also support this assignment. It has been shown[7] that Michael-type ring closures may lead initially to the kinetically favored product, but that under the reaction conditions equilibration occurs, leading to the irreversible formation of the thermodynamically more stable product. In this case the more stable ring-closure product is the 2-cis isomer **4a**; and its more stable conformation, as in **5a**, places the sulfone group in the equatorial position necessary for γ-elimination,[8] which leads to **2a** with 2-cis stereochemistry.

The symmetrical compound **7**, which lacks a *gem*-dimethyl group, does not undergo this elimination reaction under the relatively mild conditions employed (sodium ethoxide, 25 °C). This result is consistent with Woodward's observation[8] that γ-elimination of sulfones requires more drastic conditions. On the other hand, in Martel's synthesis of chrysanthemic acid[9] via the diester **8**, γ-elimination of the sulfone occurred readily under the conditions of the Michael reaction. This supports our conclusion that the elimination is both accelerated and directed by the influence of the *gem*-dimethyl group at C_6.

Experimental Section

Melting points were determined with a Kofler hot-stage apparatus, IR spectra with Perkin-Elmer 137B and 281 spectrometers, and ^1H NMR spectra (Me_4Si as internal standard) with a Varian T60A or a Bruker WM 360 instrument. Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5985 instrument.

***c*-2,6,6-Trimethyl-4-oxobicyclo[3.1.0]hexane-*r*-1-carbonitrile (2a).**[10] A suspension of [(4-methylbenzene)sulfonyl]-acetonitrile (40 g) in 2-methyl-2,5-heptadien-4-one (25 g) and ethanol (200 mL) was treated with a 20-mL aliquot of a sodium ethoxide solution [sodium (5 g) in ethanol (200 mL)] and stirred until the suspended material dissolved. The remainder of the sodium ethoxide solution was added, and the mixture was allowed to stand overnight. Dilution with water (1 L) and extraction with dichloromethane (2 × 150 mL), followed by distillation, gave 19.25 g (58.5%) of **2a**: bp 95–100 °C (0.3 mmHg); GLC showed two main components (91 + 5%); GLC/mass spectra (CI) indicated *m/e* 164 (M + 1) for both components; ^1H NMR ($CDCl_3$) δ 1.25 (s, 3 H), 1.44 (s, 3 H), 1.44 (d, 3 H, J = 7 Hz), 2.08 (br d, 1 H, J = 18 Hz), 2.30 (s, 1 H), 2.44 (dd, 1 H, J = 18, 9 Hz), 2.50 (m, 1 H); other spectroscopic data and elemental analyses previously reported.[1]

***c*-2,5,6,6-Tetramethyl-4-oxobicyclo[3.1.0]hexane-*r*-1-carbonitrile (2b).** The title compound was prepared by a method similar to that employed for **2a**. The crude product was crystallized from petroleum ether (bp 65–90 °C) in 52% yield: mp 83–84 °C; GLC/mass spectra (CI) as before showed one main component, *m/e* 178 (M + 1); ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.35 (s, 3 H), 1.37 (s, 3 H), 1.40 (d, 3 H, J = 7 Hz), 2.06 (dd, 1 H, J = 18, 3 Hz), 2.50 (m, 1 H), 2.52 (dd, 1 H, J = 18, 8 Hz); IR (Nujol mull) 2220, 1720, 1470, 1380, 1300, 1110, 850 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.61; H, 8.51; N, 8.20.

2,6,6-Trimethyl-4-oxo-3-(phenylmethylene)bicyclo[3.1.0]-hexane-1-carbonitrile (6a). A mixture of the nitrile **2a** (1.63 g) and benzaldehyde (1.1 g) was treated with 10% sodium ethoxide in ethanol (1 mL). An immediate exotherm was observed, and the mixture solidified. Recrystallization from ethanol gave 1.61 g (64%) of **6a**: mp 159–161 °C; mass spectrum, *m/e* 251 (M^+); ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.42 (d, 3 H, J = 7 Hz), 1.43 (s, 3 H), 2.42 (s, 1 H), 3.63 (dq, 1 H, J_q = 7, J_d = 2 Hz), 7.28 (d, 1 H, J = 2 Hz), 7.45 (br s, 5 H); spin-decoupling irradiation at δ 1.42 collapses the signal at δ 3.63 to a doublet, irradiation at δ 7.28 collapses the signal at δ 3.63 to a quartet, and irradiation at δ 3.63 collapses the signals at δ 1.42 and 7.28 to singlets; IR (Nujol mull) 2210, 1705, 1615, 940 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.40; H, 7.02; N, 5.53.

