$Co_2(CO)_8$-mediated *Endo* Mode Cyclization of Epoxy-alcohol: Synthesis of 2-Ethynyl-3-hydroxy-2-methyltetrahydropyran and 2-Ethynyl-3-hydroxy-3-methyltetrahydropyran Derivatives

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Successive treatment of 4,5-epoxy-5-methyl-7-trimethylsilyl-6-heptyne-1-ol with $Co_2(CO)_8$ at 0 °C and a catalytic amount of $BF_3 \cdot OEt_2$ at −78 °C gave the tetrahydropyran derivatives with the cobalt-complexed moiety. Similarly 4,5-epoxy-4-methyl-7-trimethylsilyl-6-heptyne-1-ol underwent ring closure under the above conditions to provide the corresponding tetrahydropyran derivatives. The preferential *endo* mode cyclization over the *exo* one was observed in these experiments.

Key words *endo* mode cyclization; cobalt complex; tetrahydropyran ring; epoxy alkyne

Recent studies performed in our laboratory[1,2] disclosed that the epoxy-alkyne derivatives **1** (n=1—3; R^1=H) underwent *endo* mode cyclization upon successive treatment with dicobaltoctacarbonyl [$Co_2(CO)_8$], Lewis acids such as boron trifluoride-diethyl ether ($BF_3 \cdot OEt_2$), and cerium (IV) ammonium nitrate (CAN), ending up with the exclusive formation of the corresponding oxygen-containing heterocycles **2** (n=1—3; R^1=H). Thus the tetrahydrofuran and tetrahydropyran frameworks **2** (n=1,2; R^1=H)[1a—d] possessing the 2-ethynyl-3-hydroxy functionality could be prepared with high stereoselectivity as well as in a stereospecific manner. Although stereoselective but not stereospecific formation of the oxepane **2** (n=3; R^1=H)[1e] could also be realized, this novel *endo* mode procedure was found not to be applicable to the construction of larger ring-sized oxacycles like oxocane.[1e] The fact that many natural occurring polyether species[3] have the methyl group at the ring junction prompted us to investigate if this *endo* mode cyclization method could be used for the preparation of oxacycles **2** (R^1=Me) having the methyl substitutent at C-2 or C-3 position. This paper reports the results of the cyclization reaction of the cobalt complexes of 4,5-epoxy-5-methyl-7-trimethylsilyl-6-heptyne-1-ol (**10**) and 4,5-epoxy-4-methyl-7-trimethylsilyl-6-heptyne-1-ol (**11**) in the presence of a Lewis acid where the corresponding *endo* mode cyclized products were exclusively formed.

Results and Discussion

The starting *epoxy* derivatives **10** and **11** for the *endo* mode cyclization were synthesized as follows. The mono-*tert*-butyldimethylsilyl (TBDMS)-protected alcohol **3**[4] was oxidized under Swern conditions to give the labile aldehyde, which was consecutively exposed to Horner-Emmons conditions with ethyl 2-(diethylphosphono)propionate and to diisobutylaluminum hydride (DIBAL-H) affording the allylic alcohol (*E*)-**4** in 74% yield. Transformation of the alcohol moiety of (*E*)-**4** to an ethynyl group was realized by oxidation then use of the Ramirez-Corey dibromoolefination[5] and base treatment to provide the acetylide. The anion at the triple bond terminus was then quenched by trimethylsilyl (TMS) chloride and the resulting product was hydrolyzed with 1% hydrochloric acid to produce (*E*)-**5** in a 50% overall yield. On the other hand, (*Z*)-**5** was prepared as a major product from **6**. The Swern oxidation and methyllithium addition of **6**[1e] gave the secondary alcohol (64%), which was subsequently oxidized under Swern conditions and treated with lithium TMS-acetylide to provide **7** in 86% yield. Dehydration of **7** with thionyl chloride was followed by acidic hydrolysis to afford (*Z*)-**5** (52%) along with (*E*)-**5** (15%). The stereochemistry of **5** was determined on the basis of an NOE experiment. An NOE experiment with (*Z*)-5 revealed a 3.2% enhancement between the methyl group and the vinylic proton, whereas no enhancement was observed between these protons of (*Z*)-**5** thus strongly supporting the assigned structures as shown in Chart 2. Upon exposure to *m*-chloroperbenzoic acid (*m*CPBA) in methylene chloride, (*E*)-**5** and (*Z*)-**5** underwent epoxidation to afford *trans*-**10** and *cis*-**10** in 74 and 75% yields, respectively. The other staring epoxy-alkyne derivative **11** was also prepared from **3**. The keto derivative **8**, easily available from **3** by conventional means, was exposed to the Wittig reagent, adjusted from (3-trimethylsilyl-2-propynyl)triphenylphosphonium bromide and *n*-butyllithium, to give after desilylation with 1% hydrochloric acid (*E*)-**9** and (*Z*)-**9** in 45 and 11% yields, respectively. The stereochemistry of **9** could be established by an NOE consideration: (*Z*)-**9** showed a 5.8% enhancement of the methyl signal when the vinylic proton was irradiated. However, no enhancement was observed between the vinylic proton and the methyl group in (*E*)-**9**. Both the obtained (*E*)- and (*Z*)-**9** were subsequently converted into *trans*-**11** and *cis*-**11** in rather lower yield (41 and 35% yields, respectively) for some unknown reasons.

