Stereospecific Dicobalt Octacarbonyl Mediated Enyne Cyclization for the Synthesis of Methyl Deoxynorpentalenolactone H

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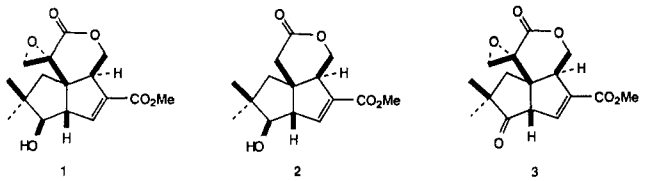
Ethyl isobutyrate was converted into the enyne **13** through a straightforward sequence of transformations. Treatment of **13** with $Co_2(CO)_8$/CO/85 °C gave the bicyclo[3.3.0]enone **15** (64%), in a completely stereospecific reaction. The enone **15** was converted into **18** by photochemical addition of allene and oxidative fragmentation. The *exo*-methylene ketone **18** was converted into its enol triflate derivative **24** and carboxymethylated to give the ester **25**. Epoxidation of **25** and BF_3·OEt_2-induced rearrangement followed by $NaBH_4$ treatment gave a mixture of the δ-lactone **27**, the γ-lactone **28**, and the alcohol **29**. Acid hydrolysis of **27** gave deoxynorpentalenolactone H methyl ester **2**.

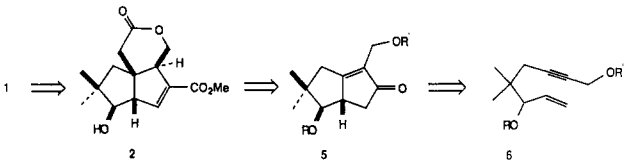
During the past four years we have described several examples of the dicobalt octacarbonyl mediated cyclization of 1,6-enynes (Pausen–Khand reaction) to provide bicyclo[3.3.0]oct-2-en-3-ones in a single step.[2] This increasingly popular organometallic process is currently being investigated by a number of groups.[3] Our own interests have focused on the observed stereoselectivity with respect to both allylic and propargylic substituents. Here we report on the effect on allylic oxygen functionality and its application to the construction of an advanced pentalenolactone H system (**1**), namely, methyl deoxynor-



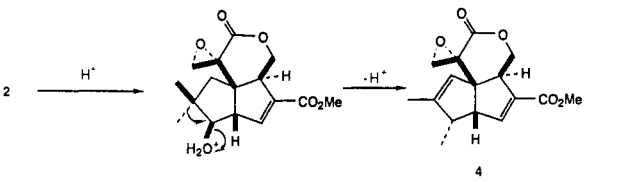
1 **2** **3**

pentalenolactone H (**2**). The pentalenolactones are antibiotics that have been popular synthetic objectives during the past decade. Prior literature is given in ref 4. Pentalenolactone G (**3**) has recently been synthesized by Pirrung, and this is the first synthesis of a pentalenolactone bearing a 4β-oxygen substituent.[5] The importance of the neopentyl β-oxygen functionality can be better appreciated when it is realized that it is not at all unreasonable to suggest that Wagner–Meerwein rearrangement of **1** can provide a plausible biogenetic pathway to pentalenolactone **4**.[6]

Scheme I



2 **5** **6**



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The question we are asking of the Pauson–Khand reaction is the following: If we assemble a suitably functionalized 1,6-enyne, will the allylic oxygen substituent appear on the exo face of the resulting bicyclo[3.3.0]octenone system? Scheme I outlines a retrosynthetic analysis of pentalenolactone H (**1**), where the key transformation is the conversion of **6** into **5**, and its attendant stereoselectivity.

On the basis of our previous experience and using the mechanistic hypothesis we have proposed for the Pauson–Khand reaction, it can be reasonably predicted that the substrate **6**, on treatment with dicobalt octacarbonyl [$Co_2(CO)_8$], will form its derived dicobalt hexacarbonyl adduct, which upon thermolysis should produce the therodynamically more stable bicyclo[3.3.0]enone **5**.[7] It

(1) Address correspondence to this author at The Department of Chemistry, The University of Texas at Austin, Austin, TX 78712-1167.

(2) For references to the original discovery of the Pauson–Khand reaction for the synthesis of cyclopentenones see: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 975. Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Forman, M. I. *Ibid.* **1973**, 977. Pauson, P. L.; Khand, I. U. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 2. Blandon, P.; Khand, I. U.; Pauson, P. L. *J. Chem. Res., Synop.* **1977**, 8. Pauson, P. L. *Tetrahedron.* **1985**, *41*, 5855. For the first intramolecular example see: Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. For examples of the stereoselectivity of the Pauson–Khand see: Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851. Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483. Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7495.

(3) For a comprehensive recent review of this area see: Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. Kraft, M. E. *Tetrahedron Lett.* **1988**, *29*, 999. Kraft, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 968. Sampath, V.; Lund, E. C.; Knudsen, M. J.; Olmstead, M. M.; Schore, N. E. *J. Org. Chem.* **1987**, *52*, 3595. Keyaniyan, S.; Apel, M.; Richmond, J. P.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 770. Montaña, A.-M.; Moyana, A.; Pricàs, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995. Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. Hua, D. H.; Coulter, M. J.; Badejo, *Tetrahedron Lett.* **1987**, *28*, 5465. Smit, N. A.; Gybin, A. S.; Shaskkov, A. S.; Strychkov, Y. T.; Kuz'mina, L. G.; Mikaelian, G. S.; Caple, R.; Swanson, E. D. *Tetrahedron Lett.* **1986**, *27*, 1241. Simonian, S. O.; Smit, W. A.; Gybin, A. S.; Shashkov, A. S.; Mikaelian, G. S.; Tarasov, V.; Ibrajimov, I. I.; Caple, R.; Froem, D. E. *Tetrahedron Lett.* **1986**, *27*, 1245. Smit, W. A.; Kireev, S. L.; Nefedov, O. M.; Tarasov, V. *Tetrahedron Lett.*, submitted for publication. Veretenov, A. L.; Gybin, A. S.; Smit, W. A.; Shashkov A. S.; Caple, R.; Wütala, *Tetrahedron Lett.*, submitted for publication. Knudsen, M. J.; Schore, N. E. *J. Org. Chem.* **1984**, *49*, 5025. Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569. Schore, N. E.; Rowley, E. G. *J. Am. Chem. Soc.* **1988**, *110*, 5224. Carcellar, E.; Centellas, V.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron Lett.* **1985**, *26*, 2475. Carcellar, E.; Garcia, M. L.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1986**, *42*, 1831.