2,5,6,6-Tetramethyl-4-oxo-3-(phenylmethylene)bicyclo-[3.1.0]hexane-1-carbonitrile (6b) was prepared from the nitrile **2b** by a similar procedure to that employed for **6a**. The product was recrystallized from ethanol to give 69% **6b**: mp 119–121 °C; ^1H NMR δ 1.17 (s, 3 H), 1.39 (s, 3 H), 1.39 (d, 3 H, J = 7 Hz), 1.50 (s, 3 H), 3.72 (q, 1 H, J = 7 Hz), 7.5 (complex, 6 H); IR (Nujol mull) 2220, 1705, 1610, 1040, 940 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.48; H, 7.30; N, 5.47.

Acknowledgment. We thank Mr. N. Secord and his colleagues for recording GC/mass spectra and Dr. W. Bremser of BASF, Ludwigshafen, for the 360-MHz ^1H NMR spectra.

Registry No. 1a, 66031-92-3; **1b**, 79255-57-5; **2a**, 79255-58-6; **2b**, 79255-59-7; **4a**, 73583-67-2; **6a**, 79255-60-0; **6b**, 79255-61-1; [(4-methylbenzene)sulfonyl]acetonitrile, 5697-44-9.

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Ozonolysis of Tetraphenylcyclopentadienone

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Received April 17, 1981

At the present time the only established examples of the 1,4 addition of ozone to conjugated diene systems are with aromatic compounds of the anthracene type, such as anthracene itself, various 9,10-disubstituted anthracenes, and certain benzoanthracenes.[1,2] No similar additions to aliphatic systems have been reported. In the hope of discovering such, we investigated the ozonation of tetraphenylcyclopentadienone (**1**). Although our anticipation was not fulfilled, the results of the ozonation were unusual enough to be of interest.

Ozonation of **1** in dichloromethane at −78 °C with 1 mol equiv of ozone resulted in two products: 5-(benzoyloxy)-3,4,5-triphenyl-1-oxacyclopent-3-en-2-one (**12**, 56% yield) and the known 1,2,3-triphenylpropane-1,3-dione (**14**, 32% yield).

The stucture of **12** was established through elemental analysis, NMR, IR, and mass spectra, a positive hydroxamic acid[3] test for an ester function, and hydrolysis to benzoic acid and known lactol **13**. The NMR spectrum of **12** revealed only aromatic protons centered at δ 8.0 (2 H) and 7.3 (18 H); the IR spectrum showed two carbonyl stretching bands at 1767 and 1745 cm^{-1}; and the mass spectrum contained a parent peak at *m/e* 432 and fragmentation peaks at *m/e* 404, 327, 311, 282, 265, 253, 207, 178, 121, 105, 77, and 51. The compound gave negative peroxide tests with KI and HI and no molecular oxygen was evolved during the ozonolysis. The structure assignment was confirmed by X-ray crystallography.[4]

