n = 9, R^2 = Me) with MeI: bp 97.0–99.0 °C (0.002 mm, Kugelrohr); IR (neat) 1738 (ester C=O), 1710 (C=O) cm^{-1}; ^{1}H NMR (100 MHz) δ 0.90, 0.97, 1.55 (s, 3, CH_3), 1.31

(br s, 18, CH_2), 2.75–3.26 (m, 2, $COCH_2$), 3.71 (s, 3, OCH_3). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.92; H, 10.59.

Methyl 1-pentyl-2-oxocycloheptane-1-carboxylate (3b, n = 4, R^1 = n-C_5H_{11}, R^2 = Me) was prepared in the same manner as described above in 87% yield by the reaction of **3a**[7] (n = 4, R^2 = Me) with pentyl bromide in the presence of KI: bp 55.0–58.5 °C (0.017 mm, Kugelrohr); IR (neat) 1738 (ester C=O), 1714 (C=O) cm^{-1}; ^1H NMR (100 MHz) δ 0.89 (t, 3, J = 6 Hz, CH_3), 1.30 (br s, 8, CH_2), 1.50–2.30 (m, 8, CH_2), 2.39–2.76 (m, 2, $COCH_2$), 3.78 (s, 3, OCH_3). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 70.08; H, 10.25.

Methyl 1-hexyl-2-oxocyclopentane-1-carboxylate (3b, n = 2, R^1 = n-C_6H_{13}, R^2 = Me) was prepared in the same manner as described above in 93% yield by the reaction of **3a**[8] (n = 2, R^2 = Me) with hexyl bromide in the presence of KI: bp 90.0–93.0 °C (2 mm, Kugelrohr); IR (neat) 1755 (C=O), 1730 (ester C=O) cm^{-1}; ^1H NMR (60 MHz) δ 0.86 (t, 3, J = 6 Hz, CH_3), 1.28 (br s, 8, CH_2), 1.35–2.70 (m, 8, CH_2), 3.68 (s, 3, OCH_3). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.80; H, 9.80.

Methyl 2-Hydroxy-1-methylcyclopentadecane-1-carboxylate (4a, n = 12, R^1 = R^2 = Me). To a cold solution (0–5 °C) of **3b** (n = 12, R^1 = R^2 = Me; 106 mg, 0.36 mmol) in MeOH (2 mL) was added dropwise a solution of $NaBH_4$ (48 mg, 1.27 mmol) in water (0.5 mL). The mixture was stirred for 3 h at room temperature, quenched with cold aqueous 10% AcOH, and worked up in the usual manner to give 96 mg (89%) of **4a** (n = 12, R^1 = R^2 = Me) as an oil: bp 112.0–114.5 °C (0.004 mm, Kugelrohr); IR (neat) 3500 (OH), 1730 (shoulder), 1714 (ester C=O) cm^{-1}; ^1H NMR (60 MHz) δ 1.13 (s, 3, CH_3), 1.33 (br s, 26, CH_2), 2.80 (br s, 1, OH), 3.69 (s, 3, OCH_3), 3.35–4.10 (m, 1, CHO). Anal. Calcd for $C_{18}H_{34}O_3$: C, 72.44; H, 11.48. Found: C, 72.54; H, 11.49.

Methyl 2-hydroxy-1-methylcyclododecane-1-carboxylate (4a, n = 9, R^1 = R^2 = Me) was prepared in the same manner as described above in 96% yield: mp 115.5–116.5 °C; IR (Nujol) 3510 (OH), 1710 (ester C=O) cm^{-1}; ^1H NMR (100 MHz) δ 1.17 (s, 3, CH_3), 1.36 (br s, 20, CH_2), 2.88 (br, 1, OH), 3.72 (s, 3, OCH_3), 4.22 (d, 1, J = 9 Hz, CHO). Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 70.15; H, 11.02.

Methyl 2-hydroxy-1-pentylcycloheptane-1-carboxylate (4a, n = 4, R^1 = n-C_5H_{11}, R^2 = Me) was prepared in the same manner as described above in 90% yield: bp 96.0–98.0 °C (0.03 mm, Kugelrohr); IR (neat) 3500 (OH), 1727 (ester C=O), 1710 (shoulder) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.26 (br, 8, CH_2), 1.40–2.25 (m, 10, CH_2), 2.59 (br, 1, OH), 3.70 (s, 3, OCH_3), 3.84–4.16 (m, 1, CHO). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.48; H, 10.86.

Ethyl 2-hydroxy-1-pentylcyclohexane-1-carboxylate (4a, n = 3, R^1 = n-C_5H_{11}, R^2 = Et) was prepared in the same manner in 94% yield by the reaction of **3b**[9] (n = 3, R^1 = n-C_5H_{11}, R^2 = Et) and $NaBH_4$: bp 77.5–79.0 °C (0.006 mm, Kugelrohr); IR (neat) 3500 (OH), 1725, 1701 (ester C=O) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.00–2.30 (m, 16, CH_2), 1.26, 1.29 (t, 3, J = 7 Hz, CH_3), 3.15 (br, 1, OH), 3.48, 3.88 (dd, 1, J = 8 and 4 Hz, CHO), 4.02, 4.04 (q, 2, J = 7 Hz, CH_2O). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.47; H, 10.96.

