Electrooxidative Cleavage of Carbon–Carbon Linkages. 1. Preparation of Acyclic Oxoalkanoates from 2-Hydroxy- and 2-Acetoxy-1-cycloalkanones and Cycloalkanone Enol Acetates

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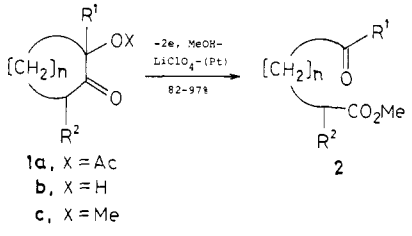
A methodology is described for the synthesis of acyclic oxoalkanoates **2** by electrooxidative cleavage of carbon–carbon linkages of 2-oxocycloalkan-1-ols **1** and cycloalkanone enol acetates **3**. The electrolysis of **1** was carried out in a MeOH–$LiClO_4$–(Pt) system at a constant applied voltage of 20 V by using a divided cell, giving **2** in 82–97% yields. On the other hand, **3** was electrolyzed in MeOH–AcOH (10:1)–$LiClO_4$–(Pt) at 2–8 °C to give **2** in 72–79% yields. Electrolysis of 4-hydroxy-*p*-menth-8-ene afforded methyl (3*R*)-3,7-dimethyl-6-oxo-7-octenoate, a chiral synthetic block for the synthesis of (+)-rose oxide, in 84% yield. Similarly, the procedure could be applied to the preparation of methyl (+)-6-oxo-6,7-dihydrocitronellate from (+)-menthone enol acetate (74%) as well as 4-hydroxy-*p*-menthone (94%). Other lithium salts, i.e., $LiBF_4$ and CF_3CO_2Li, can be used for the present purpose, but there are some difficulties in producing **2** with Et_4NOTs and Et_4NClO_4. A plausible mechanism of the formation of **2** from **1** is also discussed.

Cleavage of carbon–carbon bond at the α-position of 2-oxy-1-cycloalkanones **1**, giving oxoalkanoates **2**,[1] has been carried out by using lead tetraacetate,[2] sodium periodate,[3] and perbenzoic acid.[4] Instead of the chemical method, we have been investigating a general procedure for the preparation of the keto esters **2** from the 2-oxycycloalkanones **1a** and **1b** and the cycloalkanone enol acetates

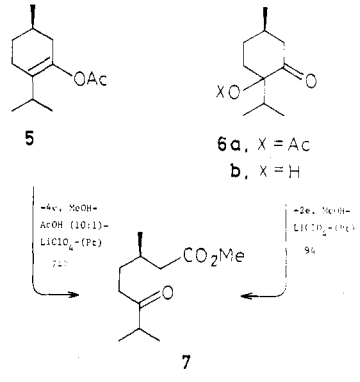


1a, X = Ac
b, X = H
c, X = Me

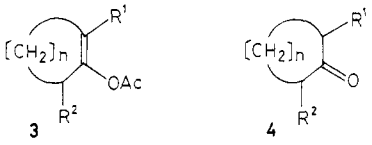
2

3 by electrolysis. So far, investigations of electrochemical carbon–carbon bond cleavage reactions have concentrated on 1,2-diols,[5] 2-alkoxyalkan-1-ols,[5a,6] 2-amino-1-ols,[6,7] 1,2-diamino derivatives,[7] 2-alkoxy 1-acetals,[8] and 2-oxoalk-1-enoic acids.[9] We report here a potential procedure of the electrooxidative cleavage of carbon–carbon linkages of the α-position of **1** and **3**, which can cut a significant path to chiral synthetic blocks.

Scheme I



Electrooxidative Cleavage of 2-Oxy-1-cycloalkanones 1 (X = H, Ac). 2-Oxy-1-cycloalkanones **1** (X = Ac, H) were prepared from cycloalkanones **4** by the



following method: epoxidation of the enol acetate **3** of **4** with monoperphthalic acid in methylene chloride and subsequent acid-catalyzed rearrangement of the epoxide[10] into **1a** on treatment with acetic acid, whose hydrolysis gave **1b** in 62–70% overall yields.

The electrocleavage of the carbon–carbon bond of **1a** (n = 3, R^1 = Me, R^2 = H) in a MeOH–0.23 M $LiClO_4$–(Pt) system at a constant applied voltage of 20 V (anode potential 2.00–2.05 V vs. Ag/0.1 M AgCl) afforded the desired **2** (n = 3, R^1 = Me, R^2 = H) in 82% yield (entry 2, Table I). As shown in Table I, a small change in the concentration of supporting electrolyte ($LiClO_4$) causes a decrease in the yield of **2** (n = 3, R^1 = Me, R^2 = H; entries 1 and 3). We also found that under the same supporting electrolyte concentration, i.e., 0.23 M $LiClO_4$ in methanol, the conversion yields of **1a** to **2** depend on the magnitude of

(1) (a) L. F. Fieser and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **70**, 3352 (1948); (b) I. Ugi, R. Huisgen, and D. Pawellek, *Justus Liebigs Ann. Chem.*, **641**, 63, (1961); (c) R. Huisgen and D. Pawellek, *ibid.*, **641**, 71 (1961); (d) R. G. Carlson and A. V. Prabhu, *J. Org. Chem.*, **39**, 1753 (1974); (e) R. D. Clark and C. H. Heathcock, *ibid.*, **41**, 1396 (1976); (f) J. R. Handley, A. A. Swigar, and R. M. Silverstein, *ibid.*, **44**, 2954 (1979).

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(4) L. Knof, *Justus Liebigs Ann. Chem.*, **656**, 183 (1962).

(5) (a) T. Shono, Y. Matsumura, T. Hashimoto, K. Hibino, H. Hamaguchi, and T. Aoki, *J. Am. Chem. Soc.*, **97**, 2546 (1975). (b) The cleavage procedure has been improved by using the MeOH–H_2SO–(Pt) system: S. Torii, K. Uneyama, H. Tanaka, T. Yamanaka, T. Yasuda, M. Ono, and Y. Kohmoto, *J. Org. Chem.*, **46**, 3312 (1981).