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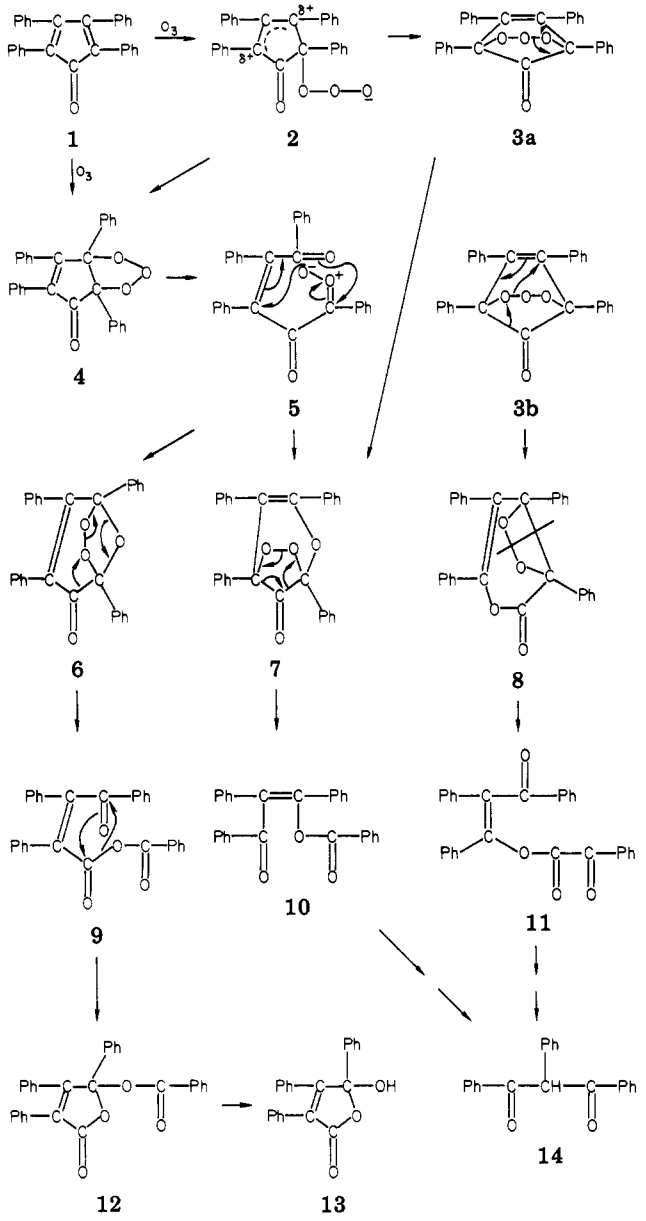
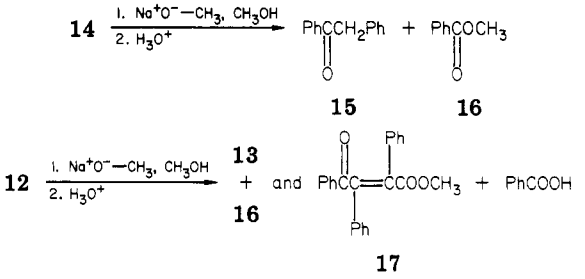
0022-3263/81/1946-5028$01.25/0

Scheme I



Scheme II



The reactions involved in the conversion of 1 to 12 and 14 during ozonation obviously include rearrangements of peroxidic intermediates. The route to 12 is best rationalized by 1 → 4 → 5 → 6 → 9 → 12 (Scheme I). The rearrangement involves the normal ozonide (or some precursor to it such as 5) to afford 9, which isomerizes to 12. Such rearrangements and isomerizations also occur during ozonation of indenones.[5]

The formation of 14 also can be rationalized via 4 and 5, which, however, cyclizes to 7 rather than 6. Rearrangement of peroxide 7 yields 10, which hydrolyzes to 14 and/or its enol tautomer. Unfortunately, it was never possible to isolate 10 due to the difficulties inherent in separating the ozonation products.

The route to 14 just outlined involves only 1,2 addition of ozone. It is also possible to rationalize the formation of 14 via 1,4 addition of ozone (1 → 2 → 3). Two pathways from 3 to 14 are possible: 3a → 7 → 10 → 14 and 3b → 8 → 11 → 14. It is not possible at this time to decide which type of reaction provided 14 since all efforts to isolate intermediates failed.

Experimental Section

Ozonation of Tetraphenylcyclopentadienone (1). Ten millimoles of ozone was passed into a solution of 10 mmol of 1 (Aldrich, mp 217–220 °C) in 100 mL of dichloromethane at −78 °C by the usual procedure (earlier papers of senior author). The ozone absorption was generally quantitative and the reaction mixture changes from deep purple to light gold. The solvent was removed via a rotary evaporator and the red-gold residue was crystallized from methanol by addition of a trace of water. Recrystallization from methanol–water afforded clear prisms melting at 134–135 °C.

Anal. Calcd for $C_{29}H_{20}O_4$: C, 80.56; H, 4.63; O, 14.81; mol wt 432.1362. Found: C, 80.42; H, 4.84; O, 14.72; mol wt (high-resolution mass spectroscopy), parent peak at m/e 432.1358.

Partial evaporation of the filtrate yielded crystals which melted at 149–150 °C after several recrystallizations.

