mixture with sodium methoxide in methanol. The reactions shown in Scheme II are involved. Compounds **15**, **16**, and **17** showed characteristic sharp NMR singlets at δ 4.15, 3.8, and 3.4, respectively. Quantitative determination of these, using acetophenone as the standard (singlet at δ 2.45) led to the yields reported in the discussion. The yield of **15** represented the yield of **14**; and the yield of **16**, over and above that of **15**, plus the yield of **17** represented the yield of **12**.

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Registry No. 1, 479-33-4; **12**, 79255-64-4; **13**, 30336-09-5; **14**, 4888-39-5; **15**, 451-40-1; **16**, 93-58-3; **17**, 52422-24-9.

Synthesis of *dl*-Malyngolide, a Marine Antibiotic δ-Lactone, from 3-Methylcyclopentane-1,2-dione

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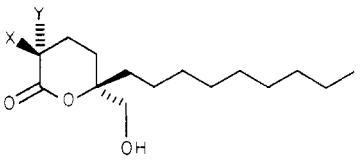
Previous studies of the electrooxidative cleavage of α-hydroxycycloalkanones in our laboratory have provided examples of the preparation of oxoalkanoates.[1] The possibility of 5-oxoalkanoates prepared by the electrolysis of α-alkyl-α-hydroxycyclopentanone to form the corresponding δ-lactones has spurred investigation into their use as a synthon of *dl*-malyngolide synthesis.[2]

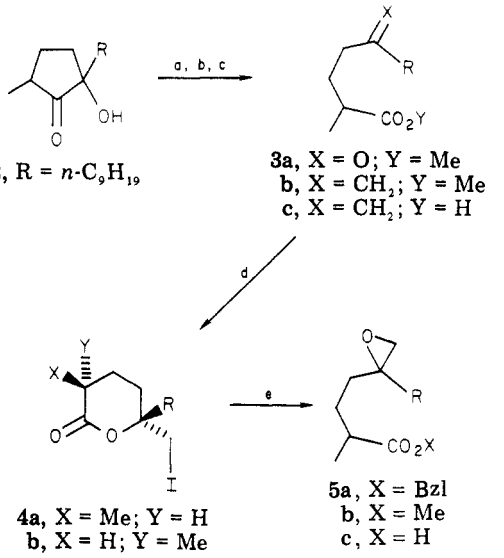


1a, X = Me; Y = H
b, X = H; Y = Me

Most syntheses of malyngolide **1a** have focused on construction of the δ-hydroxymethyl δ-lactone moiety. Recently, two papers have reported the synthesis of **1a**: one involves the elegant, asymmetric synthesis of **1a** from (*S*)-2-hydroxy-2-nonyl-6-heptanal by using (*S*)-2-(anilinomethyl)pyrrolidine as an auxiliary reagent;[3a] the other was the first example of the synthesis of *dl*-malyngolide, the procedure of which has inherent limitations for obtaining δ-hydroxymethyl δ-lactone **1a** due to the acid-catalyzed isomerization of the epoxy acid.[3b] This paper deals with the efficient synthesis of *dl*-malyngolide **1a**, which involves the electrosynthesis of methyl 2-methyl-5-oxotetradecanoate **3a** leading to **1a** and the novel procedure for the construction of the δ-hydroxymethyl δ-lactone moiety of **1a**.

The electrooxidation of 2-hydroxy-5-methyl-2-nonylcyclopentanone **2**, obtained by the reaction of sodium 3-methylcyclopentane-1,2-dionoate with nonylmagnesium bromide,[4] at 20 V (1.8–7.7 mA/cm^2, 3.6 F/mol of electricity) with platinum electrodes at room temperature in a divided cell afforded the cleavage product **3a** in 93% yield (Scheme I). Treatment of **3a** with methylenetriphenylphosphorane gave an unsaturated ester **3b** in 89% yield.

Scheme I[a]



2, R = *n*-C_9H_{19}

3a, X = O; Y = Me
b, X = CH_2; Y = Me
c, X = CH_2; Y = H

4a, X = Me; Y = H
b, X = H; Y = Me

5a, X = Bzl
b, X = Me
c, X = H

[a] a, -2e, MeOH-$LiClO_4$-(Pt) (93%); b, $(Ph)_3PCH_2$ (89%); c, KOH-H_2O (91%); d, I_2-KI-aqueous $NaHCO_3$ (92%); e, BzlOK-DMF (86%).