(4) For a general review of polyquinane synthesis see: Paquette, L. A. *Topics in Current Chemistry*, Springer-Verlag: Berlin, Heidelberg, 1984; Vol. 119. Synthesis of (±)-pentalenolactone E methyl ester: Paquette, L. A.; Schostarez, H.; Annis, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 6526; **1982**, *104*, 6646. Cane, D. E.; Thomas, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 5295. Ohtsuka, T.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1983**, *24*, 3851. Taber, D. F.; Schuchardt, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5289. Marino, J. P.; Silveiro, C.; Comasseto, J.; Petragnani, N. *J. Org. Chem.* **1987**, *52*, 4140. Pentalenolactone: Danishefsky, S.; Hirama, M.; Gombatz, K.; Harayama, T.; Berman, E.; Schuda, P. F. *J. Am. Chem. Soc.* **1979**, *101*, 7020. Parsons, W. H.; Schlessinger, R. H.; Quesada, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 889.

(5) Pirrung, M. C.; Thomson, S. A. *J. Org. Chem.* **1988**, *53*, 227.

(6) Cane, D. E.; Tillman, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 122. Cane, D. E.; Rossi, T.; Tillman, A. M.; Pachlatko, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 1838.

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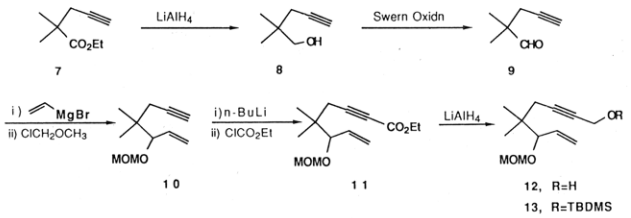
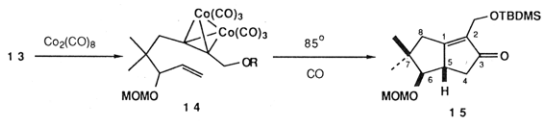
appears to be a trend in these reactions that both allylic and propargylic substituents appear on the exo face of the product bicyclo[3.3.0]enone.

The synthesis of **6** (R = MOM; R′ = TBDMS) is described briefly, since it was accomplished by standard transformations. Ethyl isobutyrate was converted into its derived lithium enolate by addition to lithium diisopropylamide in THF at −78 °C. Addition of propargyl bromide to this solution gave **7** (94%). Reduction of **7**



($LiAlH_4$) gave **8** (96%), which was oxidized by using the Swern modification of the Moffat oxidation to give the aldehyde **9** (95%). Treatment of **9** with vinylmagnesium bromide in ether, followed by chloromethyl methyl ether, provided the 1,6-enyne **10** (74%). Generation of the lithium acetylide derivative of **10** with *n*-butyllithium, followed by quenching with ethyl chloroformate, gave **11** (93%), which was reduced with $LiAlH_4$ to give **12** (91%). Finally, protection of **12** (TBDMSCl/imidazole/CH_2Cl_2) gave **13** (83%).

Addition of **13** to Brønsted heptane solution of $Co_2(CO)_8$ containing 0.1 equiv of 4-methyl-2,6-di-*tert*-butylpyridine resulted in complete complexation to give the adduct **14**.



The function of the Brønsted base is to minimize any untoward acid-catalyzed degradation (cleavage of protecting groups) that might be caused by $HCo(CO)_4$. The complex **14** was heated under an atmosphere of CO in a resealable tube for 50 h at 85 °C. Chromatography of the reaction mixture gave **15** (64%); we could not detect any other bicyclo[3.3.0]enones in the reaction mixture.

The relative stereochemistry between C-5 and C-6 was initially assigned on the basis of comparing the vicinal coupling constant between H-6 and H-5, 10.1 Hz, which is close to that of pentalenolactone H (**1**), whereas the opposite relative stereochemistry between H-6 and H-5 (cis) would have a considerably smaller coupling of ca. 4.0 Hz. Later in the sequence, shown below, we confirmed the assignment by single-crystal X-ray crystallographic structural analysis of **19**, a compound derived from **15** (see Figure 1). The bicyclo[3.3.0]octenone **15** proved to be susceptible to decomposition, due to small amounts of cobalt-derived residues that cochromatographed with **15**. Removal of these contaminants by oxidation using *N*-methyl morpholine *N*-oxide gave pure **15**, which could be chemically manipulated without unwanted decomposition.

A number of methods were tried that should have had the overall effect of adding $-CH_2CO_2R$ to C-1 of the enone **15**, but they did not work. Consequently, we returned to a strategy that we used several years ago, namely, the [2 + 2] photoaddition of allene to cyclopentenones.[8] Irradiation (Hanovia 450-W lamp) of a mixture of **15** in hexane/THF and allene at −40 °C gave the photoadduct **16** (80%). The structure of **16** (regiochemistry) is well pre-

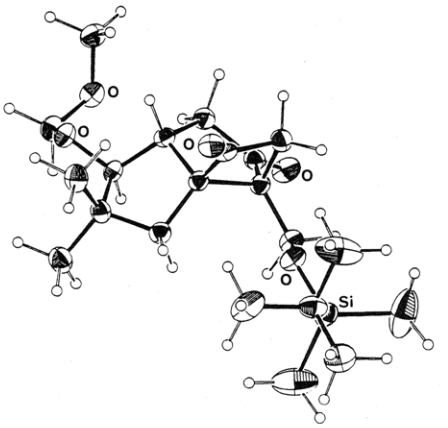
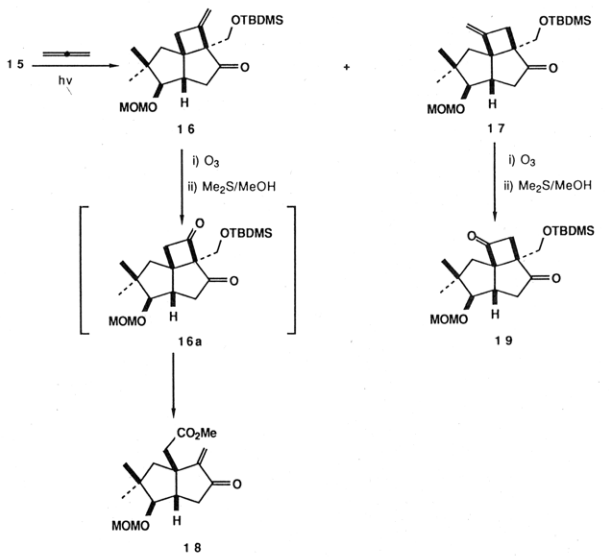


Figure 1.