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Table I. Conditions and Results of Electrooxidative Cleavage of 2-Hydroxy- and/or 2-Acetoxy-1-cycloalkanones[a]

entry	compd	substrate			current, mA/cm²	electricity, F/mol[h]	temp, °C	product (yield,[b] %)
		n	R¹	R²				
1	1a	3	Me	H	4.2-10.0	4.5	30-34	2 (71)[c]
2	1a	3	Me	H	5.3-11.3	5.5	30-34	2 (82)
3	1a	3	Me	H	16.0-18.9	6.0	30-34	2 (64)[d]
4	1a	2	n-C_5H_{11}	H	6.0-10.7	5.4	10-15	2 (90)
5	1b	3	n-C_5H_{11}	H	6.3-13.3	5.3	30-34	2 (97)
6	1b	3	Me	Me	10.0-15.0	4.2	29-32	2 (83)[e]
7	1b	3	Me	Me	4.7-11.3	2.9	3-5	2 (93)[f]
8	1b	4	n-C_5H_{11}	H	6.2-15.5	5.2	30-34	2 (94)
9	1b	9	Me	H	5.6-17.5	7.5	30-34	2 (94)
10	1b	9	H	H	11.7-26.0	6.8	29-32	2 (90)[g]
11	6b				11.0-15.0	5.0	26-29	7 (94)
12	11				10.0-11.3	4.8	8-10	12 (84)

[a] Unless otherwise noted, electrolyses were carried out in MeOH containing 0.23 M $LiClO_4$ under a constant applied voltage of 20 V with Pt electrodes (3 cm²) in the anode compartment of a divided cell. [b] Based on isolated products in complete conversion of 0.3-1.1 mmol of the substrates. [c] Carried out by using 0.16 M $LiClO_4$. [d] Carried out by using 0.33 M $LiClO_4$. [e] Yield based on consumed **3b** (75% conversion). [f] Carried out in a mixed solution of MeOH-AcOH (10:1). [g] A mixture of aldehyde and dimethyl acetal (4:6) was obtained. [h] Faradays/mole during preparative run.

Table II. Conditions and Results of Electrooxidative Cleavage of Enol Acetates[a]

entry	compd	substrate			current, mA/cm²	electricity, F/mol[d]	temp, °C	product (yield,[b] %)
		n	R¹	R²				
1	3	3	Me	Me	16.0-17.3	7.2	24-26	2 (25)[c]
2	3	3	Me	Me	3.3-16.7	6.6	22-29	2 (55)
3	3	3	Me	Me	3.0-12.0	6.7	2-3	2 (72)
4	3	2	n-C_5H_{11}	H	3.3-9.0	6.6	2-3	2 (75)
5	3	3	n-C_5H_{11}	H	3.7-11.0	7.4	2-3	2 (79)
6	3	4	n-C_5H_{11}	H	4.0-10.7	7.2	3-8	2 (75)
7	5				2.7-12.0	6.9	2-3	7 (74)

[a] All electrolyses were carried out in MeOH-AcOH (10:1) solutions of 0.23 M $LiClO_4$ under a constant applied voltage of 20 V with Pt electrodes (3 cm²) in a divided cell. [b] Based on isolated products in complete conversion of 0.38-0.93 mmol of the substrates. [c] Electrolyzed in MeOH solution. [d] Faradays/mole during preparative run.

the current density. The best result was obtained in the electrolysis conditions of entry 2. Interestingly, a change of the supporting electrolyte from $LiClO_4$ (entry 4) to Et_4NOTs in the electrolysis of **1a** (n = 2, R^1 = n-C_5H_{11}, R^2 = H) provided 2-pentyl-2-cyclopentenone in 55% yield. This electrochemical method is also advantageous for the cleavage of the cycloalkanone **1b** (n = 9, R^1 = R^2 = H), which lacks substituents at the α-position of the carbonyl groups (entry 10).[11]

This procedure was also used in the preparation of the methyl ester **7** (Scheme I), an enantiomer of (−)-6-oxo-6,7-dihydrocitronellic acid,[12] a new constituent of Reunion germanium oil (*Pelargonium graveolens*), from (+)-menthone by the electrooxidative cleavage of its enol acetate **5** as well as 4-hydroxymenthone **6b**.

Electrooxidative Cleavage of Cycloalkanone Enol Acetates 3. Electrolytic oxidation of the enol acetates **3** in acetic acid has been shown to give the corresponding α-acetoxy and α,β-unsaturated ketones,[13] but there is no report of a direct electrocleavage of **3**. Now, we find that the enol acetates **3** represent excellent precursors for the electrosynthesis of the oxoalkanoates **2**. As shown in entry 1 of Table II, electrolysis of **3** (n = 3, R^1 = R^2 = Me) in a MeOH–$LiClO_4$–(Pt) system provided the corresponding **2** (n = 3, R^1 = R^2 = Me) in poor yield (25%), but a mixed solvent of MeOH–AcOH (10:1) improves the yield of the desired **2** (entry 2). Strikingly, the same electrolysis (applied voltage 20 V, anode potential 2.00–2.20 V vs. Ag/0.1 M AgCl) at 2–3 °C gave **2** (n = 3, R^1 = R^2 = Me) in 72% yield along with 18% yield of **9** and **10** (entry 3). Other results are shown in entries 4–7 of Table II. The distribution of the major product **2**, along with those of the minor products **1c** (n = 3, R^1 = R^2 = Me) and **8**–**10** ob-

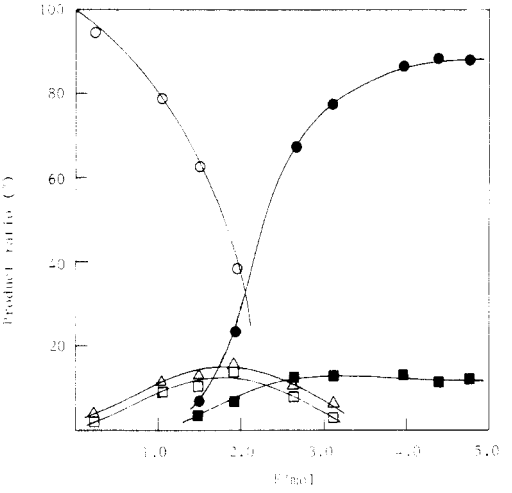
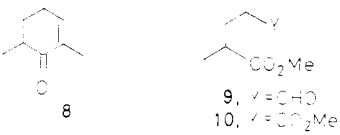
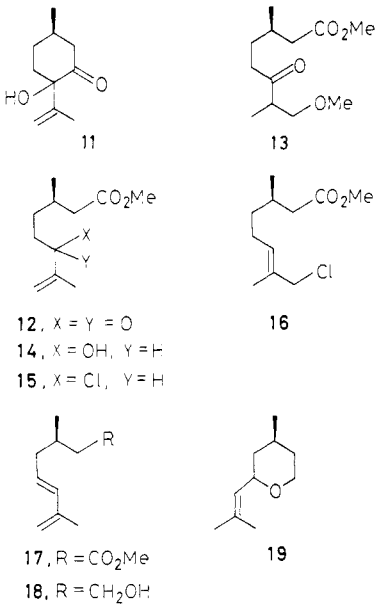


Figure 1. Plots of product distribution of the anodic oxidation of **3** (n = 3, R^1 = R^2 = Me) with passed electricity (F/mol): ○, **3** (n = 3, R^1 = R^2 = Me). Two-electron oxidation products: △, **1c** (n = 3, R^1 = R^2 = Me); □, **8**. Four-electron oxidation product: ●, **2**, (n = 3, R^1 = R^2 = Me). Four- and six-electron oxidation products: ■, **9** + **10**.