With the required epoxy-alkyne derivatives **10** and **11** available, the $Co_2(CO)_8$-mediated ring closure was undertaken. Treatment of *trans*-**10** with $Co_2(CO)_8$ in methylene chloride at room temperature gave the corresponding cobalt complex, which was subsequently exposed to a catalytic amount of $BF_3 \cdot Et_2O$ (0.10 eq) at −78°C for 10 min to produce the *endo* mode cyclized products, *trans*-**12** and *cis*-**12** (90%: *trans*-**12** : *cis*-**12**=46 : 54). A similar nonstereoselec-

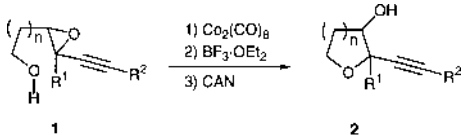

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Chart 1

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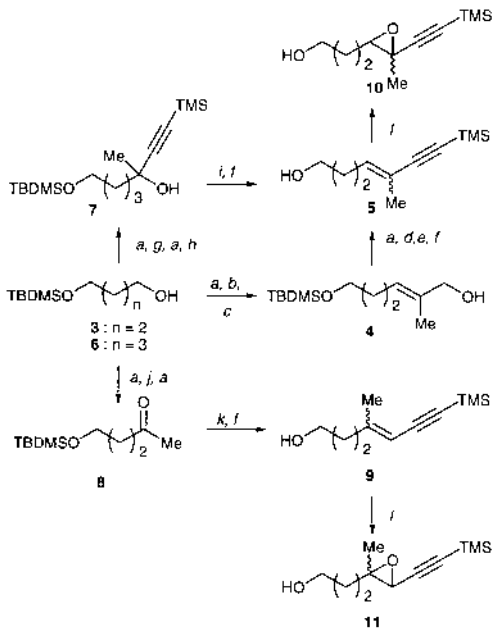