Methyl 1-hexyl-2-hydroxycyclopentane-1-carboxylate (4a, n = 2, R^1 = n-C_6H_{13}, R^2 = Me) was prepared in 96% yield by the reaction of **3b** (n = 2, R^1 = n-C_6H_{13}, R^2 = Me) and $LiAl(t\text{-}BuO)_3H$: bp 59.0–61.0 °C (0.003 mm, Kugelrohr); IR (neat) 3450 (OH), 1725, 1715 (ester C=O) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.27 (br s, 8, CH_2), 1.40–2.30 (m, 8, CH_2), 2.27 (br, 1, OH), 3.67, 3.70 (s, 3, OCH_3), 3.99–4.40 (m, 1, CHO). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.20; H, 10.53.

Methyl 1-Methyl-2-(methanesulfonoxy)cyclopentadecane-1-carboxylate (4b, n = 12, R^1 = R^2 = Me). A solution of **4a** (n = 12, R^1 = R^2 = Me; 196 mg, 0.66 mmol) and $MeSO_2Cl$ (226 mg, 1.97 mmol) in pyridine (3 mL) was stirred for 30 min at 0–5 °C and for 3 h at room temperature. The mixture was quenched with cold water and worked up in the usual manner to give 247 mg (100%) of **4b** (n = 12, R^1 = R^2 = Me): IR (neat) 1729 (ester C=O), 1341, 1171 (SO_2) cm^{-1}; ^1H NMR (60 MHz) δ 1.20, 1.24 (s, 3, CH_3), 1.30 (br, 26, CH_2), 2.93, 3.01 (s, 3, SO_2CH_3), 3.69 (s, 3, OCH_3), 4.60–5.20 (m, 1, CHO). Anal. Calcd for $C_{19}H_{36}O_5S$: C, 60.61; H, 9.64. Found: C, 60.79; H, 9.67.

Methyl 1-methyl-2-(methanesulfonoxy)cyclododecane-1-carboxylate (4b, n = 9, R^1 = R^2 = Me) was prepared in the same manner as described above in 98% yield: IR (neat) 1730 cm^{-1} (ester); ^1H NMR (100 MHz) δ 1.24 (s, 3, CH_3), 1.38 (br s, 20, CH_2), 2.96, 3.06 (s, 3, SO_2CH_3), 3.70 (s, 3, OCH_3), 4.86, 5.38 (d, 1, J = 8 Hz, CHO). Anal. Calcd for $C_{16}H_{30}O_5S$: C, 57.47; H, 9.04. Found: C, 57.76; H, 8.82.

Methyl 2-(methanesulfonoxy)-1-pentylcycloheptane-1-carboxylate (4b, n = 4, R^1 = n-C_5H_{11}, R^2 = Me) was prepared in the same manner as described above in 99% yield: IR (neat) 1735 cm^{-1} (ester C=O); ^1H NMR (100 MHz) δ 0.87 (t, 3, J = 6 Hz, CH_3), 1.23 (br, 8, CH_2), 1.40–2.36 (m, 10, CH_2), 2.92, 2.97 (s, 3, SO_2CH_3), 3.66 (s, 3, OCH_3), 5.00, 5.16 (d, 1, J = 6 Hz, CHO). Anal. Calcd for $C_{15}H_{28}O_5S$: C, 56.23; H, 8.81. Found: C, 56.06; H, 8.94.

Ethyl 2-(methanesulfonoxy)-1-pentylcyclohexane-1-carboxylate (4b, n = 3, R^1 = n-C_5H_{11}, R^2 = Et) was prepared in the same manner as described above in 97% yield: IR (neat) 1730 cm^{-1} (ester C=O); ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.05–2.30 (m, 16, CH_2), 1.29 (t, 3, J = 7 Hz, CH_3), 2.98, 3.03 (s, 3, SO_2CH_3), 4.02–4.37 (m, 2, CH_2O), 5.01, 5.24 (d, 1, J = 6 Hz, CHO). Anal. Calcd for $C_{15}H_{28}O_5S$: C, 56.23; H, 8.81. Found: C, 56.44; H, 8.88.

Methyl 1-hexyl-2-(methanesulfonoxy)cyclopentane-1-carboxylate (4b, n = 2, R^1 = n-C_6H_{13}, R^2 = Me) was prepared in the same manner as described above in 98% yield: IR (neat) 1727 cm^{-1} (ester C=O); ^1H NMR (100 MHz) δ 0.86 (t, 3, J = 6 Hz, CH_3), 1.26 (br, 8, CH_2), 1.56–2.32 (m, 8, CH_2), 2.96, 3.02 (s, 3, SO_2CH_3), 3.70 (s, 3, OCH_3), 4.89, 5.28 (t, 1, J = 4 Hz, CHO). Anal. Calcd for $C_{14}H_{26}O_5S$: C, 54.89; H, 8.55. Found: C, 54.87; H, 8.55.