(11) (a) H. D. Law, *J. Chem. Soc.*, **89**, 1437 (1906); (b) J. Holubek and J. Volke, *Collect. Czech. Chem. Commun.*, **25**, 3293 (1960).
(12) E. Klein, W. Rojahn, *Dragoco Rep. (Engl. Ed.)* **24**, 55 (1977); *Chem. Abstr.*, **87**, 23525 (1977).
(13) (a) T. Shono, Y. Matsumura, and Y. Nakagawa, *J. Am. Chem. Soc.*, **96**, 3532 (1974); (b) T. Shono, M. Okawa, and I. Nishiguchi, *ibid.*, **97**, 6144 (1975).

Chart I



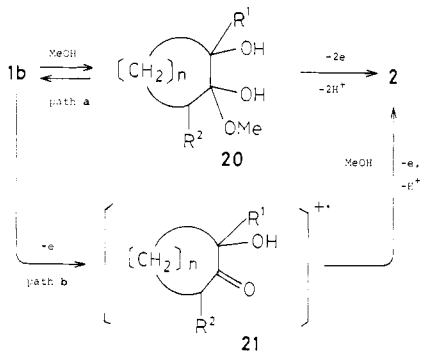
tained in the electrolysis of **3** (n = 3, $R^1 = R^2$ = Me), is shown in Figure 1 and indicates that under these conditions the further two-electron oxidation of **1c** proceeds smoothly, with an increase of the amount of **1c** in the media. The products **9** and **10** may result from the cleavage of the α,β-unsaturated double bond of **8**, derived from the demethoxylation of the intermediate **1c** (n = 3, $R^1 = R^2$ = Me) in the acidic electrolysis media. The electrolysis afforded a mixture of **1c** (n = 3, $R^1 = R^2$ = Me, 18%), **8** (14%), **9** (4%), **10** (4%), **2** (n = 3, $R^1 = R^2$ = Me, 20%), and the starting material **3** (n = 3, $R^1 = R^2$ = Me, 40%), after passing 2F/mol of electricity through the mixture. However, prolonged electrolysis can improve the yields of **2** (n = 3, $R^1 = R^2$ = Me) along with the minor products **9** and **10** in contrast a decrease in the amounts of **1c** (n = 3, $R^1 = R^2$ = Me) and **8**.

We were stimulated to explore the versatility of the electrolytic cleavage procedure in an attempt to prepare the chiral synthetic block **12** (see Chart I) from readily available chiral natural products. The desired chiral block **12** for (+)-rose oxide synthesis[14] was obtained in 84% yield by electrolysis of **11**[15] in a MeOH–$LiClO_4$–(Pt) system at 8–10 °C, but higher temperatures (30–33 °C) provided a mixture of **12** (64%) and **13** (23%) in the same media.

The conversion of the keto ester **12** into (+)-rose oxide (**19**) through the diene intermediate **17** conducted as follows. The reduction of **12** with sodium borohydride in the presence of ceric(III) chloride[16] gave the allyl alcohol **14** quantitatively. The key intermediate **17** was obtained by the chlorination of **14** with methanesulfonyl chloride in DMF followed by dehydrochlorination on treatment of mixture of **15** and **16** with DBU[17] at 100 °C in 74% yield (from **14**). Cyclization of **18** after the reduction of **17** with lithium aluminum hydride was carried out in 30% sulfuric acid[18] at 17–18 °C, giving a mixture of *cis*-(+)-rose oxide **19** (83% yield from **17**) and *trans*-(+)-rose oxide (9%).

As shown in Table I, most of the electrolyses of **1** in a MeOH–$LiClO_4$–(Pt) system required 4.2–7.5 F/mol of electricity for 100% conversion yields. It is interesting to

Scheme II



note that employment of an acidic solvent system such as MeOH–AcOH (10:1) improved the current efficiency in producing the cleavage product **2** (n = 3, $R^1 = R^2$ = Me; entry 7). The electrolysis using other supporting electrolytes such as Et_4NOTs and Et_4NClO_4 instead of $LiClO_4$ met with some difficulties in producing the desired **2**, and most of the electrolyses gave the recovered **1**. It is likely that dissociation of $LiClO_4$ as a strong electrolyte would provide a stable solvated perchlorate ion along with a lithium cation in methanol, in contrast with the formatin of solvated ion pairs from the ammonium salts.[19] If the dissociated perchlorate ion was oriented to the surface of the anode, one might expect the outer Helmholtz layer[20] to act as an acid catalyst. Other lithium salts derived from strong acids, i.e., $LiBF_4$ and CF_3CO_2Li, can be used for this purpose. The electrolysis of **1b** (n = 3, $R^1 = R^2$ = Me) with those electrolytes afforded the cleavage product **2** (n = 3, $R^1 = R^2$ = Me) in 80–88% yields.

The mechanism of the formation of **2** from **1b** is not completely understood. A plausible reaction path is depicted in Scheme II. The hemiacetal **20** (path a) would be produced by equilibration near the acidic anode in a MeOH–$LiClO_4$–(Pt) system. The formation of **2** can readily be rationalized by assuming anodic cleavage of the 1,2-diol[5] group of **20**. This occurs more readily than the direct oxidation of the carbonyl group of **1b**. This is supported by the reported cleavage of 1,2-diols at 2.00–2.20 V vs. SCE in a MeOH–Et_4NOTs–(C) system.[5] On the other hand, cyclic voltammetric data of the carbonyl group of alkanones shows $E_{p/2}$ values at 2.15–2.36 V vs. Ag/0.1 M $AgNO_3$ in a MeCN–0.1 M $LiClO_4$–(Pt) system.[21] Because of the proximity of the oxidation potentials of **1b** [anode potential 2.00–2.20 V vs. Ag/0.1 M $AgNO_3$ in MeCN–0.1 M $LiClO_4$–(Pt)] with those of the 1,2-diols and the alkanones, we cannot rule out the possibility of competitive electrooxidation of the both functional groups of **1b** (path b) under the macroelectrolysis conditions.

A variety of the enol acetates **3** have been shown to be oxidized at 1.44–2.09 V vs. SCE in an AcOH–Et_4NOTs–(C) system, giving principally α-acetoxy and α,β-unsaturated ketones.[13] In contrast with these results, the electrolysis

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(15) W. Reusch, D. F. Anderson, and C. K. Johnson, *J. Am. Chem. Soc.*, **90**, 4988 (1968).
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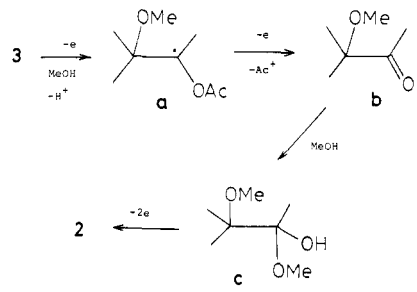
(21) (a) L. L. Miller, V. R. Koch, M. E. Larscheid, and J. F. Wolf, *Tetrahedron Lett.*, 1389 (1971); (b) J. Y. Becker, L. L. Miller, and T. M. Siegel, *J. Am. Chem. Soc.*, **97**, 849 (1975); (c) M. M. Green, G. J. Mayotte, L. Meites, and D. Forsynth, *ibid.*, **102**, 1464 (1980).