cedented by the work of Wiesner and others.[8] The cis stereochemistry between the two five-membered rings is obviously the less strained photoadduct. In general, it has been observed in [2 + 2] allene photoadditions to α,β-unsaturated ketones that the thermodynamically more stable adduct is the major, if not the sole isolated product. Unexpectedly, we found that in subsequent allene photoadditions the adduct **16** was accompanied by variable amounts of its regioisomer **17**, if the starting enone **15** was not carefully purified and the cobalt residues oxidatively destroyed. While we could not separate **17** from **16**, its presence was shown in the following way: Ozonolysis of a mixture of **16** and **17** followed by reductive workup with dimethyl sulfide in methanol gave exocyclic enone **18**, and the cyclobutanone **19** (ν_{max} 1780 cm^{-1}) as a crystalline solid. Single-crystal X-ray crystallography established its structure. Since both **18** and **19** exhibit doublets at 3.23 (J = 8.1 Hz) and 3.22 (J = 8.5 Hz), the stereochemical assignment between C-5 and C-6 is the same in both compounds.



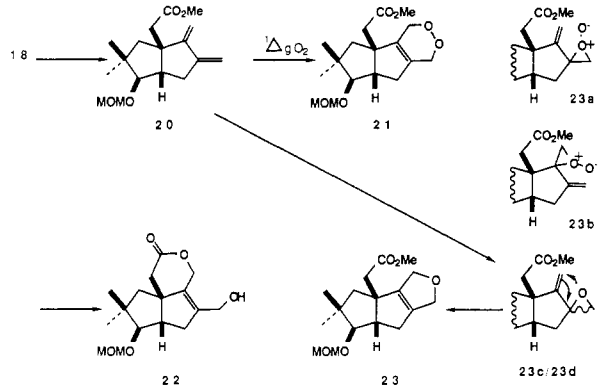
The enone **18** was treated with the Lombardo reagent ($CH_2Br_2/Zn/TiCl_4$)[10] to give the exo-cyclic diene **20** in

(7) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(8) Eaton, P. E. *Tetrahedron Lett.* **1964**, 3695. Wiesner, K. *Tetrahedron* **1975**, *31*, 1655.

(9) Complete details of the single-crystal X-ray structural determination of **19** may be obtained from Dr. John Huffman, Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. Please ask for report No. 86180.

(10) Lombardo, L. *Tetrahedron Lett.* **1982**, 4293. *Org. Synth.* **1987**, *65*, 81. Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417.

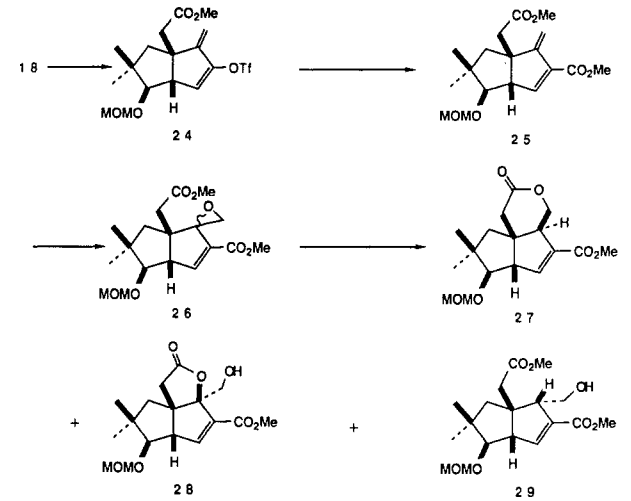


excellent yield (94%). It was anticipated that singlet oxygen addition to **20** would take place in a [2 + 4] manner to give the *endo*-peroxide **21**, which upon reductive cleavage followed by lactonization should provide **22**. While **22** has the tetrasubstituted double bond in the "wrong" place, it was reasoned that this could be rectified by manipulation of the allylic primary alcohol group. However, when the diene **20** was exposed to singlet oxygen ($^1\Delta gO_2$) generated photochemically by irradiation in MeOH or pyridine containing rose bengal or hematoporphyrin as sensitizers, no definable products were isolated. Nevertheless, by changing the solvent to dichloromethane and the sensitizer to *meso*-tetraphenylporphine, a single adduct **20** was rapidly formed (70%).

Its formation may be rationalized by the intermediacy of the perepoxide intermediates (**23a**/**23b**), which are reduced to the epoxides (**23c**/**23d**). The *exo*-cyclic diene has an extinction coefficient of 5300 at 248 nm, whereas coplanar dienes have ϵ values of 10000–12000. The low value reflects poor π-overlap between the adjacent exo-cyclic methylene groups, which prevents the usual [2 + 4] cycloaddition of singlet oxygen.[11]

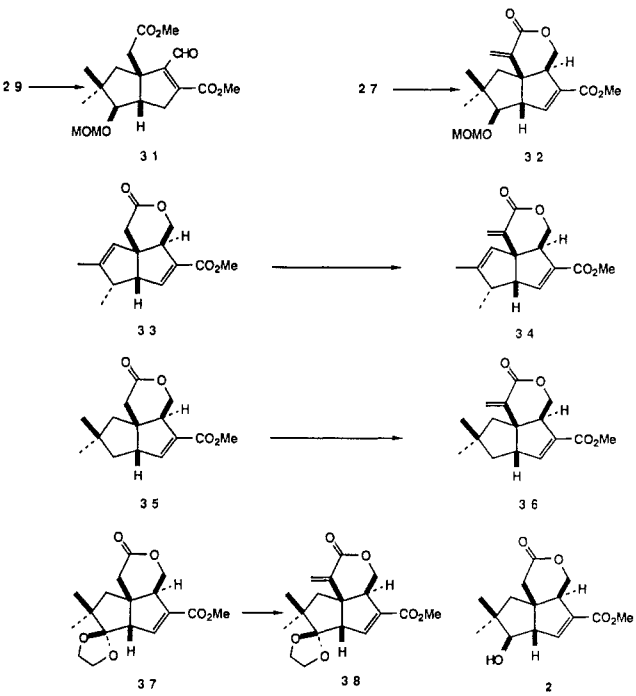
Treatment of the enone **18** with triflic anhydride/4-methyl-2,6-di-*tert*-butylpyridine at 0 °C gave the enol triflate **24**, which was directly subjected to carboxymethylation conditions, MeOH/DMF/Ph_3P/$Pd(OAc)_2$/Et_3N under CO, to give the unsaturated methyl ester **25** (52% from **18**).[12] Attempts to hydroborate the *exo*-methylene group using a wide variety or hydroborating agents failed.