Methyl (*E*)- and (*Z*)-1-Methyl-2-cyclopentadecene-1-carboxylates (1a, n = 12, R^1 = Me). A mixture of **4b** (n = 12, R^1 = R^2 = Me; 220 mg, 0.59 mmol) and Me_2SO (2 mL) was heated at 135–140 °C for 3 h and worked up in the usual manner to give 162 mg (99%) of **1a** (n = 12, R^1 = Me): bp 73.0–75.5 °C (0.0035 mm, Kugelrohr); IR (neat) 1733 cm^{-1} (ester C=O); ^1H NMR (100 MHz) δ 1.26 (s, 3, CH_3), 1.32 (br s, 22, CH_2), 2.12 (m, 2, CH_2C=C), 3.66 (s, 3, OCH_3), 5.25–5.77 (m, 2, HC=C). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.02; H, 11.60.

Methyl (*E*)- and (*Z*)-1-methyl-2-cyclododecene-1-carboxylates (1a, n = 9, R^1 = Me) were prepared in the same manner as described above in 97% yield: bp 139.0–141.0 °C (2 mm, Kugelrohr); IR (neat) 1730 cm^{-1} (ester C=O); ^1H NMR (100 MHz) δ 1.26 (s, 3, CH_3), 1.29 (br, 14, CH_2), 1.61–2.30 (m, 4, CH_2), 3.66 (s, 3, OCH_3), 5.12–5.86 (m, 2, HC=C). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.74; H, 11.17.

Methyl 1-pentyl-2-cycloheptene-1-carboxylate (1a, n = 4, R^1 = n-C_5H_{11}) was prepared in the same manner as described above in 97% yield: bp 96.0–98.0 °C (2 mm, Kugelrohr); IR (neat) 3020, 1732 (ester C=O), 1650 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 0.87 (t, 3, J = 6 Hz, CH_3), 1.25 (br, 6, CH_2), 1.40–1.80 (m, 10, CH_2), 1.90–2.17 (m, 2, CH_2C=C), 3.63 (s, 3, OCH_3), 5.49–5.89 (m, 2, HC=C). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.05; H, 10.84.

Ethyl 1-pentyl-2-cyclohexene-1-carboxylate (1b, n = 3, R^1 = n-C_5H_{11}) was prepared in the same manner as described above in 91% yield: bp 83.0–85.0 °C (2 mm, Kugelrohr); IR (neat) 3020, 1730 (ester C=O), 1651 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.23 (br, 6, CH_2), 1.25 (t, 3, J = 7 Hz, CH_3), 1.41–1.81 (m, 5, CH_2), 1.95–2.28 (m, 3, CH_2), 4.17 (q, 2, J = 7 Hz, CH_2O), 5.79 (br s, 2, HC=C). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.19; H, 10.91.

Methyl 1-hexyl-2-cyclopentene-1-carboxylate (1a, n = 2, R^1 = n-C_6H_{13}) was prepared in the same manner as described above in 98% yield: bp 92.0–94.0 °C (3 mm, Kugelrohr); IR (neat) 3040, 1732 (ester C=O), 1619 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.28 (br, 8, CH_2), 1.50–1.97 (m, 3, CH_2), 2.24–2.56 (m, 3, CH_2), 3.72 (s, 3, OCH_3), 5.68–5.94 (m, 2, HC=C). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.20; H, 10.60.

(*E*)- and (*Z*)-1-Methyl-2-cyclopentadecene-1-carboxylic Acids (1c, n = 12, R^1 = Me). A solution of **1a** (n = 12, R^1 = Me; 240.5 mg, 0.86 mmol) and KOH (290 mg, 5.17 mmol) in MeOH (7 mL) and water (0.6 mL) was stirred for 5 h at 60–65 °C. After the solvent was removed, the mixture was washed with benzene and the aqueous layer was acidified with cold aqueous 10% HCl and worked up in the usual manner to give 218 mg (95%) of **1c** (n = 12, R^1 = Me) as a solid: mp 69.5–71.5 °C; IR (Nujol) 3400–2600 (COOH), 1700 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 1.31 (s, 3, CH_3), 1.33 (br s, 22, CH_2), 2.00–2.32 (m, 2, CH_2C=C), 5.40–5.72 (m, 2, HC=C), 11.40 (br, 1, COOH). Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.77; H, 11.57.

(*E*)- and (*Z*)-1-Methyl-2-cyclododecene-1-carboxylic acids (1c, n = 9, R^1 = Me) were prepared in the same manner as described above in 86% yield: IR (neat) 3600–2500 (COOH), 1697 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 1.26, 1.36 (s, 3, CH_3), 1.31 (br s, 16, CH_2), 1.90–2.29 (m, 2, CH_2C=C), 5.10–5.84 (m, 2, HC=C), 11.76 (br, 1, COOH). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.88; H, 10.83.