Scheme III



of **3** in a MeOH–AcOH (10:1)–$LiClO_4$–(Pt) system affords the cleavage products **2** exclusively. A plausible mechansim of the formation of **2** in the later electrolysis system is shown in Scheme III. The intermediate b would be produced by the oxidation of the radical intermediate a, which arises from nucleophilic attack of methanol to a cation-radical intermediate derived from one-electron discharge of **3** on the anode. Actually, the electrolysis of **3** (n = 3, $R^1 = R^2$ = Me) provided **1c** (n = 3, $R^1 = R^2$ = Me) as an initial reaction product. As we suggested above, the presence of strong electrolytes has a great influence upon the hemiacetal formation. It is most likely that the hemiacetal c partly produced by acid-catalyzed equilibration with b in methanol would undergo further two-electron oxidation to provide the cleavage products **2** smoothly.

Experimental Section

Melting points are uncorrected and boiling points are indicated by an air-bath temperature without correction. IR spectra were determined with a JASCO IRA-1 grating spectra. ^1H NMR spectra were obtained with Hitachi R-24 (60 MHz) and/or JEOL FX-100 (100 MHz) spectrometers. ^{13}C NMR spectra were recorded with a JEOL FX-100 (25.05 MHz) spectrometer. Samples were dissolved in $CDCl_3$ and chemicl shifts (δ) are expressed in parts per million downfield from internal Me_4Si. Optical rotations were taken on a JASCO DIP-140 digital polarimeter in $CHCl_3$. Elemental analyses were performed in our laboratory.

General Procedure for the Preparation of Enol Acetates 3.[22] A solution of 2-pentylcyclopentanone (700 mg, 4.55 mmol) in Ac_2O (10 mL) containing *p*-TsOH (25 mg) was heated at 110–125 °C for 6 h. The mixture was poured into cold aqueous $NaHCO_3$ and taken up in hexane. The extract was washed with $NaHCO_3$, dried (Na_2SO_4), and concentrated. The crude product was distilled at 125–130 °C (19 mm), and the distillate was chromatographed (SiO_2, hexane–AcOEt 20:1) to give 660 mg (74%) of **3** [n = 2, R^1 = n-C_5H_{11}, R^2 = H; bp 115–117 °C (19 mm) [lit.[23] bp 65 °C (0.2 mm)]] and 134 mg (15%) of 2-acetyl-2-pentylcyclopentanone: bp 118–120 °C (19 mm); IR (neat) 1739 (C=O), 1700 (C=O), 1134, 1114 cm^{-1}; ^1H NMR (60 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.05–2.80 (m, 14, CH_2), 2.09 (s, 3, $COCH_3$); ^{13}C NMR δ 14.0 (q), 19.6 (t), 22.4 (t), 24.8 (t), 25.7 (q, Ac), 30.5 (t), 32.1 (t), 35.3 (t), 38.5 (t), 69.3 (s), 203.9 (s), 215.6 (s). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.60; H, 10.23.

2,6-Dimethyl-1-cyclohexen-1-yl acetate (3, n = 3, $R^1 = R^2$ = Me) was obtained in 93% yield from **4** (n = 3, $R^1 = R^2$ = Me): bp 64–66 °C (9 mm); IR (neat) 1755 (OAc), 1698 (C=C), 1210, 1105, 1085, 908 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.97 (d, 3, J = 7 Hz, CH_3), 1.10–2.60 (m, 7, CH_2, CH), 1.50 (complex s, 3, CH_3), 2.13 (s, 3, $COCH_3$). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.53; H, 9.58.

2-Pentyl-1-cyclohepten-1-yl acetate (3, n = 4, R^1 = n-C_5H_{11}, R^2 = H) was obtained in 90% yield from **4** (n = 4, R^1 = n-C_5H_{11}, R^2 = H): bp 157–158 °C (24 mm); IR (neat) 1750 (OAc), 1698 (C=C), 1209, 1134 cm^{-1}; ^1H NMR (60 MHz) δ 0.88 (t, 3, J = 7 Hz, CH_3), 1.05–2.35 (m, 18, CH_2), 2.02 (s, 3, $COCH_3$). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.00; H, 10.91.

2- and 12-Methyl-1-cyclododecen-1-yl acetate (3, n = 9, R^1 = Me, R^2 = H and R^1 = H, R^2 = Me) was obtained in 94% yield from **4** (n = 9, R^1 = Me, R^2 = H): bp 123–125 °C (1 mm); IR (neat) 1758 (OAc), 1685 (C=C), 1365, 1205, 1110 cm^{-1}; ^1H NMR (60 MHz) δ 0.96 (d, J = 7 Hz, CH_3), 1.10–2.50 (m, CH_2, CH), 1.46 (s, CH_3), 2.03, 2.07 (s, 3, $COCH_3$), 4.70–5.08 (m, HC=C). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.68; H, 11.14.

2-Acetoxy-2-pentylcyclopentanone (1a, n = 2, R^1 = n-C_5H_{11}, R^2 = H). To a solution of **3** (n = 2, R^1 = n-C_5H_{11}, R^2 = H; 1.96 g, 10 mmol) in CH_2Cl_2 (30 mL) was added an ethereal 1 N monoperphthalic acid (1.8 mL, 18 mmol) solution at 0–5 °C for 12 h. The mixture was filtered off, and the filtrate was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. To the residue was added AcOH (2 mL). The mixture was stirred at room temperature for 4 h, poured into cold water, and taken up in benzene–AcOEt (1:1). The usual workup gave 1.8 g (85%) of **1a** after chromatography (SiO_2; hexane–AcOEt, 20:1): 78–80 °C (0.015 mm); IR (neat) 1755 (OAc), 1735 (C=O), 1371, 1257, 1195, 1162, 1099, 1021 cm^{-1}; ^1H NMR (60 MHz) δ 0.89 (t, 3, J = 6 Hz, CH_3), 1.10–2.75 (m, 14, CH_2), 2.02 (s, 3, $COCH_3$). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.69; H, 9.59.

2-Acetoxy-2-methylcyclohexanone (1a, n = 3, R^1 = Me, R^2 = H) was obtained in 93% yield by the same manner as described above from **3** (n = 3, R^1 = Me, R^2 = H); bp 81–83 °C (3 mm) [lit.[24] bp 115–118 °C (15 mm)].