Epoxidation of **25** using *m*-chloroperoxybenzoic acid gave **26**, and this was treated directly with BF_3·OEt_2 at −78 °C followed by $NaBH_4$/MeOH to reduce the intermediate aldehydes.[13] Three products were isolated from this experiment: the desired δ-lactone **27** (δ 7.01); the γ-lactone **28** (δ 7.25); the epimeric alcohol **29** (δ 6.94), with each resonance corresponding to the proton attached to the trigonally hybridized carbon atom (β to the CO_2Me group). When the BF_3·OEt_2 was added to **26** at 0 °C, significantly less of the five-membered ring lactone **28** was formed, and at 25 °C it's formation was entirely eliminated. The decreased formation of **28** was accompanied by small increases in the yield of the required δ-lactone **27**, although



the yield remained modest since the epimeric alcohol **29** became the major product. (Table I) A mechanism that is consistant with these observations is outlined in Scheme II.

The allylic epoxide **26** can readily open to give the allylic cation **26a**, which can be trapped by the adjacent ester carbonyl group, leading to the γ-lactone **28** via the oxonium ion **26b**. Alternatively, a 1,2-hydride shift in **26a** leads to the epimeric aldehydes **30**, which upon hydride reduction ($NaBH_4$) produces the δ-lactone **27** and the homoallylic alcohol **29**. Attempts to recycle the undesired epimer **29** by reoxidation to **30** and equilibration failed, because of competitive conjugation of the double bond to give the derived α,β-unsaturated aldehyde **31**. The δ-lactone **27** could not be converted into the α-methylene derivative **32** by using procedures (Stille's reagent and Bredereck's reagent)[14] that had successfully converted **33** and **35** into their corresponding α-methylene derivatives **34** and **36** respectively.



(11) Wasserman, H. H.; Murray, R. W. *Singlet Oxygen*; Academic Press: New York, 1979, p 200–237. Kearns, D. R. *J. Am. Chem. Soc.* **1969**, 91, 6554. Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381. Bartlett, P. D.; Shimizu, N. *J. Am. Chem. Soc.* **1976**, *98*, 4193. Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1975**, *97*, 3978.

(12) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1985**, *26*, 1109. For the synthesis of enol triflates see: Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.

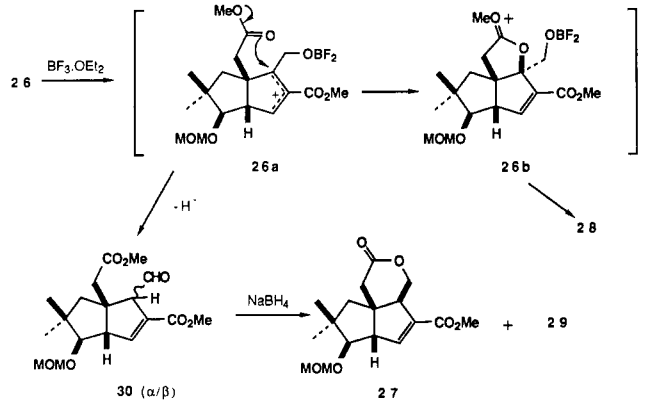
(13) House, H. O.; Blaker, J. W.; Madden, D. A. *J. Am. Chem. Soc.* **1958**, *80*, 6386. Reif, D. J.; House, H. O. *Org. Syn. Coll. Vol. 4*, 1963, 375. Ryerson, G. D.; Wasson, R. L.; House, H. O. *Org. Synth.* **1963**, *Coll. Vol. IV*, 957.

(14) Johnson, F.; Martin, F.; Watts, P. C. *Chem. Commun.* 1970, 27. Finkbeiner, H. L.; Stiles, M. *J. Org. Chem.* **1963**, *85*, 616. Bredereck, H.; Simchen, G.; Rebstat, S.; Kantlehner, W.; Horn, P.; Wahl, R.; Hoffman, H.; Grieshaber, P. *Chem. Ber.* **1968**, *101*, 41. Gutzwiller, J.; Pizzolato, G.; Uskokovic, M. *J. Am. Chem. Soc.* **1971**, *93*, 5907.

Table I. Ratios of 27/28/29 at Various Temperatures

temp, °C	27	28	29
−78	1	2	4
0	3	2	8
25	1	0	3

Scheme II



During the course of this final part of the synthesis we became aware that Pirrung had converted **37** into **38** using LDA/Eschenmoser's salt followed by elimination (MeI/MeOH/THF and DBU/THF).[5] Given the very close similarity between the Pirrung strategy and our own work, and the difficulties in obtaining sufficient quantities of material, namely, **27**, we decided not to continue further. Acid hydrolysis of **27** gave **2**, which is deoxynorpentalenolactone methyl ester.

Experimental Section

Melting points were measured on a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded for solutions in CCl_4 on a Perkin-Elmer 298 spectrophotometer. Nuclear magnetic resonance spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-300 spectrometer using $CHCl_3$ as an internal standard. Ultraviolet spectra were recorded for solutions in MeOH on a Perkin-Elmer 552 spectrophotometer. Mass spectra were obtained on a Kratos MS 80 spectrometer.

Ethyl 4,4-Dimethylpent-1-yn-5-oate (7). To a solution of lithium diisopropylamide prepared by the addition of *n*-butyllithium (2.5 M in hexane; 75.6 mL, 1.05 equiv) to diisopropylamine (19.4 g, 1.10 equiv) at −78 °C was added ethyl isobutyrate (20.9 g, 1.0 equiv) in THF (200 mL) over 3 h. The mixture was warmed to 0 °C and cooled to −78 °C, and propargyl bromide (22.5 g, 1.05 equiv freshly distilled) in THF (100 mL) added. The resulting mixture was warmed to 20 °C and kept at this temperature for 3 h. Workup in the usual manner gave **7**, which was filtered through silica (200 g) eluting with petroleum ether. Distillation of the eluate gave **7** (25.1 g, 94%): bp 35–37 °C (3 mmHg); IR 3330, 1738 cm^{-1}; ^1H NMR δ 4.14 (2 H, q, J = 6.6 Hz), 2.40 (2 H, d, J = 3.0 Hz), 1.95 (1 H, t, J = 3.0 Hz), 1.25 (6 H, s), 1.22 (3 H, t, J = 6.6 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.13; H, 9.18.