1-Pentyl-2-cycloheptene-1-carboxylic acid (1c, n = 4, R^1 = n-C_5H_{11}) was prepared in the same manner as described above in 88% yield: IR (neat) 3400–2400 (COOH), 1697 (COOH) cm^{-1}; ^1H NMR

(100 MHz) δ 0.87 (t, 3, J = 6 Hz, CH_3), 1.28 (br, 6, CH_2), 1.48–1.92 (m, 10, CH_2), 2.00–2.22 (m, 2, CH_2C=C), 5.50–6.00 (m, 2, HC=C), 10.18 (br, 1, COOH). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.49; H, 10.70.

1-Pentyl-2-cyclohexene-1-carboxylic acid (1c, n = 3, R^1 = n-C_5H_{11}) was prepared in the same manner as described above in 93% yield: IR (neat) 3400–2400 (COOH), 1695 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 0.91 (t, 3, J = 6 Hz, CH_3), 1.30 (br, 6, CH_2), 1.46–1.79 (m, 5, CH_2), 1.88–2.30 (m, 3, CH_2), 5.76–6.04 (m, 2, HC=C), 10.70 (br, 1, COOH). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.43; H, 10.38.

1-Hexyl-2-cyclopentene-1-carboxylic acid (1c, n = 2, R^1 = n-C_6H_{13}) was prepared in the same manner as described above in 83% yield: IR (neat) 3400–2400 (COOH), 1698 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 0.90 (t, 3, J = 6 Hz, CH_3), 1.28 (br, 8, CH_2), 1.48–1.99 (m, 3, CH_2), 2.44 (m, 3, CH_2), 5.76–5.96 (m, 2, HC=C), 9.95 (br, 1, COOH). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.40; H, 10.46.

8,8a-Epoxy-2,2-(ethylenedioxy)-4a-decalylcarboxylic Acid (6). To a solution of **8b** (105 mg, 0.44 mmol) in CH_2Cl_2 (5 mL) was added 85% m-chloroperbenzoic acid (120 mg, 0.59 mmol), and the mixture was stirred for 20 h at 5 °C. Removal of the solvent and subsequent chromatography (SiO_2, 1:1 hexane–AcOEt) gave 99.6 mg (89%) of **6** as an oil: IR (neat) 3600–2400 (COOH), 1710 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 1.19–3.04 (m, 13, CH_2, CHO), 3.97–4.16 (m, 4, CH_2O), 6.16 (br s, 1, COOH). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.41; H, 7.14. Found: C, 61.51; H, 7.20.

2,2-(Ethylenedioxy)-1,2,3,4,4a,5,6,7-octahydronaphthalene-4a-carboxylic Acid (8b). To a solution of **8a**[10] (416 mg, 1.56 mmol) in MeOH (15 mL) was added a solution of KOH (530 mg, 9.46 mmol) in water (1 mL). The mixture was stirred for 24 h at 55–60 °C and worked up in the usual manner to give 292 mg (79%) of **8b** as a solid: mp 71.5–73.5 °C; IR (Nujol) 3400–2500 (COOH), 1680 (COOH) cm^{-1}; ^1H NMR (100 MHz) δ 1.30–3.05 (m, 12, CH_2), 3.96 (s, 4, CH_2O), 5.69 (br s, 1, HC=C), 9.56 (br s, 1, COOH). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.80; H, 7.88.

Electrolysis Apparatus. An undivided cell was equipped with a platinum anode (3 cm^2), a platinum cathode (3 cm^2), and/or a SUS-27 stainless steel cathode (11 cm^2), a gas lead pipe, and a thermometer. Regulated dc power was supplied by a Metronix 543B instrument.

General Procedure for Electrochemical Synthesis of 2a from 1c in AcOH–AcOEt–t-BuOH. A stirred solution of **1c** (n = 12, R^1 = Me; 26 mg, 0.098 mmol) and Et_3N (436 mg, 4.3 mmol) in AcOH (1.5 mL), AcOEt (3.5 mL), and t-BuOH (0.19 mL) was electrolyzed in a beaker fitted with two platinum electrodes at a constant applied voltage of 30 V, current density 36–54 mA/cm^2, for 3 h (~153 F/mol) at 19–22 °C. After electrolysis, the mixture was concentrated and taken up in ether. The extracts were washed with brine, dried (Na_2SO_4), and shaken over solid K_2CO_3. Removal of the solvent and subsequent chromatography (SiO_2, 5:1 hexane–AcOEt) gave 21.8 mg (79%) of **2a** (n = 12, R^1 = Me) as an oil: bp 110.0–111.0 °C (0.03 mm, Kugelrohr); IR (neat) 1735 (ester C=O), 1670 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 1.32 (br, 24, CH_2), 1.70 (s, 3, CH_3), 2.01 (s, 3, $COCH_3$), 2.00–2.18 (m, 2, CH_2), 5.12 (d, 1, J = 10 Hz, HC=C), 5.38–5.60 (m, 1, CHO). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.25; H, 11.41.