Anal. Calcd for $C_{21}H_{16}O_2$: mol wt 300.1150. Found: mol wt (high-resolution mass spectroscopy), parent peak at m/e 300.1146.

Further evaporation of the filtrate yielded crystals melting at 115–117 °C. These resisted further purification, but the IR spectrum indicated the material to be a mixture of the two substances just described.

5-(Benzoyloxy)-3,4,5-triphenyl-1-oxacyclopent-3-en-2-one (12). The compound melting at 134–135 °C was characterized as 12 as already described. The hydrolysis was performed in *p*-dioxane with 5% sodium hydroxide. After acidification, extraction with ether, and extraction of the ether layer with bicarbonate, benzoic acid was isolated from the bicarbonate layer: mp 119–121 °C; identification by mixture melting point and IR spectrum. From the ether layer was isolated lactol 13: mp 175–175.5 °C after recrystallization from ethanol. Identification of this known compound[6] was via melting point and various spectra: IR 3268 (OH), 1730 (C=O), and 1642 cm^{-1} (C=C); mass spectrum, parent peak at m/e 328 and fragmentation peaks at m/e 300, 223, 178, 105, 77, and 51; NMR δ 4.7 (br s, 1 H), 7.25 (aromatic m, 15 H).

1,2,3-Triphenylpropane-1,3-dione (14). The compound melting at 149–150 °C was identified as the known compound 14[7] via its melting point and molecular weight (above) and its IR spectrum: carbonyl absorptions at 1689 and 1661 cm^{-1} (as expected from 14 and its enol tautomer) and aromatic absorption at 1590 cm^{-1}. In addition the NMR spectrum revealed aromatic multiplets at δ 8.1 (4 H) and 7.5 (11 H) and a singlet at δ 6.63 (1 H); the mass spectrum included the parent peak at m/e 300 and fragmentation peaks at m/e 281, 223, 195, 178, 165, 152, 105, 77, and 51.

Quantitative Determination of 12 and 14. The product yields obtained as described above were very low and no improvement was realized through thin-layer or elution chromatography. Quantitative IR determinations on the crude oily product were impossible because the carbonyl region bands were not well enough defined.

After much effort it was found that the mixture of 12 and 14 could be analyzed through quantitative NMR determination of the products formed by treatment of the ozonation reaction

(4) We thank Professor Raymond Davis and Dr. Paul Riley of the University of Texas at Austin for this determination.

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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**.

Acknowledgment. This work was supported by Grant F-042 from the Robert A. Welch Foundation, for which the authors are grateful.

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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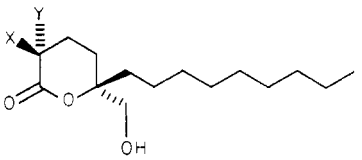
Received June 1, 1981

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]

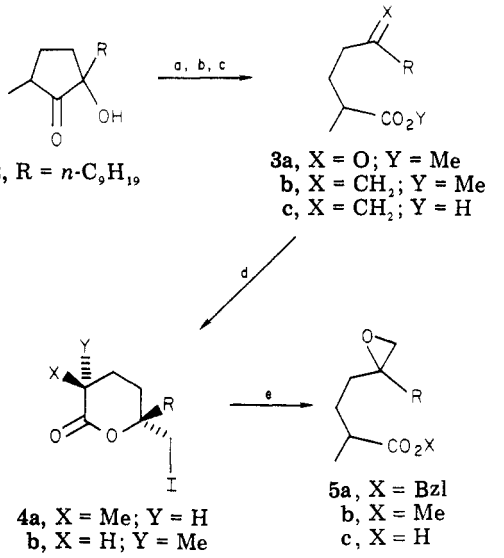


1a, X = Me; Y = H
b, X = H; Y = Me

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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(2) Cardillina II, J. H.; Moore, R. E; Arnold, E. V.; Clardy, J. *J. Org. Chem.* **1979**, *44*, 4039.
(3) (a) Sakito, Y.; Tanaka, S.; Asami, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 1223. (b) Babler, J. H.; Invergo, B. J.; Sarussi, S. J. *J. Org. Chem.* **1980**, *45*, 4241. (c) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *Ibid.* **1981**, *46*, 2439.
(4) Carlson, R. G.; Prabhu, A. V. *J. Org. Chem.* **1974**, *39*, 1753.
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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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