2-Acetoxy-2-pentylcyclohexanone (1a, n = 3, R^1 = n-C_5H_{11}, R^2 = H) was obtained in 94% yield by the same manner as described above from **3** (n = 3, R^1 = n-C_5H_{11}, R^2 = H): bp 67–69 °C (0.02 mm); IR (neat) 1739 (OAc), 1719 (C=O), 1258, 1240, 1130, 1013 cm^{-1}; ^1H NMR (60 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.00–2.80 (m, 16, CH_2), 2.01 (s, 3, $COCH_3$). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.96; H, 9.94.

2-Acetoxy-2,6-dimethylcyclohexanone (1a, n = 3, $R^1 = R^2$ = Me)[25] was obtained in 81% yield by the same manner as described above: bp 79–81 °C (3.5 mm); IR (neat) 1738 (OAc), 1719 (C=O), 1370, 1250, 1225, 1138, 1118, 1011, 948, 859 cm^{-1}; ^1H NMR (60 MHz) δ 0.95 (d, 3, J = 7 Hz, CH_3), 1.00–2.87 (m, 7, CH_2, CH), 1.35 (s, 3, CH_3), 2.02 (s, 3, $COCH_3$).

2-Acetoxy-2-pentylcycloheptanone (1a, n = 4, R^1 = n-C_5H_{11}, R^2 = H) was obtained in 91% yield by the same manner as described above from **3** (n = 4, R^1 = n-C_5H_{11}, R^2 = H): bp 85–87 °C (0.25 mm); IR (neat) 1738 (OAc), 1710 (C=O), 1378, 1245, 1155 cm^{-1}; ^1H NMR (60 MHz) δ 0.89 (t, 3, J = 7 Hz, CH_3), 1.27 (br s, 8, CH_2), 1.83 (br s, 8, CH_2), 2.01 (s, 3, $COCH_3$), 2.12–2.70 (m, 2, $COCH_2$). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 70.09; H, 10.29.

2-Hydroxy-2-pentylcyclohexanone (1b, n = 3, R^1 = n-C_5H_{11}, R^2 = H). To a solution of **1a** (n = 3, R^1 = n-C_5H_{11}, R^2 = H, 452 mg, 2.0 mmol) in MeOH (5 mL) was added a solution of KOH (448 mg, 8.0 mmol) in H_2O (1.0 mL) at 0–5 °C. After being stirred for 12 h at room temperature, the mixture was poured into ice–water and taken up in ether–benzene (1:1). The usual workup gave 291 mg (79%) of **1b** after chromatography (SiO_2; hexane–AcOEt, 5:1): bp 84–86 °C (0.15 mm); IR (neat) 3500 (OH), 1708 (C=O), 1244, 1160, 1130, 1047 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.86 (t, 3, J = 6 Hz, CH_3), 1.00–2.60 (m, 16, CH_2), 3.53 (br s, 1, OH). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.57; H, 11.07.

2-Hydroxy-2,6-dimethylcyclohexanone (1b, n = 3, $R^1 = R^2$ = Me)[26] was obtained in 84% yield by the same manner as described above from **1a** (n = 3, $R^1 = R^2$ = Me): bp 75–77 °C (12 mm); IR (neat) 3480 (OH), 1703 (C=O), 1370, 1311, 1225, 1138, 1118, 1011, 948, 859 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.08 (d, 3, J = 6 Hz, CH_3), 1.20–2.30 (m, 6, CH_2), 1.40 (s, 3, CH_3), 2.40–2.90 (m, 1, COCH), 3.74 (s, 1, OH).

2-Hydroxy-2-pentylcycloheptanone (1b, n = 4, R^1 = n-C_5H_{11}, R^2 = H) was prepared from **1a** (n = 4, R^1 = n-C_5H_{11}, R^2 = H) in 86% yield in the same manner as described above: bp 63–65 °C (0.005 mm); IR (neat) 3500 (OH), 1700 (C=O), 1172,

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946 cm^{-1}; ^1H NMR (100 MHz) δ 0.85 (t, 3, J = 7 Hz, CH_3), 1.00–2.16 (m, 16, CH_2), 2.32–2.68 (m, 2, $COCH_2$), 3.54 (br, 1, OH). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.84; H, 11.29.

4-Hydroxy-*p*-menth-3-one (6b). To a soln. of **5** (1.96 g, 10.0 mmol) in CH_2Cl_2 (30 mL) was added an ethereal solution of 1 M monoperphthalic acid (18 mL, 18 mmol) at 0–5 °C. After being stirred at 5–10 °C for 12 h, the mixture was worked up in the usual manner and then treated with AcOH (2.0 mL) to give 1.23 g (58%) of **6a** [bp 57–59 °C (0.002 mm) [lit.[13b] bp 81–82 °C (2 mm)]] and 720 mg (34%) of 3,4-epoxy-*p*-menth-3-yl acetate: bp 47–49 °C (0.002 mm); IR (neat) 1750 (OAc), 1370, 1224, 1189, 1104, 1087, 1007, 829 cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (d, 3, J = 7 Hz, CH_3), 0.96 (d, 3, J = 7 Hz, CH_3), 1.03 (d, 3, J = 7 Hz, CH_3), 1.15–2.48 (m, 8, CH_2, CH), 2.07 (s, 3, $COCH_3$). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.82; H, 9.63.

Hydrolysis of **6a** (212 mg, 1.0 mmol) with KOH (224 mg, 4.0 mmol) in MeOH (3 mL) and H_2O (0.3 mL) gave **6b** in 91% yield: bp 63–65 °C (0.002 mm); $[\alpha]_D^9$ –123.7° (*c* 2.6); IR (neat) 3490 (OH), 1710 (C=O), 1380, 1364, 1252, 1152, 1094, 1008 cm^{-1}; ^1H NMR (100 MHz) δ 0.70 (d, 3, J = 6.6 Hz, CH_3), 0.96 (d, 3, J = 6.6 Hz, CH_3), 1.01 (d, 3, J = 6.6 Hz, CH_3), 1.30–2.82 (m, 9, CH_2, CH, OH). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.52; H, 10.74. Hydrolysis of 3,4-epoxy-*p*-menth-3-yl acetate with aqueous alcoholic KOH also afforded **6b** in 93% yield.

2-Hydroxy-2-methylcyclododecanone (1b, n = 9, R^1 = Me, R^2 = H) was obtained in 43% yield by epoxidation of **3** (n = 9, R^1 = Me, R^2 = H and R^1 = H, R^2 = Me) with monoperphthalic acid followed by hydrolysis with aqueous KOH: mp 43.5–45.5 °C; IR (Nujol) 3480 (OH), 1706 (C=O), 1410, 1346, 1150, 1008 cm^{-1}; ^1H NMR (60 MHz) δ 1.29 (br s, 14, CH_2), 1.36 (s, 3, CH_3), 1.47–2.46 (m, 5, CH_2), 2.76–3.27 (m, 1, CH_2), 3.90 (br s, 1, OH). Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.64; H, 11.57.