4,4-Dimethylpent-1-yn-5-al (9). To a stirred suspension of $LiAlH_4$ (5.11 g, 0.134 mol) in diethyl ether (200 mL) at 0 °C was added a solution of the ester **7** (20.0 g, 0.128 mol) in diethyl ether (100 mL). Workup in the usual way gave **8** (13.7 g, 96%): IR 3440, 3330, cm^{-1}; ^1H NMR δ 3.40 (2 H, s), 2.15 (2 H, t, J = 2.7 Hz), 2.13 (1 H, s), 1.95 (1 H, t, J = 2.7 Hz), 0.95 (6 H, s). The alcohol **8** (12.0 g 0.107 mol) in CH_2Cl_2 (100 mL) was added to a solution of dimethyl sulfoxide (18.8 mL, 0.243 mol) in CH_2Cl_2 (200 mL) containing oxalyl chloride (10.64 mL, 0.12 mol) at −50 °C. After 0.5 h triethylamine (75.0 mL, 0.636 mol) was added, and the mixture warmed to room temperature. Conventional workup gave the aldehyde **9** (11.2 g, 95%) purified by distillation: bp 49–51 °C (30 mmHg): IR 330, 2710, 2115, 1723 cm^{-1}; ^1H NMR δ 9.58 (1 H, s), 2.33 (2 H, d, J = 2.7 Hz), 2.02 (1 H, t, J = 2.7 Hz), 1.05 (6 H, s). Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.08.

4,4-Dimethyl-5-(methoxymethoxy)hept-6-en-1-yne (10). The aldehyde **9** (11.0 g, 0.10 mol) in diethyl ether (50 mL) was treated with vinylmagnesium bromide (1.0 M, in THF, 105 mL) in diethyl ether (250 mL) at −30 °C. After the above mixture was stirred at 20 °C for 3 h, chloromethyl methyl ether (freshly distilled twice from CaH_2, 22.8 mL) was added, and the mixture heated at reflux for 24 h. Conventional workup gave **10**, which was purified by distillation through a short Vigraeux column to give **10** (10.5 g, 58%), bp 43–46 °C) (0.5 mmHg). The distillation residue was dissolved in Hünigs base (30 mL), and chloromethyl methyl ether (10 mL) added to 0 °C. After the above mixture was stirred for 24 h, workup and distillation gave additional **10** (total 13.4 g, 74%): IR 3080, 2115, 1670 cm^{-1}; ^1H NMR δ 5.88–5.46 (1 H, m), 5.34–5.05 (2 H, m), 4.57 (2 H, AB q, $\Delta\nu_{AB}$ = 15.9 Hz, J_{AB} = 6.0 Hz), 3.80 (1 H, d, J = 8.4 Hz), 3.34 (3 H, s), 2.17 (2 H, t, J = 2.7 Hz), 1.94 (2 H, t, J = 2.7 Hz), 0.97 (3 H, s), 0.94 (3 H, s). Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.10; H, 9.73.

Ethyl 5,5-Dimethyl-6-(methoxymethoxy)oct-7-en-2-ynoate (11). *n*-Butyllithium (1.55 M in hexane, 36.1 mL) was added to a solution of **10** (9.1 g, 0.05 mol) in THF (250 mL) at −78 °C. After 0.5 h, ethyl chloroformate (freshly distilled from CaH_2: 8.1 g, 0.075 mol) was added to the above mixture, and the resulting solution warmed to 20 °C. Conventional workup gave **11**, which was purified by distillation providing **11** (11.8, 93%): bp 110–116 °C (0.5 mmHg); IR 3080, 2215, 1710, 1245, 1030 cm^{-1}; ^1H NMR δ 5.88–5.46 (1 H, m), 5.34–5.05 (2 H, m), 4.57 (2 H, AB, q, $\Delta\nu_{AB}$ = 15.9 Hz, J_{AB} = 6.0 Hz), 4.14 (2 H, q, J = 7.5 Hz), 3.72 (1 H, d, J = 8.4 Hz), 3.34 (3 H, s), 2.30 (2 H, d, J = 2.4 Hz), 1.22 (3 H, t, J = 7.5 Hz), 0.95 (6 H, s). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.87; H, 8.85.

1-((*tert*-Butyldimethylsilyl)oxy)-5,5-dimethyl-6-(methoxymethoxy)oct-7-en-2-yne (13). The ester **11** (10.2 g, 0.04 mol) was reduced with $LiAlH_4$ (1.68 g) in diethyl ether (100 mL) at −78 °C in the standard manner to give **12** (7.72 g, 91%): IR 3360, 3080, 2220, 1210 cm^{-1}; ^1H NMR δ 5.85–5.60 (1 H, m), 5.35–5.20 (2 H, m), 4.57 (2 H, AB, q, $\Delta\nu_{AB}$ = 65.4 Hz, J_AB = 6.8 Hz), 4.21 (2 H, AB q, $\Delta\nu_{AB}$ = 2.2 Hz, J_{AB} = 2.4 Hz), 3.89 (1 H, d, J = 8.2 Hz), 3.34 (3 H, s), 2.55 (1 H, t, J = 5.9 Hz), 2.23 (2 H, ABX_2, $\Delta\nu$ = 61.9, $J_{AX} \approx J_{BX}$ = 2.0 Hz), 1.01 (3 H, s), 0.98 (3 H, s). The alcohol **12** (6.39 g 0.03 mol) in dry CH_2Cl_2 (100 mL) containing imidazole (5.1 g, 0.075 mol) at 0 °C was treated with *tert*-butyldimethylsilyl chloride (5.4 g, 0.036 mol) in dry CH_2Cl_2 (25 mL). After 10 h at 20 °C the above mixture was worked up in the usual way, and the residue chromatographed over silica gel (100 g) eluting with 4% ether/petroleum to give **13** (8.14 g, 83%): IR 3080, 2225, 1460, 1365, 1250, 840 cm^{-1}; ^1H NMR δ 5.75–5.60 (1 H, m), 5.35–5.20 (2 H, m), 4.59 (2 H, AB q, $\Delta\nu_{AB}$ = 62.5 Hz, J_{AB} = 6.8 Hz), 4.32 (2 H, s), 3.82 (1 H, d, J = 8.2 Hz), 3.38 (3 H, s), 2.23 (2 H, AB q, $\Delta\nu_{AB}$ = 35.0 Hz, J_{AB} = 16.6 Hz), 0.99 (3 H, s), 0.95 (3 H, s), 0.90 (9 Hz, s), 0.12 (6 H, s). Anal. Calcd for $C_{18}H_{34}O_3Si$: C, 66.20; H, 10.49. Found: C, 65.87; H, 10.28.