(*E*)- and (*Z*)-3-Methyl-2-cyclododecen-1-ol Acetates (2a, n = 9, R^1 = Me): bp 45.0–47.0 °C (0.0015 mm, Kugelrohr); IR (neat) 1735 (ester C=O), 1660 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 1.28 (br, 16, CH_2), 1.53, 1.73 (s, 3, CH_3), 1.90–2.10 (m, 2, CH_2), 2.01 (s, 3, $COCH_3$), 5.26 (d, 1, J = 10 Hz, HC=C), 5.34–5.65 (m, 1, CHO). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.53; H, 11.07.

3-Pentyl-2-cyclohepten-1-ol Acetate (2a, n = 4, R^1 = n-C_5H_{11}): bp 57.0–59.0 °C (0.002 mm, Kugelrohr); IR (neat) 1730 (ester C=O), 1370, 1241, 1025 cm^{-1}; ^1H NMR (100 MHz) δ 0.90 (t, 3, J = 6 Hz, CH_3), 1.20–2.24 (m, 10, CH_2), 1.29 (br, 6, CH_2), 2.03 (s, 3, $COCH_3$), 5.41 (br s, 2, HC=C, CHO); ^{13}C NMR δ 14.0 (q), 21.4 (q, acetyl CH_3), 22.6 (t), 26.1 (t), 27.2 (t), 27.3 (t), 31.5 (t), 32.5 (t), 32.9 (t), 40.1 (t, C-7), 74.0 (d, C-1), 127.0 (d, C-2), 144.0 (s, C-3), 170.4 (s, acetyl C=O). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.11; H, 10.76.

3-Pentyl-2-cyclohexen-1-ol Acetate (2a, n = 3, R^1 = n-C_5H_{11}): bp 51.0–53.0 °C (0.011 mm, Kugelrohr); IR (neat) 1730 (ester C=O), 1664 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 0.89 (t, 3, J = 6 Hz, CH_3), 1.29 (br, 6, CH_2), 1.71 (br, 4, CH_2), 1.91–2.40 (m, 4, CH_2), 2.03 (s, 3, $COCH_3$), 5.27 (br, 1, HC=C), 5.44 (br s, 1, CHO); ^{13}C NMR δ 14.0 (q), 19.2 (t), 21.5 (q, acetyl CH_3), 22.6 (t), 27.1 (t), 28.4 (t, 2C), 31.6 (t, C-4), 37.7 (t, C-6), 68.9 (d, C-1), 119.2 (d, C-2), 144.9 (s, C-3), 170.8 (s, acetyl C=O). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.39; H, 10.62.

3-Hexyl-2-cyclopenten-1-ol Acetate (2a, n = 2, R^1 = n-C_6H_{13}): bp 49.0–51.0 °C (0.006 mm, Kugelrohr); IR (neat) 1730 (ester C=O), 1682 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 0.90 (t, 3, J = 6 Hz, CH_3), 1.31 (br, 8, CH_2), 1.50–2.55 (m, 6, CH_2), 1.92 (s, 3, $COCH_3$), 5.41 (complex s, 1, HC=C), 5.52 (broad m, 1, CHO). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.35; H, 10.45.

General Procedure for Electrosynthesis of 2c and/or 5 from 1c in MeOH. A stirred solution of **1c** (n = 12, R^1 = Me; 27.8 mg, 0.104 mmol) in MeOH (15 mL) containing Et_3N (210 mg, 2.08 mmol) was electrolyzed in a beaker fitted with a platinum anode and a SUS-27 stainless steel cathode at a constant applied voltage of 20 V, current density 41–44 mA/cm^2, for 3 h (~140 F/mol) at 20–26 °C. The electrolysis solution was concentrated, and the residue was taken up in ether–benzene. The organic layer was washed with brine and dried (Na_2SO_4). Removal of the solvent and subsequent chromatography (SiO_2, 7:1 hexane–AcOEt) gave 21.9 mg (83%) of a mixture of **2c** and **5** (n = 12, R^1 = Me) [the ratio of **2c/5** was estimated to be 1:2 based on ^1H NMR signals at δ 3.16 (s, OCH_3) and 3.22 (s, OCH_3)]: bp 70.5–73.0 °C (0.003 mm, Kugelrohr); IR (neat) 1660 (C=C), 1458, 1371, 1088, 976 cm^{-1}; ^1H NMR (100 MHz) δ 1.20, 1.68 (s, 3, CH_3), 1.30 (br, 22, CH_2), 2.13 (m, 2, CH_2), 3.16, 3.22 (s, 3, OCH_3), 3.94 (m, CHO), 4.99–5.67 (m, HC=C). Anal. Calcd for $C_{17}H_{32}O$: C, 80.89; H, 12.78. Found: C, 80.97; H, 12.91.

(*E*)- and (*Z*)-3-Methoxy-1-methyl-2-cyclododecenes (2c, n = 9, R^1 = Me) and/or (*E*)- and (*Z*)-1-methoxy-1-methyl-2-cyclododecenes (5, n = 9, R^1 = Me) (2c/5 = 1:2): bp 75.0–77.5 °C (0.005 mm, Kugelrohr); IR (neat) 1660 (C=C), 1460, 1443, 1371, 1080, 982 cm^{-1}; ^1H NMR (100 MHz) δ 1.21, 1.71 (s, 3, CH_3), 1.29 (br, 16, CH_2), 2.10 (m, 2, CH_2), 3.19, 3.26 (s, 3, OCH_3), 3.79–4.04 (m, CHO), 5.12–5.48 (m, HC=C). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.91; H, 12.27.