In order to prepare the δ-hydroxymethyl δ-lactone moiety of **1a**, we examined Lewis acid-catalyzed isomerization of benzyl 5,6-epoxy-5-nonylhexanoate **5a**. Iodolactonization of **3c**, prepared by hydrolysis of **3b**, under a kinetically controlled condition (I_2–KI–$NaHCO_3$) at 10 °C[5] gave a mixture of **4a** (61%) and **4b** (31%). Attempted replacement of iodine of **4** by treatment with silver trifluoroacetate failed.[6] Alcoholysis of **4** with potassium benzyl oxide in DMF provided the benzyl ester **5a** in 86% yield. Lactonization of **5a** by treating with boron tribromide at −60 °C for 1 h furnished a 1:1 mixture of **1a** and its C-2 epimer **1b** in 92% yield as the result of hydrolysis of benzyl ester and subsequent intramolecular attack of carboxylate on the epoxy group.[7] However, either the lactonization of **5b** with boron tribromide at room temperature for 3 h or the lactonization of epoxy acid **5c**[3b] catalyzed by *m*-chloroperbenzoic acid in a refluxing toluene–cyclohexane mixture for 24 h afforded inferior yields of **1a** and **1b** (32–38%).[8]

Experimental Section

The boiling points are indicated by an air-bath temperature without correction. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^{1}H NMR spectra were obtained with a Hitachi R-24 (60 MHz) spectrometer and ^{13}C NMR spectra were determined with a JEOL FX-100 (25.05 MHz) spectrometer. Samples were dissolved in $CDCl_3$ and the chemical shift values are expressed in δ values (ppm) relative to Me_4Si as an internal standard. Elemental analyses were performed in our laboratory.

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(6) After the manuscript was submitted, the successful conversion of iodo lactone **4** to the corresponding hydroxy lactone **1** (91% yield) by use of mercury(II) perchlorate in aqueous dimethoxyethane is reported; see ref 3c.
(7) The C-2 epimer **1b** can be epimerized to an approximate 1:1 mixture of **1a** and **1b** on treatment with *t*-BuOK in Me_2SO; see ref 3a.
(8) In contrast to the difficulty in obtaining the δ-lactone **1** from 5,6-epoxyalkanoic acid, 4,5-epoxyalkanoic acid can smoothly lead to γ-hydroxymethyl γ-lactone: Collum, D. E.; McDonald, J. H.; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118.

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3-Methyl-1-nonyl-2-oxocyclopentan-1-ol (2). A mixture of 3-methylcyclopentane-1,2-dione (434 mg, 3.87 mmol) and NaH (191 mg, 7.96 mmol) in ether (12 mL) was stirred at room temperature for 3 h until H_2 evolution ceased and to this solution was added a solution of nonylmagnesium bromide prepared from 1-bromononane (1.63 g, 7.87 mmol) and magnesium (230 mg, 9.47 mmol) in ether (5 mL). The refluxing mixture was stirred for 48 h, quenched with cold 10% NH_4Cl, acidified with 10% HCl, and extracted with AcOEt-hexane (1:1). The usual workup gave 785 mg (84%) of **2** as an oil, after chromatography (SiO_2, hexane-AcOEt 20:1): bp 125 °C (0.26 mm, decomposition on distillation); IR (neat) 3420 (OH), 1738 cm^{-1} (C=O); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.14 (d, J = 6 Hz, 3, CH_3), 1.28 (br s, 12, CH_2), 1.40-2.40 (m, 9, CH_2, CH), 2.33 (br, 1, OH). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.83; H, 11.97.

Methyl 2-Methyl-5-oxotetradecanoate (3a). A solution of **2** (410 mg, 1.71 mmol) and $LiClO_4$ (500 mg) in MeOH (20 mL) was charged in a H-type of anode compartment. To the cathode compartment was added a solution of $LiClO_4$ (250 mg) in MeOH (15 mL). The mixture was electrolyzed with platinum electrodes (1.5 × 2.0 cm^2) under a constant applied voltage of 20 V (1.8-7.7 mA/cm^2) at room temperature. After 3.6 F/mol of electricity passed, the anode solution was concentrated and the residue was taken up in AcOEt-benzene (1:1). The extracts were worked up in the usual manner and the following chromatography (SiO_2, hexane-AcOEt, 10:1) gave 425 mg (93%) of **3a**: bp 173-176 °C (0.03 mm); IR (neat) 1732 (COO), 1710 cm^{-1} (C=O); ^1H NMR δ 0.90 (br t, 3, CH_3), 1.14 (d, J = 6 Hz, 3, CH_3), 1.27 (br s, 16, CH_2), 2.10-2.67 (m, 5, CH_2CO, CHCO), 3.59 (s, 3, OCH_3). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.15; H, 11.39.