2-Hydroxycyclododecanone (1b, n = 9, R^1 = R^2 = H) was obtained in 69% yield by the same procedure as described above from **1a** (n = 9, R^1 = R^2 = H), mp 75–76 °C (lit.[27] mp 78–79 °C).

4-Hydroxy-*p*-menth-8-en-3-one (11).[15] A solution of pulegone oxide (2.2 g, 11.89 mmol) in benzene (30 mL) containing *dl*-10-camphorsulfonic acid (100 mg) was heated at 50–60 °C for 3 h. The mixture was washed with cold aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2; hexane–AcOEt, 7:1) to give 1.66 g (83%) of a mixture of 1,4-*trans*- and 1,4-*cis*-**11**: bp 68–70 °C (2 mm); $[\alpha]_D^{18}$ –109.8° (*c* 1.0).

Electrolysis Apparatus.[28] A modified H-type two comparment cell (100 mL volume) was used. The anode compartment, fitted with a drying tube ($CaCl_2$), a thermometer, and a magnetic stirrer bar was divided from the cathode by 1.8 cm diameter glass-frits plate (No. 5G). Two platinum electrodes (3 cm^2) were placed parallel to each other 3 cm apart. Regulated dc power was supplied by a Metronix Model 543B instrument. The integration of the current was carried out by accumulating the amount of electric currents appeared on the time–current diagrams.

General Procedure for Electrolysis of 2-Acetoxy-2-alkyl-1-cycloalkanone Analogues. A solution of **1a** (n = 3, R^1 = Me, R^2 = H; 85 mg, 0.5 mmol) and $LiClO_4$ (500 mg) in dry MeOH (19 mL) was charged into the anode compartment. Into the cathode compartment was charged a solution of $LiClO_4$ (200 mg) in dry MeOH (16 mL). The mixture was electrolyzed under a constant applied voltage of 20 V at a current of 5.3–11.3 mA/cm^2 at 20–25 °C. After 5.0 F/mol of electricity was passed, the mixture was concentrated, and the residue was taken up in benzene–AcOEt (1:1). The extract was washed with brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2; hexane–AcOEt, 10:1) to give 65 mg (82%) of **2** (n = 3, R^1 = Me, R^2 = H), bp 110–112 °C (19 mm) [lit.[29] bp 140–142 °C (8 mm)].

Details of the reaction conditions and results are given in Table I. Physical properties and spectral data of the electrolysis products **2** are as follows.

Methyl 5-oxodecanoate (2, n = 2, R^1 = n-C_5H_{11}, R^2 = H), bp 128–130 °C (19 mm) [lit.[30] bp 135–142 °C (10 mm)].

Methyl 6-oxoundecanoate (2, n = 3, R^1 = n-C_5H_{11}, R^2 = H):[31] bp 133–135 °C (19 mm); IR (neat) 1738 (COO), 1710 (C=O), 1340, 1199, 1171 cm^{-1}; ^1H NMR (60 MHz) δ 0.91 (t, 3, J = 6 Hz, CH_3), 1.05–1.79 (m, 10, CH_2), 2.10–2.45 (m, 6, $COCH_2$), 3.61 (s, 3, OCH_3). Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.46; H, 10.54.

Methyl 2-methyl-6-oxoheptanoate (2, n = 3, R^1 = R^2 = Me): bp 98–100 °C (6 mm) [lit.[32] bp 106–107 °C (11 mm)]; ^{13}C NMR δ 17.1 (q, C-2 Me), 21.5 (t, C-4), 29.8 (q, C-7), 33.2 (t, C-3), 39.3 (d, C-2), 43.4 (t, C-5), 51.5 (q, OMe), 176.9 (s, C-1), 208.4 (s, C-6).

Methyl 7-oxododecanoate (2, n = 4, R^1 = n-C_5H_{11}, R^2 = H): bp 139–141 °C (19 mm); IR (neat) 1739 (COO), 1711 cm^{-1} (C=O); ^1H NMR (60 MHz) δ 0.89 (t, 3, J = 7 Hz, CH_3), 1.05–1.83 (m, 12, CH_2), 2.11–2.39 (m, 6, $COCH_2$), 3.58 (s, 3, OCH_3). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.59; H, 10.76.

Methyl 12-oxotridecanoate (2, n = 9, R^1 = Me, R^2 = H): mp 29.0–30.5 °C (lit.[33] mp 32.6–33.2 °C).

Methyl 12-oxodecanoate (2, n = 9, R^1 = R^2 = H)[34] and methyl 12,12-dimethoxydodecanoate: IR (neat) 2700, 1738, (COO), 1718 cm^{-1} (C=O); ^1H NMR (60 MHz) δ 1.28 (br s, 16, CH_2), 1.95–2.40 (m, $COCH_2$), 3.17 (s, OCH_3), 3.57 (s, 3, OCH_3), 4.21 (t, J = 6 Hz, CHO), 9.66 (m, CHO).

Methyl (3*R*)-3,7-dimethyl-6-oxooctanoate (7):[1f] bp 87–89 °C (3 mm); $[\alpha]_D^{11}$ +9.7° (*c* 1.3); IR (neat) 1739 (COO), 1710 (C=O), 1380, 1364, 1252, 1152, 1094, 1008 cm^{-1}; ^1H NMR (100 MHz) δ 0.94 (d, 3, J = 6 Hz, CH_3), 1.09 (d, 6, J = 7 Hz, CH_3), 1.10–2.05 (m, 3, CH_2, CH), 2.12–2.72 (m, 5, $COCH_2$, COCH), 3.67 (s, 3, OCH_3); ^{13}C NMR δ 18.3 (q, C-8, C-7 Me), 19.5 (q, C-3 Me), 30.0 (d, C-3), 30.3 (t, C-4), 37.8 (t, C-5), 40.8 (d, C-7), 41.4 (t, C-2), 51.4 (q, OMe), 173.2 (s, C-1), 214.2 (s, C-6). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.93; H, 10.25.

Methyl (3*R*)-3,7-dimethyl-6-oxo-7-octenoate (12): bp 82–84 °C (2 mm); $[\alpha]_D^{10}$ +95° (*c* 0.95); IR (neat) 3100, 1735 (COO), 1675 (C=O), 1630 (C=C), 1368, 1283, 1206, 1158, 1007, 955 cm^{-1}; ^1H NMR (60 MHz) δ 0.93 (d, 3, J = 6 Hz, CH_3), 1.35–1.95 (m, 3, CH_2, CH), 1.43 (d, 3, J = 1 Hz, CH_3), 1.98–2.25 (m, 2, $COCH_2$), 2.36–2.86 (m, 2, $COCH_2$), 3.57 (s, 3, OCH_3), 5.65, 5.85 (br s, 2, H_2C=C); ^{13}C NMR δ 17.6 (q, C-7 Me), 19.7 (q, C-3 Me), 30.1 (d, C-3), 31.1 (t, C-4), 35.0 (t, C-5), 41.4 (t, C-2), 51.3 (q, OMe), 124.3 (t, C-8), 144.4 (s, C-7), 173.2 (s, C-1), 201.5 (s, C-6). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.51; H, 9.36.