1-Methoxy-3-pentyl-2-cyclohexene (2c, n = 3, R^1 = n-C_5H_{11}): bp 73.5–75.0 °C (0.006 mm, Kugelrohr); IR (neat) 1666 (C=C), 1468, 1452, 1378, 1354, 1194, 1095, 934, 912 cm^{-1}; ^1H NMR (100 MHz) δ 0.89 (t, 3, J = 6 Hz, CH_3), 1.14–2.03 (m, 14, CH_2), 3.37 (s, 3, OCH_3), 3.72 (br, 1, CHO), 5.50 (br, 1, HC=C). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.11; H, 12.37.

1-Methoxy-1-pentyl-2-cyclohexene (5, n = 3, R^1 = n-C_5H_{11}): bp 72.0–74.5 °C (0.006 mm, Kugelrohr); IR (neat) 3010, 1648 (C=C), 1468, 1454, 1074, 908 cm^{-1}; ^1H NMR (100 MHz) δ 0.98 (t, 3, J = 6 Hz, CH_3), 1.10–2.16 (m, 14, CH_2), 3.17, 3.18 (s, 3, OCH_3), 5.57 (d, 1, J = 10 Hz, HC=C), 5.88 (dt, 1, J = 10 and 4 Hz, HC=C). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.26; H, 12.28.

Electrolysis of 6 in MeOH. A solution of **6** (77.6 mg, 0.306 mmol) in MeOH (12 mL) containing Et_3N (210 mg, 2.08 mmol) was electrolyzed with two platinum electrodes at a constant applied voltage of 20 V, current density 23–32 mA/cm^2, for 7 h (~120 F/mol) at 44–49 °C. The mixture was concentrated, and the residue was worked up in the usual manner to give 53.5 mg (84.2%) of **7** as an oil after chromatography (SiO_2, 10:1 hexane–AcOEt): bp 73.5–76.0 °C (0.007 mm, Kugelrohr); IR (neat) 1664 (C=O), 1635 (C=C) cm^{-1}; ^1H NMR (60 MHz) δ 1.20–2.60 (m, 12, CH_2), 3.97 (complex s, 4, CH_2O); ^{13}C NMR δ 22.2 (t), 30.7 (t, 2C), 31.1 (t), 32.3 (t), 37.3 (t), 64.4 (t, 2C), 107.9 (s, C-2), 130.0 (s, C-8a), 155.7 (s, C-4a), 198.4 (s, C-8). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.34; H, 7.76.

Electrolysis of 8b in MeOH. A solution of **8b** (102.5 mg, 0.43 mmol) in MeOH (12 mL) and Et_3N (291 mg, 2.88 mmol) was electrolyzed using two platinum electrodes at a constant applied voltage of 20 V, current density 23–33 mA/cm^2, for 5 h (~82 F/mol). The usual workup and subsequent chromatography (SiO_2, 10:1 hexane–AcOEt) gave 27.2 mg (28.6%) of **9** and 37.8 mg (39.7%) of **10** as a oil product. Physical constants together with elemental analyses of **9** and **10** are as follows.

2,2-(Ethylenedioxy)-4a-methoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (9): bp 41.0–42.5 °C (0.01 mm, Kugelrohr); IR (neat) 3050, 1376, 1311, 1265, 1202, 1167, 1130, 1088, 1068, 1000, 974, 965, 948, 869, 811 cm^{-1}; ^1H NMR (60 MHz) δ 1.23–2.75 (m, 12, CH_2), 3.17 (s, 3, OCH_3), 3.93 (s, 4, CH_2O), 5.69 (br s, 1, HC=C); ^{13}C NMR δ 19.9 (t), 25.3 (t), 30.5 (t), 31.6 (t), 33.7 (t), 41.2 (t, C-1), 49.5 (q, OCH_3), 64.3 (t, 2C), 73.0 (s, C-4a), 109.2 (s, C-2), 127.4 (d, C-8), 135.4 (s, C-8a). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.63; H, 8.89.

2,2-(Ethylenedioxy)-8-methoxy-1,2,3,4,5,6,7,8-octahydronaphthalene (10): bp 41.0–43.5 °C (0.006 mm, Kugelrohr); IR (neat) 1365, 1329, 1251, 1215, 1197, 1141, 1130, 1098, 1080, 1017, 947, 900, 842 cm^{-1}; ^1H NMR (60 MHz) δ 1.27–2.73 (m, 12, CH_2), 3.32 (s, 3, OCH_3), 3.45 (m, 1, CHO), 3.97 (s, 4, CH_2O); ^{13}C NMR δ 18.6 (t), 26.6 (t), 29.7 (t), 29.9 (t), 31.0 (t), 37.5 (t, C-1), 59.4 (q, OCH_3), 64.3 (t, 2C), 77.8 (d, C-8), 108.6 (s, C-2), 126.5 (s, C-4a), 132.4 (s, C-8a). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.69; H, 8.90.