Methyl 2-Methyl-5-methylenetetradecanoate (3b). To a solution of **3a** (278 mg, 1.03 mmol) in benzene (1 mL) was added a solution of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide (708 mg, 1.98 mmol) and $NaNH_2$ (238 mg, 6.1 mmol) in benzene (10 mL). The mixture was stirred at room temperature for 12 h and worked up in the usual manner to give 246 mg (89%) of **3b**, after chromatography (SiO_2, hexane-AcOEt 20:1): bp 155-157 °C (2 mm); IR (neat) 3060 (H_2C=C), 1735 (COO), 1637 cm^{-1} (C=C); ^1H NMR δ 0.91 (br t, 3, CH_3), 0.93-2.55 (m, 21, CH_2, CH), 1.14 (d, J = 6 Hz, 3, CH_3), 3.59 (s, 3, OCH_3), 4.65 (br s, 2, H_2C=C). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.26; H, 12.20.

2-Methyl-5-methylenetetradecanoic Acid (3c). Hydrolysis of **3b** (104 mg, 0.39 mmol) in MeOH (2 mL)-KOH (105 mg, 1.81 mmol)-H_2O (0.6 mL) system was carried out at room temperature for 24 h, acidified with cold aqueous 10% HCl, and extracted with hexane-AcOEt (1:2). The usual workup gave 90 mg (91%) of **3c**.[3b]

2,5-*trans*- and 2,5-*cis*-5-(Iodomethyl)-2-methyltetradecan-5-olides (4a,b). To a solution of **3c** (62 mg, 0.244 mmol) in aqueous 0.5 N $NaHCO_3$ (1.0 mL) was added a mixture of KI (415 mg, 2.50 mmol), I_2 (190 mg, 0.75 mmol), and H_2O (0.6 mL) at 0 °C. The mixture was stirred at 15 °C for 48 h and extracted with ether. The extract was worked up in the usual manner to give 31 mg (33.6%) of **4b** (R_f 0.57, Merck PF 254, hexane-AcOEt 20:1) and 59 mg (62.3%) of **4a** (R_f 0.49). Physical constants together with elemental analyses of **4a** and **4b** are as follows. **4b**: bp 159-160 °C (0.015 mm); IR (neat) 1735 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.29 (br s, 12, CH_2), 1.31 (d, J = 6 Hz, 3, CH_3), 1.40-2.70 (m, 9, CH_2, CH), 3.35 (br s, 2, CH_2I); ^{13}C NMR δ 11.7 (t, CH_2I), 14.1 (q, C-14), 17.3 (q, C-2 Me), 22.6 (t, 3C), 25.0 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t), 31.8 (t), 35.1 (d), 39.9 (t), 83.7 (s, C-5), 173.7 (s, C-1). Anal. Calcd for $C_{16}H_{29}IO_2$: C, 50.53; H, 7.69. Found: C, 50.55; H, 7.77.

4a: bp 161-162 °C (0.02 mm); IR (neat) 1735 cm^{-1} (COO); ^1H NMR δ 0.88 (br t, 3, CH_3), 1.29 (br s, 12, CH_2), 1.26 (d, J = 6 Hz, 3, CH_3), 1.40-2.70 (m, 9, CH_2, CH), 3.50 (br s, 2, CH_2I); ^{13}C NMR δ 14.1 (q, C-14), 15.3 (t, CH_2I), 17.2 (q, C-2 Me), 22.7 (t), 23.3 (t), 25.4 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.7 (t), 30.6 (t), 31.9 (t), 35.1 (d, C-2), 38.7 (t), 83.3 (s, C-5), 173.7 (s, C-1). Anal. Calcd for $C_{16}H_{29}IO_2$: C, 50.53; H, 7.69. Found: C, 50.41; H, 7.98.