Methyl (3*R*)-3,7-dimethyl-8-methoxy-6-oxooctanoate (13): bp 139–141 °C (19 mm); $[\alpha]_D^{10}$ +9.1° (*c* 0.66); IR (neat) 1735 (COO), 1710 (C=O), 1206, 1161, 1108, 1009, 935 cm^{-1}; ^1H NMR (100 MHz) δ 0.93 (d, 3, J = 6 Hz, CH_3), 1.06 (d, 3, J = 6 Hz, CH_3), 1.20–2.08 (m, 3, CH_2, CH), 2.23 (dd, 2, J = 8, 6 Hz, $COCH_2$), 2.51 (t, 2, J = 7 Hz, $COCH_2$), 2.64–3.00 (m, 1, COCH), 3.28–3.51 (m, 2, CH_2O), 3.30 (s, 3, OCH_3), 3.67 (s, 3, OCH_3). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.60; H, 9.76.

General Procedure for Electrolysis of Enol Acetates 3. A solution of 700 mg of $LiClO_4$ in 36 mL of MeOH/AcOH (10:1) was poured into both compartments of a divided electrolysis cell. To the anode comparment was added **3** (n = 3, R^1 = R^2 = Me, 128 mg, 0.76 mmol), and the mixture was electrolyzed under a constant applied voltage of 20 V at a current of 2.2–12.0 mA/cm^2. After 6.0 F/mol of electricity was passed, the electrolyzed solution in the anode comparment was concentrated, neutralized with cold aqueous $NaHCO_3$, and extracted with hexane–ether (1:1). The extract was worked up in the usual manner to give 94 mg (72%) of **2** (n = 3, R^1 = R^2 = Me).

The constituents (Figure 1) of the mixture after 2.0 F/mol of electricity had been passed were analyzed by GLC (silicon GE, 10% SE-30 coated on 80–100-mesh Chamelite, 4 m × 4 mm, 120 °C, carrier gas H_2 at 20 mL/min). Retention times and spectral

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data of the constituents are as follows.

2,6-Dimethyl-2-cyclohexenone (8): t_R = 4.4 min; IR (neat) 1670 cm^{-1} (C=O); ^1H NMR (100 MHz) δ 1.02 (d, 3, J = 7 Hz, CH_3), 1.20–2.55 (m, 5, CH_2, CH), 1.79 (complex s, 3, CH_3), 6.70 (m, 1, HC=C).

2,6-Dimethyl-2-methoxycyclohexanone 1c (n = 3, R^1 = R^2 = Me): t_R = 4.4 min; IR (neat) 2812, 1700 (C=O), 1170, 1080, 1015, 994 cm^{-1}; ^1H NMR (100 MHz) δ 1.17 (d, 3, J = 7 Hz, CH_3), 1.10–2.40 (m, 7, CH_2, CH), 1.21 (s, 3, CH_3), 3.14 (s, 3, OCH_3).

Methyl 2-methyl-5-oxopentanoate (9): t_R = 10.4 min; IR (neat) 2720, 1730, (COO), 1720 cm^{-1} (C=O); ^1H NMR (100 MHz) δ 1.20 (d, 3, J = 7.5 Hz, CH_3), 1.72–2.10 (m, 2, CH_2), 2.40–2.65 (m, 3, CH_2, CH), 3.68 (s, 3, OCH_3), 9.76 (t, 1, J = 1 Hz, CHO).

Dimethyl 2-methylglutarate (10): t_R = 17 min; IR (neat) 1745 cm^{-1} (COO); ^1H NMR (100 MHz) δ 1.19 (d, 3, J = 7 Hz, CH_3), 1.70–2.64 (m, 5, CH_2, CH), 3.68 (s, 6, OCH_3).

Methyl (3*R*)-6-Hydroxy-3,7-dimethyl-7-octenoate (14). To a methanolic solution of **12** (60 mg, 0.3 mmol) and 0.4 M $CeCl_3 \cdot 7H_2O$ (0.75 mL, 0.3 mmol) was added $NaBH_4$ (11.4 mg, 0.3 mmol) at 0 °C. The mixture was stirred for 5 min, quenched with cold aqueous 10% AcOH, and extracted with AcOEt–benzene (1:1). The extract was worked up in the usual manner to give 59.4 mg (99%) of **14**: bp 95–97 °C (2 mm); $[\alpha]_D^{10}$ +8.8° (c 1.6); IR (neat) 3440 (OH), 3070, 1735 (COO), 1640 (C=C), 1199, 1151, 1088, 1000, 892 cm^{-1}; ^1H NMR (60 MHz) δ 0.95 (d, 3, J = 6 Hz, CH_3), 1.10–2.43 (m, 8, CH_2, CH, OH), 1.71 (br s, 3, CH_3), 3.68 (s, 3, OCH_3), 4.05 (t, 1, J = 6 Hz, CHO), 4.85–4.93 (m, 2, H_2C=C); ^{13}C NMR δ 17.4, 17.5 (q, C-7 Me), 19.7 (q, C-3 Me), 30.3, 30.4 (d, C-3), 32.2 (t), 32.5 (t), 41.5 (t, C-2), 51.4 (q, OMe), 75.6, 75.9 (d, C-6), 110.9, 111.1 (t, C-8), 147.5, 147.6 (s, C-7), 173.7 (s, C-1). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.92; H, 10.29.

Methyl (3*R*)-6-Chloro-3,7-dimethyl-7-octenoate (15) and Methyl (3*R*)-8-Chloro-3,7-dimethyl-6-octenoate (16). To a solution of **14** (95 mg, 0.48 mmol) and Et_3N (220 mg, 1.92 mmol) in DMF (3 mL) was added MsCl (97 mg, 0.96 mmol) at 0 °C. The mixture was stirred for 8 h at 45–50 °C, poured into cold aqueous $NaHCO_3$, and extracted with AcOEt–benzene (1:1). The extract was worked up in the usual manner and the crude product was chromatographed (SiO_2, hexane-AcOEt 10:1) to give 91 mg (88%) of a 42:58 mixture of **15** and **16**: bp 117–119 °C (16 mm); $[\alpha]_D^{17}$ +11.1° (c 0.97); IR (neat) 3075, 1735 (COO), 1640 (C=C), 1284, 1198, 1170, 1085, 1006, 904 cm^{-1}; ^1H NMR (60 MHz) δ 0.95 (d, 3, J = 6 Hz, CH_3), 1.10–2.40 (m, CH_2, CH), 1.72, 1.79 (br s, 3, CH_3), 3.63 (s, 3, OCH_3), 3.99 (s, CH_2Cl), 4.32 (t, J = 7 Hz, CHCl), 4.85, 4.96 (m, H_2C=C), 5.46 (t, J = 7 Hz, HC=C). Anal. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76. Found: C, 60.75; H, 8.75.