(*E*)- and (*Z*)-3-Methyl-2-cyclopentadecen-1-ols (2b, n = 12, R^1 = Me). A solution of **2a** (n = 12, R^1 = Me; 20 mg, 0.071 mmol) and KOH (50 mg, 0.89 mmol) in 25% aqueous MeOH (2 mL) was stirred

for 8 h at 5–10 °C. The mixture was worked up in the usual manner to give 16 mg (93%) of **2b** (n = 12, R^1 = Me) as an oil: bp 51.5–53.5 °C (0.005 mm, Kugelrohr); IR (neat) 3320 (OH), 1668 (C=C), 1460, 1380, 1015, 720 cm^{-1}; ^1H NMR (100 MHz) δ 1.32 (br s, 23, CH_2, OH), 1.68 (s, 3, CH_3), 2.04–2.15 (m, 2, CH_2), 4.28–4.54 (m, 1, CHO), 5.18 (d, 1, J = 10 Hz, HC=C). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.54; H, 12.55.

***(E)*- and *(Z)*-3-Methyl-2-cyclopentadecen-1-ones (11).**[11] To a stirred suspension of pyridinium chlorochromate (30 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) was added dropwise a solution of **2b** (n = 12, R^1 = Me; 15 mg, 0.063 mmol) in CH_2Cl_2 at 0–5 °C. The mixture was stirred for 30 min at 5 °C and for 2 h at room temperature and worked up in the usual manner to give 9.7 mg (65%) of **11** as an oil: bp 75.0–78.0 °C (0.005 mm, Kugelrohr) [lit.[11a] 100–105 °C (0.01 mm)]; IR (neat) 3050, 1685 (C=O), 1617 (C=C) cm^{-1}; ^1H NMR (100 MHz) δ 1.30 (br, 22, CH_2), 2.14 (s, 3, CH_3), 2.28, 2.41 (d, 2, J = 5 Hz, $COCH_2$), 6.17 (br s, 1, HC=C).

***dl*-Muscone.**[12] A mixture of **11** (7 mg, 0.03 mmol) and 10% palladium on charcoal in EtOH (1.5 mL) was treated with excess H_2 (2 mL). The mixture was filtered, and the filtrate was concentrated to give 6.8 mg (97%) of *dl*-muscone:[13] bp 77.5–79.0 °C (0.005 mm, Kugelrohr) [lit.[11a] 100–105 °C (0.01 mm)]; IR (neat) 1715 cm^{-1} (C=O); ^1H NMR (60 MHz) δ 0.92 (d, 3, J = 6 Hz, CH_3), 1.29 (br, 23, CH_2, CH), 2.00–2.52 (m, 4, CH_2).