5β*H*-2-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-6β-(methoxymethoxy)-7,7-dimethylbicyclo[3.3.0]oct-1-en-3-one (15). A solution of dicobalt octacarbonyl (95 wt % $Co_2(CO)_8$, 5 wt % hexanes, 3.95 g, 0.011 mol) and 4-methyl-2,6-di-*tert*-butylpyridine (0.2 g, 0.001 mol) in dry heptane (80 mL, purged with CO for 2 h) was prepared in a large (500 mL) resealable tube under an atmosphere of CO. The enyne **13** (3.27 g, 0.01 mol) was added to the above solution, and the mixture stirred for 3 h until the evolution of CO is complete. This procedure ensures formation of the adduct **14**, which can be isolated, although in this procedure it was not. The resealable tube was sealed (screw-cap) and heated in an oil bath at 85 °C for 50 h. After the tube was cooled to 20 °C it was opened, the content filtered, the residue washed with 10% ether/petrol, and the filtrate placed directly on a bed of silica gel (125g). The cobalt residues were eluted with 2% ether/petrol. The enone **15** was eluted with 25% ether/petrol. Crude **15** was dissolved in dichloromethane (30 mL), *N*-methylmorpholine *N*-oxide (1.5 g) added, and the resulting mixture stirred at 20 °C for 0.5 h. The solution was washed with brine (10 mL) and water

(3 × 10 mL), and the washings were extracted with ether. The combined organic extracts were dried ($MgSO_4$) and filtered through Celite. Evaporation in vacuo gave **15** (2.27 g, 64%): IR 1700, 1665, 1260, 1100, 840 cm^{-1}; ^1H NMR δ 4.68 (2 H, AB q, $\Delta\upsilon_{AB}$ = 22.3 Hz, J_{AB} = 6.7 Hz), 4.38 (2 H, AB q unresolved), 3.37 (3 H, s), 3.25 (1 H, d, J = 10.1 Hz), 3.12 (1 H, m), 2.66 (2 H, s), 2.50 (2 H, ABX, $\Delta\upsilon_{AB}$ = 119 Hz, J_{AB} = 18.2 Hz, J_{AX} = 6.1 Hz, J_{BX} = 2.9 Hz), 1.19 (3 H, s), 1.15 (3 H, s), 0.91 (9 H, s), 0.08 (6 H, s); MS, calcd for $C_{19}H_{34}O_4Si$ 354.3317, found 354.3291.

8a-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-3,3-dimethyl-5βH-9-methylidene-4β-(methoxymethoxy)tricyclo-[6.2.0.0^{1,5}]decan-7-one (16). A solution of **15** (1.0 g 2.82 mmol) in a mixture of hexane (20 mL) and THF (1 mL) was purged with N_2 for 1 h in a resealable tube. Allene (3 mL) was condensed, and the liquified gas poured into the above solution at −40 °C. The tube was sealed, and the mixture irradiated (Hanovia 450-W UV lamp) for 4 h while the temperature was maintained below 20 °C. The tube was recooled to −40 °C, and opened, and the contents were allowed to warm to room temperature to remove the volatile material. The resulting residue was purified by chromatography over silica gel (20 g) eluting with 4% ether/petrol to give **16** (890 mg 80%): mp 46–48 °C; IR 1725, 1670, 1460, 1260, 1150, 1040 and 835 cm^{-1}. ^1H NMR δ 4.87 (1 H, t, unresolved), 4.81 (1 H, t, unresolved), 4.60 (2 H, AB q $\Delta\upsilon_{AB}$ = 40.7 Hz, J_{AB} = 6.6 Hz), 3.80 (2 H, AB q, $\Delta\upsilon_{AB}$ = 54.1 Hz, J_{AB} = 10.0 Hz), 3.31 (3 H, s), 3.21 (1 H, d, J = 7.9 Hz), 2.79 (2 H, ABX, $\Delta\upsilon$ = 40.7 Hz, J_{AB} = 15.7 Hz, $J_{AX} \approx J_{BX}$ = 2.8 Hz), 2.64 (2 H, m), 2.45 (2 H, m), 1.85 (2 H, AB q, $\Delta\upsilon_{AB}$ = 180 Hz), J_{AB} = 13.8 Hz), 1.00 (3 H, s), 0.95 (3 H, s), 0.84 (9 H, s), 0.02 (3 H, s), 0.01 (3 H, s). Anal. Calcd for $C_{22}H_{38}O_4Si$: C, 66.96; H, 9.71. Found: C, 66.93; H, 9.30.

1β-((Carbomethoxy)methyl)-3,3-dimethyl-5βH-8-methylene-4β-(methoxymethoxy)bicyclo[3.3.0]octan-7-one (18). A solution of **16** (500 mg, 1.27 mmol) in dry CH_2Cl_2 (20 mL) was treated with ozone at −78 °C for 15 min in the presence of 4-Å molecular sieves. After consumption of **16** excess ozone was removed by purging with N_2. Dimethyl sulfide (2 mL) was added to the above mixture, and the resulting solution warmed to 20 °C. Dry methanol (20 mL) was added, and the resulting solution stirred for 60 h. The mixture was filtered, and the crude product chromatographed over silica gel (10 g) eluting with 25% ether/petrol to give **18** (245 mg, 62%) as white crystals: mp 49–51 °C; IR 1725, 1630, 1150, 1090, 1040 cm^{-1}; ^1H NMR δ 6.06 n1 H, s), 5.29 (1 H, s), 4.64 (2 H, m), 3.60 (3 H, s), 3.36 (3 H s), 3.23 (1 H, d, J = 8.1 Hz), 2.77 (1 H, m), 2.71 (2 H, d, J = 5.0 Hz), 2.61 (2 H, ABX, unresolved), 1.86 (2 H, AB q, $\Delta\upsilon_{AB}$ = 101 Hz, J_{AB} = 13.7 Hz), 1.04 (3 H, s), 0.98 (3 H, s). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.37; H, 8.30. Compound **19** was separated in a less polar fraction (20% ether/petrol). Crystallization from ether/petrol gave **19** (20%): mp 45–46 °C; IR 1780, 1730, 1260, 1150, 1650, 840 cm^{-1}; ^1H NMR δ 4.61 (2 H, AB q, $\Delta\upsilon_{AB}$ = 7.1 Hz, J_{AB} = 6.6 Hz), 3.91 (2 H, AB q, $\Delta\upsilon_{AB}$ = 19.7 Hz, J_{AB} = 11.1 Hz), 3.34 (3 H, s), 3.22 (1 H, d, J = 8.5 Hz), 3.03 (2 H, AB q, $\Delta\upsilon_{AB}$ = 41.7 Hz, J_{AB} = 17.6 Hz), 2.25 (3 H, m), 1.82 (2 H, AB q, $\Delta\upsilon_AB$ = 40.1 Hz, J_{AB} = 14.7 Hz), 1.06 (3 H, s), 1.05 (3 H, s), 0.87 (9 H, s), 0.06 (3 H, s), 0.05 (3 H, s). Anal. Calcd for $C_{21}H_{38}O_5Si$: C, 63.59; H, 9.15. Found: C, 63.44; H, 9.02.