Methyl (3*R*,5*E*)-3,7-Dimethyl-5,7-octadienoate (17). A solution of **15** and **16** (30 mg, 0.14 mmol) in DBU (43 mg, 0.28 mmol) was heated for 30 min at 100 °C. The mixture was extracted with ether–benzene (2:1), and the extract was washed with cold aqueous 5% HCl and brine, dried (Na_2SO_4), and concentrated to give 21 mg (84%) of **17** after chromatography (SiO_2; hexane–ether, 10:1): bp 104–106 °C (16 mm); $[\alpha]_D^{17}$ +19.8° (c 0.83); IR (neat) 3055, 3010, 1735 (COO), 1605 (C=C), 1245, 1198, 1150, 1012, 962, 880 cm^{-1}; ^1H NMR (100 MHz) δ 0.96 (d, 3, J = 6 Hz, CH_3), 1.83 (t, 3, J = 1 Hz, CH_3), 1.60–2.50 (m, 5, CH_2, CH), 3.64 (s, 3, OCH_3), 4.88 (br s, 2, H_2C=C), 5.61 (dt, 1, J = 15, 7 Hz, HC=C), 6.15 (d, 1, J = 15 Hz, HC=C). ^{13}C NMR δ 18.7 (q, C-7 Me), 19.8 (q, C-3 Me), 30.7 (d, C-3), 40.0 (t, C-4), 41.0 (t, C-2), 51.4 (q, OMe), 114.8 (t, C-8), 128.1 (d, C-5), 134.9 (d, C-6), 142.0 (s, C-7), 173.6 (s, C-1). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.56; H, 10.15.

(3*R*,5*E*)-3,7-Dimethylocta-5,7-dien-1-ol (18). To a suspension of $LiAlH_4$ (21 mg, 0.55 mmol) in THF (4 mL) was added a solution of **17** (50 mg, 0.27 mmol) in THF (1 mL). The mixture was stirred for 1 h at room temperature, quenched with AcOEt and cold aqueous $NaHCO_3$, and worked up in the usual manner to give 40 mg (96%) of **18**: bp 131–133 °C (16 mm) [lit.[18] bp 100 °C (4 mm)]; $[\alpha]_D^{17}$ +6.7° (c 0.9); IR (neat) 3300 (OH), 3065, 3010, 1372, 1050, 960, 880 cm^{-1}; ^1H NMR (60 MHz) δ 0.92 (d, 3, J = 6 Hz, CH_3), 1.10–2.35 (m, 6, CH_2, CH, OH), 1.84 (br s, 3, CH_3), 3.67 (t, 2, J = 6.5 Hz, CH_2O), 4.85 (br s, 2, H_2C=C), 5.60 (dt, 1, J = 15, 7.5 Hz, HC=C), 6.16 (d, 1, J = 15 Hz, HC=C).

(+)-Rose Oxide (19). A solution of **18** (50 mg, 0.32 mmol) in 30% H_2SO_4 (1 mL) was stirred for 4 h at 17–18 °C. The mixture was worked up in the usual manner followed by chromatography (SiO_2; hexane–ether, 10:1) to give 48 mg (96%) of **19**: bp 68–70 °C (15 mm) [lit.[18] bp 72–73 °C (15 mm)]; $[\alpha]_D^{29}$ +39° (c 0.9) (lit.[14] $[\alpha]_D^{20}$ +38.1°).

Registry No. 1a (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 74285-12-4; **1a** (n = 3; R^1 = Me; R^2 = H), 16963-12-5; **1a** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-86-1; **1a** (n = 3; R^1 = R^2 = Me), 56829-74-4; **1a** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-87-2; **1a** (n = 9; R^1 = R^2 = H), 26307-31-3; **1b** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-88-3; **1b** (n = 3; R^1 = R^2 = Me), 66633-36-1; **1b** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-89-4; **1b** (n = 9; R^1 = Me; R^2 = H), 74285-14-6; **1b** (n = 9; R^1 = R^2 = H), 19025-38-8; **1c** (n = 3; R^1 = R^2 = Me), 79664-90-7; **2** (n = 3; R^1 = Me; R^2 = H), 2046-21-1; **2** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 6093-95-4; **2** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-91-8; **2** (n = 3; R^1 = R^2 = Me), 2570-90-3; **2** (n = 4; R^1 = n-C_5H_{11};R^2 = H), 54527-02-5; **2** (n = 9; R^1 = Me; R^2 = H), 74285-16-8; **2** (n = 9; R^1 = R^2 = H), 2009-59-8; **3** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 24851-93-2; **3** (n = 3; R^1 = R^2 = Me), 6203-89-0; **3** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-92-9; **3** (n = 9; R^1 = Me; R^2 = H), 79664-93-0; **3** (n = 9; R^1 = H; R^2 = Me), 79664-94-1; **3** (n = 3; R^1 = Me; R^2 = H), 1196-73-2; **3** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 73746-55-1; **4** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 4819-67-4; **4** (n = 3; R^1 = R^2 = Me), 2816-57-1; **4** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-95-2; **4** (n = 9; R^1 = Me; R^2 = H), 16837-94-8; **5**, 53771-94-1; **6a**, 57426-90-1; **6b**, 74219-28-6; **7**, 63175-00-8; **8**, 40790-56-5; **9**, 79664-96-3; **10**, 14035-94-0; *cis*-**11**, 35736-68-6; *trans*-**11**, 35736-67-5; **12**, 79664-97-4; **13**, 79664-98-5; **14**, 73374-55-7; **15**, 79664-99-6; **16**, 79665-00-2; **17**, 79665-01-3; **18**, 79731-38-7; *cis*-**19**, 4610-11-1; *trans*-**19**, 5258-10-6; 2-acetyl-2-pentylcyclopentanone, 79665-02-4; 3,4-epoxy-*p*-menth-3-yl acetate, 79665-03-5; *dl*-10-camphorsulfonic acid, 5872-08-2; methyl 12,12-dimethoxydodecanoate, 1931-67-5.

Metallo Aldimines. 3. Coupling of Lithium Aldimines with Aryl, Vinyl, and Acetylenic Halides[1]

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tert-Butyllithium aldimine, an acyl anion equivalent derived from 1,1,3,3-tetramethylbutyl isocyanide (TMBI) and *tert*-butyllithium, couples with aryl, vinyl, and acetylenic halides to give the corresponding ketimine which upon hydrolysis affords the corresponding ketones. These coupling reactions appear to result from halogen–metal exchange followed by addition–elimination to give the observed products.

Metallo aldimines, resulting from the addition of organometallic reagents to isocyanides (eq 1), have been shown to be very versatile acyl anion equivalents.[2] They were treated with primary alkyl halides, carbon dioxide,

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