Registry No.—(*E*)-**1a** (n = 12, R^1 = Me), 69832-58-2; (*Z*)-**1a** (n = 12, R^1 = Me), 69832-59-3; (*E*)-**1a** (n = 9, R^1 = Me), 69832-60-6; (*Z*)-**1a** (n = 9, R^1 = Me), 69832-61-7; **1a** (n = 4, R^1 = n-C_5H_{11}), 69832-62-8; **1a** (n = 2, R^1 = n-C_6H_{13}), 69832-63-9; **1b** (n = 3, R^1 = n-C_5H_{11}), 69832-64-0; (*E*)-**1c** (n = 12, R^1 = Me), 69832-65-1; (*Z*)-**1c** (n = 12, R^1 = Me), 69832-66-2; (*E*)-**1c** (n = 9, R^1 = Me), 69832-67-3; (*Z*)-**1c** (n = 9, R^1 = Me), 69832-68-4; **1c** (n = 4, R^1 = n-C_5H_{11}), 69832-69-5; **1c** (n = 3, R^1 = n-C_5H_{11}), 69855-40-9; **1c** (n = 2, R^1 = n-C_6H_{13}), 69832-70-8; (*E*)-**2a** (n = 12, R^1 = Me), 69832-71-9; (*Z*)-**2a** (n = 12, R^1 = Me), 69832-72-0; (*E*)-**2a** (n = 9, R^1 = Me), 69832-73-1; (*Z*)-**2a** (n = 9, R^1 = Me), 69832-74-2; **2a** (n = 4, R^1 = n-C_5H_{11}), 69832-75-3; **2a,** (n = 3, R^1 = n-C_5H_{11}), 69832-76-4; **2a** (n = 2, R^1 = n-C_6H_{13}), 69832-77-5; (*E*)-**2b** (n = 12, R^1 = Me), 69832-78-6; (*Z*)-**2b** (n = 12, R^1 = Me), 69832-79-7; (*E*)-**2c** (n = 12, R^1 = Me), 69832-80-0; (*Z*)-**2c,** (n = 12, R^1 = Me), 69832-81-1; (*E*)-**2c** (n = 9, R^1 = Me), 69832-82-2; (*Z*)-**2c,** (n = 9, R^1 = Me), 69832-83-3; **2c** (n = 3, R^1 = n-C_5H_{11}), 69832-84-4; **3a** (n = 12, R^2 = Me), 52794-21-5; **3a** (n = 9, R^2 = Me), 62939-87-1; **3a,** (n = 4, R^2 = Me), 52784-32-4; **3a** (n = 2, R^2 = Me), 10472, 24-9; **3b** (n = 12, R^1 = R^2 = Me), 69832-85-5; **3b** (n = 9, R^1 = R^2 = Me), 69832-86-6; **3b** (n = 4, R^1 = n-C_5H_{11}, R^2 = Me), 69832-87-7; **3b** (n = 2, R^1 = n-C_6H_{13}, R^2 = Me), 69832-88-8; **3b** (n = 3, R^1 = n-C_5H_{11}, R^2 = Et), 57026-68-3; **4a** (n = 12, R^1 = R^2 = Me), 69832-89-9; **4a** (n = 9, R^1 = R^2 = Me), 69832-90-2; **4a** (n = 4, R^1 = n-C_5H_{11}, R^2 = Me), 69832-91-3; **4a** (n = 3, R^1 = n-C_5H_{11}, R^2 = Et), 69832-92-4; **4a** (n = 2, R^1 = n-C_6H_{13}, R^2 = Me), 69832-93-5; **4b** (n = 12, R^1 = R^2 = Me), 69832-94-6; **4b** (n = 9, R^1 = R^2 = Me), 69832-95-7; **4b** (n = 4, R^1 = n-C_5H_{11}, R^2 = Me), 69832-96-8; **4b** (n = 3, R^1 = n-C_5H_{11}, R^2 = Et), 69832-97-9; **4b** (n = 2, R^1 = n-C_6H_{13}, R^2 = Me), 69832-98-0; (*E*)-**5** (n = 12, R^1 = Me), 69832-99-1; (*Z*)-**5** (n = 12, R^1 = Me), 69833-00-7; (*E*)-**5** (n = 9, R^1 = Me), 69833-01-8; (*Z*)-**5** (n = 9, R^1 = Me), 69833-02-9; **5** (n = 3, R^1 = n-C_5H_{11}), 69833-03-0; **6,** 69833-04-1; **7,** 69833-05-2; **8a,** 65898-58-0; **8b,** 69833-06-3; **9,** 69833-07-4; **10,** 69833-08-5; (*E*)-**11,** 58643-70-2; (*Z*)-**11,** 58643-71-3; *dl*-muscone, 956-82-1.

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Reaction of 2,3,4,6-Tetramethoxybenzaldehyde with Aluminum Chloride. Selective Cleavage at Position 2 and Selective Ether Exchange at Position 3

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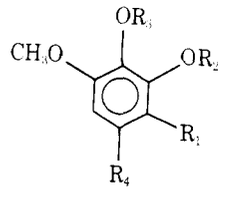
The cleavage of 2,3,4,6-tetramethoxybenzaldehyde, **1**, with aluminum chloride in ether to obtain the 2-hydroxy compound, **2**,[1] is accompanied by formation of appreciable amounts (38%) of a single ethoxy-containing compound. This compound is identified as **3**. A modification for a high yield preparation of pure **2** is described.

Polymethoxybenzaldehydes with 2-methoxy groups can cleave that group selectively with aluminum chloride.[2-4] Reichstein[2] formed the 2-hydroxy compound **4** from **5** using toluene as the solvent, but Robertson,[3] finding that toluene cleaved all the methoxy groups, used ether as the solvent.

To monocleave **1** to **2**, we tried Robertson's method. The cleavage product had a wide melting point range after some purification and showed ethoxy peaks in ^1H NMR. The simplicity of the spectra suggested a mixture containing a single ethoxy compound in 38% yield. Isolation of the dimethoxyethoxyhydroxybenzaldehyde, **3**, was accomplished via extraction with 5% sodium carbonate solution. Its identity was established by methylation and comparison with known ethoxytrimethoxybenzaldehydes. The ethoxy should be either in the 3 position (next to the phenol) or the 6 position (next to the formyl group). Accordingly, 3-ethoxy-2,4,6-trimethoxy- and 6-ethoxy-2,3,4-trimethoxybenzaldehydes, **6** and **7**, were prepared respectively from the phenols **8** and **9** via ethylation to **10** and **11** and formylation to **6** and **7**. By increasing the



	R_1	R_2	R_3	R_4
1	CHO	CH_3	CH_3	CH_3O
2	CHO	H	CH_3	CH_3O
3	CHO	H	CH_3CH_2	CH_3O
4	CHO	H	CH_3	H
5	CHO	CH_3	CH_3	H
6	CHO	CH_3	CH_3CH_2	CH_3O
7	CHO	CH_3	CH_3	CH_3CH_2O
8	H	CH_3	H	CH_3O
9	H	CH_3	CH_3	OH
10	H	CH_3	CH_3CH_2	CH_3O
11	H	CH_3	CH_3	CH_3CH_2O
12	CHO	H	H	CH_3O
13	CHO		$-CH_2-$	CH_3O

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