1β-((Carbomethoxy)methyl)-3,3-dimethyl-5βH-7,8-dimethylene-4β-(methoxymethoxy)bicyclo[3.3.0]octane (20). An excess of Lombardo's reagent (5.0 equiv) was added to a rapidly stirred solution of **18** (0.20 g, 0.67 mmol) in CH_2Cl_2 (15 mL) at 20 °C. After 0.25 min the suspension was poured into a mixture of aqueous sodium hydrogen carbonate [1.5 g in water (100 mL)] and ether (20 mL). The aqueous phase was extracted with ether (3 × 5 mL), and the organic phases were combined and dried ($MgSO_4$). Evaporation in vacuo and chromatography of the residue over silica gel (8.0 g) eluting with 10% ether/petrol gave **20** (0.185 m, 94%) as a colorless oil: IR 3100, 1735, 1620, 1440, 1040 cm^{-1}; ^1H NMR δ 5.42 (1 H, s), 5.40 (1 H, br s), 4.95 (1 H, br s), 4.65 (2 H, AB q, $\Delta\upsilon_{AB}$ = 6.0, J_{AB} = 4.3 Hz), 4.28 (1 H, s), 3.62 (3 H, s), 3.38 (3 H, s), 3.17 (1 H, d, J = 12.0 Hz), 2.68 (1 H, m), 2.50 (2 H, s), 2.48 (2 H, AB q, obscured), 1.87 (2 H, AB q, $\Delta\upsilon_{AB}$ = 69.4, J_{AB} = 14.4 Hz), 1.00 (3 H, s), 0.98 (3 H, s). MS, calcd for $C_{16}H_{26}O_4$ m/e 294.1831, found 294.1836; λ_{max} (EtOH) 248 nm (ϵ = 5300).

1β-((Carbomethoxy)methyl)-3,3-dimethyl-5βH-4β-(methoxymethoxy)tricyclo[6.3.0.0^{1,5}]-9-oxaundec-$\Delta^{7,11}$-ene (23). Dry oxygen was introduced through an immersed glass frit into a solution of **20** (60 mg, 0.2 mmol) and *meso*-tetraphenylporphine (5 mg) in dichloromethane (15 mL) at 0 °C and irradiated for 10 min with an Hanovia 450-W UV lamp. The mixture was chromatographed over silica gel (5 g) eluting with 20% ether/petrol to give **23** (50 mg 80%): IR 1740, 1150, 1100, 1050 cm^{-1}; ^1H NMR δ 4.67 (2 H, AB q, $\Delta\upsilon_{AB}$ = 16.0 Hz, J_{AB} = 6.5 Hz), 4.70–4.40 (4 H, m), 3.61 (3 H, s), 3.38 (3 H, s), 3.32 (1 H, d, J = 8.3 Hz) 2.78 (1 H, dt, J = 12.8, 2.0 Hz), 2.57 (2 H, s), 2.45 (2 H, AB q obscured), 1.63 (2 H, s), 1.04 (3 H, s), 1.01 (3 H, s); MS, calcd for $C_{17}H_{26}O_5$ 310.1780, found 310.1785.

Methyl 1β-((Carbomethoxy)methyl)-3,3-dimethyl-5βH-8-methylene-4β-(methoxymethoxy)bicyclo[3.3.0]oct-6-ene-7-carboxylate (25). A solution of 2,6-di-*tert*-butyl-4-methylpyridine (0.120 g freshly sublimed in vacuo) in dry dichloromethane (10 mL) was added to a stirred solution of **18** (85 mg) in dry dichloromethane (5 mL) at −78 °C. Triflic anhydride (0.070 mL, freshly distilled) was added by syringe, and the mixture stirred for 15 min. The mixture was warmed to 0 °C and held at that temperature for 90 min. The solution was diluted with dichloromethane (5 mL), washed with saturated aqueous sodium hydrogen carbonate solution (2 × 3 mL) and water (2 × 5 mL), and dried ($MgSO_4$). The crude enol triflate **24** was used directly.

Triphenylphosphine (15 mg), palladium acetate (6 mg), and triethylamine (0.4 mL) in methanol (10 mL) and dimethylformamide (3 mL) in resealable tube were purged with CO for 20 min. The crude enol triflate **24** in methanol (2 mL) was added to the mixture, and CO bubbled through the resulting solution for an additional 15 min. The tube was sealed, and the mixture stirred at 20 °C for 15 h. The solution was diluted with petrol (10 mL) and ether (10 mL), washed with water (3 × 10 mL), and dried ($MgSO_4$). Chromatography over silica gel eluting with 25% ether/petrol gave **25** (50 mg 52% from **18**) as a colorless oil: IR 3050, 1735 cm^{-1}; ^1H NMR δ 7.13 (1 H, br s), 5.81 (1 H, s), 4.96 (1 H, s), 4.65 (2 H, AB q, $\Delta\upsilon_{AB}$ = 31.3 Hz, H_{AB} = 7.3 Hz), 3.76 (3 H, s), 3.56 (3 H, s), 3.38 (3 H, s), 3.32 (1 H, d, J = 7.5 Hz), 3.25 (1 H, d, J = 7.5 Hz), 3.25 (1 H, m), 2.62 (2 H, s), 1.87 (2 H, AB q, FG6FRυ_{AB} = 70.5 Hz, J_{AB} = 13.2 Hz), 1.02 (3 H, s), 0.93 (3 H, s); ^{13}C NMR δ 172.0 (s), 164.7 (s), 157.2 (s), 150.5 (d), 134.5 (s), 108.5 (t), 96.8 (t), 89.9 (d), 61.0 (d), 55.7 (q), 53.0 (t), 51.6 (s), 51.5 (q), 46.6 (t), 43.9 (s), 28.2 (q), 23.8 (q). MS, calcd for $C_{18}H_{26}O_6$ 338.1729, found 338.1724.