Benzyl 5,6-Epoxy-2-methyl-5-nonylhexanoate (5a). A solution of potassium benzyl oxide prepared from benzyl alcohol (209 mg, 1.93 mmol) and *t*-BuOK (95 mg, 0.84 mmol) in DMF (2 mL) was added to **4** (151 mg, 0.4 mmol) in DMF (0.3 mL) at 0 °C. The mixture was stirred at room temperature for 24 h, poured into cold aqueous 5% tartaric acid, and extracted. The workup gave 124 mg (86%) of **5a** after chromatography (SiO_2, hexane-AcOEt 5:1): bp 187-189 °C (0.02 mm); IR (neat) 3030, 1735 cm^{-1} (COO); ^1H NMR δ 0.88 (br t, 3, CH_3), 1.16 (d, J = 6 Hz, 3, CH_3), 1.10-1.85 (m, 20, CH_2, 1.24 (top)), 2.15-2.51 (m, 1, CHCO), 2.52 (s, 2, CH_2O), 5.10 (s, 2, CH_2OCO), 7.30 (br s, 5, PhH). Anal. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.06. Found: C, 76.68; H, 10.30.

Methyl 5,6-Epoxy-2-methyl-5-nonylhexanoate (5b). To a solution of **3a** (300 mg, 1.1 mmol) in CH_2Cl_2 (3 mL) was added 80% *m*-CPBA (299 mg, 1.73 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h and worked up in the usual manner to give 307 mg (98%) of **3b**: bp 120-122 °C (0.02 mm); IR (neat) 1732 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.10-2.80 (m, 21, CH_2, 1.27 (top)), 1.16 (d, J = 6 Hz, 3, CH_3), 2.38 (m, 1, CHCO), 2.54 (s, 2, CH_2O), 3.66 (s, 3, OCH_3). Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.79; H, 11.34. Found: C, 71.73; H, 11.39.

***dl*-Malyngolide (1a) and 2-Epimalyngolide (1b).** To a solution of **5a** (55 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) was added a solution of BBr_3 (153 mg, 0.61 mmol) in CH_2Cl_2 (0.3 mL) at -70 °C. The mixture was stirred at -65 ~ -60 °C for 1 h, quenched with cold water, and extracted with AcOEt. The usual workup gave 19 mg (46%) of **1b** (R_f 0.31, Merck F254, hexane-AcOEt 4:1) and 19 mg (46%) of **1a** (R_f 0.23) after chromatography (SiO_2, hexane-AcOEt 4:1). Physical constants of **1a** and **1b** together with elemental analysis **1b** are as follows. **1b**: bp 144-146 °C (0.01 mm); IR (CCl_4) 3390 (OH), 1728, 1712 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.26 (br s, 12, CH_2), 1.27 (d, J = 6 Hz, 3, CH_3), 1.45-2.20 (m, 8, CH_2), 2.23-2.65 (m, 1, CHCO), 2.83 (br s, 1, OH), 3.57 (br s, 2, CH_2O); ^{13}C NMR δ 14.1 (q, C-14), 17.2 (q, C-2 Me), 22.7 (t), 23.6 (t), 25.3 (t), 26.3 (t), 29.3 (t), 29.5 (t, 2C), 30.1 (t), 31.9 (t), 35.6 (d, C-2), 36.7 (t), 67.7 (t, C-5 CH_2O), 86.9 (s, C-5), 175.3 (s, C-1). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.13; H, 11.29.

1a: bp 144-146 °C (0.01 mm); ^{13}C NMR δ 14.1 (q, C-14), 17.2 (q, C-2 Me), 22.7 (t), 23.2 (t), 25.4 (t), 27.2 (t), 29.3 (t), 29.5 (t, 2C), 30.0 (t), 31.9 (t), 35.2 (d, C-2), 37.7 (t), 67.6 (t, C-5 CH_2O), 86.4 (s, C-5), 175.5 (s, C-1).

Registry No. 1a, 74742-19-1; **1b**, 76984-84-4; **2**, 79299-93-7; **3a**, 76984-85-5; **3b**, 76917-12-9; **3c**, 74709-66-3; **4a**, 76917-13-0; **4b**, 76917-14-1; **5a**, 79299-94-8; **5b**, 79299-95-9; 3-methylcyclopentane-1,2-dione, 79299-96-0; 1-bromononane, 693-58-3.

An Efficient Synthesis of Conjugated Ketene Dithioacetals

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Ketene dithioacetals conjugated with functional groups have been exploited in a variety of synthetic applications. Conjugated olefin ketene dithioacetals have served as carbonyl umpolung reagents[1] and Diels-Alder dienes.[2] α-Oxoketene dithioacetals have been previously utilized for the synthesis of heterocyclic compounds,[3-5] Diels-Alder dienes,[6] and the indirect synthesis of α-tertiary alkyl substituted ketones.[7] The conjugated ketene dithioacetals contain a masked ester functionality and hold considerable potential as substrates for functional group manipulation and sequential carbon-carbon bond-forming transformations.

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