Deoxynorpentalenolactone H Methyl Ester Methoxymethyl Ether (27). The diene ester **25** (21 mg, 0.064 mmol, 1.0 equiv) was dissolved in dichloromethane (1.5 mL); potassium carbonate (freshly ignited and ground; 20 mg) and MCPBA (17 mg 0.1 mmol; 1.5 equiv) were added with stirring, under nitrogen, and the mixture was stirred until TLC (1:1 petrol/ethyl acetate) indicated complete reaction (4–10 h). Thereupon the temperature of the mixture was brought to 26 °C, and boron trifluoride etherate (freshly distilled, 9 mL) was added, and the whole stirred 4 min. Sodium borohydride (23 mg 0.64 mmol, 10.0 equiv) thoroughly dissolved in methanol (0.3 mL) was then added, stirred 20 min, and worked up by adding 0.5 N HCl, washing with water, and drying the organic phase ($MgSO_4$). Separation by preparative layer chromatography (silica, 0.5-mm layer, eluting with 1:1 ethyl acetate/petrol) gave **27** (3 mg, 15%): IR 3050, 1740, 1720, 1050; ^1H NMR (in d_6-acetone) δ 7.01 (1 H m), 4.70 (2 H, AB q, $\Delta\upsilon_{AB}$ = 29.3 Hz), J_{AB} = 7.0 Hz), 4.46 (2 H, ABX, $\Delta\upsilon_{AB}$ = 43.5 Hz, J_{AB} = 11.7 Hz, J_{AX} = 4.9 Hz, J_{BX} = J_{BX} = 4.9 Hz), 3.74 (3 H, s), 3.38 (1 H, d, obscured), 3.36 (3 H, s), 3.16 (1 H, m), 2.98 (1 H, m), 2.72 (2 H, AB q, $\Delta\upsilon_{AB}$ = 54.4 Hz, J_{AB} = 14.4 Hz), 1.86 (2 H, AB q, $\Delta\upsilon_{AB}$ = 11.7 Hz, J_{AB} = 13.1 Hz), 1.06 (3 H, s), 1.03 (3 H, s); MS, calcd for $C_{17}H_{24}O_6$, 324.1572, found 324.1570; other peaks, 303 (–OMe, 28.5%), 248 (–OMe, –MOM, 100%).

Deoxynorpentalenolactone H Methyl Ester (2). The lactone **27** (3 mg) in 5% aqueous sulfuric acid and THF (0.5 mL, 1:1) was heated at 60 °C for 7 h. The mixture was neutralized with aqueous sodium bicarbonate and extracted with chloroform (1 mL). The dried (Na_2SO_4) extract was evaporated to give **2** (2.5 mg, 90%): IR 3260, 3050, 1720, 1050 cm^{-1}; ^1H NMR (d_6-acetone) δ 6.98 (1 H, m), 4.46 (2 H, ABX, υ_{AB} = 43.9 Hz, J_{AB} = 11.8 Hz, J_{AX} = 4.9 Hz, J_{BX} = 4.9 Hz), 3.74 (3 H, s), 3.50 (1 H, d, J = 5.7 Hz), 3.17 (1 H, m), 2.69 (2 H, AB q V_{AB} = 65.0 Mz, J_{AB} = 16.6 Hz), 1.85 (2 H, υ_{AB} = 19.2 Hz, J_{AB} = 14.0 Hz), 1.03 (3 H, s), 0.98 (3 H, s); MS, calcd for $C_{15}H_{20}O_5$ 280.1311, found 280.1315.

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Supplementary Material Available: Crystal data, fractional coordinates, anisotropic thermal parameters, bond distances, bond angles, and isotropic thermal parameters for **19** (6 pages). Ordering information is given on any current masthead page.

Stereoselective Reduction of Bicyclic Ketals. A New, Enantioselective Synthesis of Isolaurepinnacin and Lauthisan Skeletons[1]

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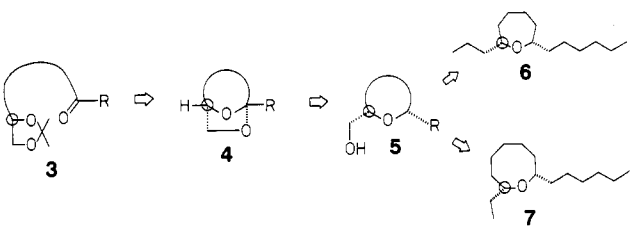
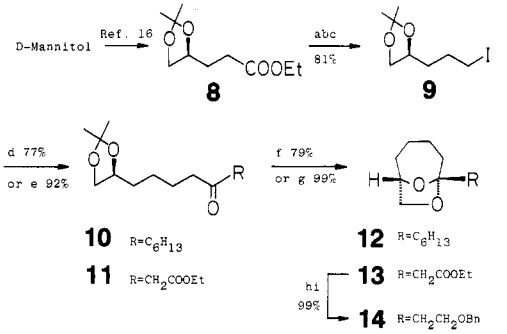
A general synthetic strategy for constructing seven- and eight-membered cyclic ether derivatives is described. The important feature of this work is a highly stereoselective reduction of bicyclic ketals, i.e., cis-selective reduction with triethylsilane/$TiCl_4$ and trans-selective reduction with diisobutylaluminum hydride (DIBAL). The procedure completed a new and efficient synthesis of isolaurepinnacin and lauthisan skeletons in optically active forms.

In view of the increasing number of biologically active marine natural products containing medium- and large-sized cyclic ether derivatives,[2] much attention has recently been focused on efficient approaches toward these systems. In particular, the lauthisan family,[3] having an eight-membered cyclic ether, which was mainly isolated from the genus *Laurencia*, has been a major synthetic challenge within the past decade.[4-11] The pioneering work in this field has been established by Masamune and co-workers, i.e., the total synthesis of *dl*-laurencin.[4] However, their

Scheme I



Scheme II[a]



[a] Conditions: (a) $LiAlH_4$, Et_2O, 0 °C; (b) *p*-TsCl, Et_3N, CH_2Cl_2; (c) KI, K_2CO_3, acetone, reflux; (d) $CH_3C(=NNMe_2)C_6H_{13}$, *n*-BuLi, THF, -78 °C → room temperature, then SiO_2, CH_2Cl_2; (e) CH_3COCH_2COOEt, LDA, THF, 0 °C; (f) *p*-TsOH·H_2O, CH_2Cl_2, reflux, 24 h; (g) *p*-TsOH·H_2O, CH_2Cl_2, reflux, 3 h; (h) $LiAlH_4$, Et_2O, 0 °C; (i) NaH, THF, 0 °C, then benzyl bromide.

(1) The preliminary work was presented at the 16th International Symposium on the Chemistry of Natural Products (IUPAC), Kyoto, Japan, May 29-June 3, 1988 (Abstract PB 90).

(2) For review, see: Moore, R. E. In *Marine Natural Products*; Scheuer, P. J., Ed.; Academic: New York, 1978; Vol. 1, Chapter 2. Erickson, K. K. *Ibid.* 1983; Vol. 5, p 131. Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251; **1986**, *3*, 1; **1988**, *5*, 613.

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