Chart 2

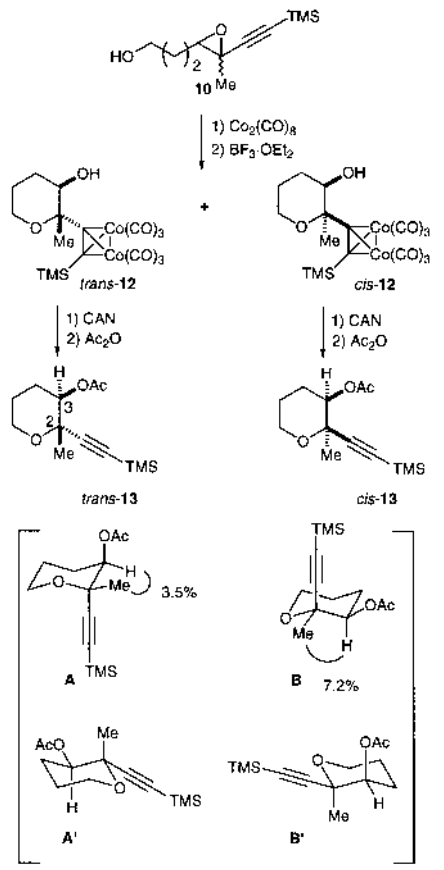

Chart 3

tive construction of the tetrahydropyran framework (88%: *trans*-**12** : *cis*-**12** = 55 : 45) was observed when *cis*-**10** was reacted with the cyclization conditions described above. The tetrahydrofuran derivatives due to the *exo* mode cyclization could not be detected in the reaction mixture. The tetrahydropyran derivatives, *trans*-**12** and *cis*-**12**, with cobalt complexation were converted into the corresponding acetates, *trans*-**13** and *cis*-**13**, by conventional means[6] in 74 and 64% yields, respectively. The stereochemistry of these cyclized products was determined by analysis of their ^{1}H-NMR spectra. The C-3 proton of *trans*-**13** appeared at δ 4.87 as a triplet with a rather small coupling constant (J = 2.4 Hz) due to an equatorial–axial and an equatorial–equatorial coupling, while that of *cis*-**13** resonated at δ 4.55 as a doublet of doublets (J = 11.7 and 2.9 Hz) attributable to an axial–axial and an axial–equatorial coupling. This simple analysis indicated that the former should have the preferred conformer **A** and the latter the preferred conformer **B**. The possibility that the former possesses structure **B′** and the latter is **A′** on the basis of coupling patterns could be ruled out by the following NOE experiment. An NOE experiment of *trans*-**13** showed a 3.5% enhancement between the C-2 methyl group and the C-3 proton, while a rather larger enhancement (7.2%) between these protons of *cis*-**13** was detected by its NOE experiment. These NOE experiments coupled with the consideration of the coupling constant unambiguously established the stereochemistries of **12** and **13**.

There are several points that should be discussed. (i) Although the *endo* mode cyclization reaction proceeded regioselectively as expected, neither the stereoselectivity nor stereospecificity could be observed. These results are in sharp contrast to the cases of the epoxy-alkyne derivative **1** (Chart 1, R^1 = H). (ii) The tetrahydropyran derivative **12** with cobalt complexation was found to be stable under the reaction conditions, thus when *trans*-**12** and *cis*-**12** were independently treated with a catalytic amount of $BF_3 \cdot OEt_2$ at −78 °C, no isomerization took place and the starting **12** was completely recovered intact. (iii) However, a mixture of *trans*-**12** and *cis*-**12** (46 : 54; obtained from the reaction of *trans*-**10**) was exposed to a stoichiometric amount of $BF_3 \cdot OEt_2$ at 0 °C for 3 h resulting in a mixture of *trans*-**12** and *cis*-**12** in the ratio of 88 to 12. A similar preferential formation of the *trans* skeleton over the *cis* one (*trans*-**12** : *cis*-**12** = 91 : 9) was observed when a mixture of *trans*-**12** and *cis*-**12** (55 : 45; obtained from the reaction of *cis*-**10**) was submitted to a stoichiometric amount of $BF_3 \cdot OEt_2$ at 0 °C for 3 h. Moreover, acetic anhydride was shown to accelerate the isomerization of the *cis* derivative to *trans* congener. Treatment of the cobalt-complexed *cis*-**10** with a catalytic amount of $BF_3 \cdot OEt_2$ at −78 °C was followed by the addition of acetic anhydride in the presence of a stoichiometric amount of $BF_3 \cdot OEt_2$ at the same temperature and demetalation with CAN[6] giving rise to the exclusive formation of *trans*-**13** in 61% yield. The exclusive formation of *trans*-**13** was also realized from the cobalt-complexed *trans*-**10** under the similar acetylation conditions.

The regioselective formation of **12** can be interpreted by the reaction pathway through the plausible intermediate **C** (R^1 = H, R^2 = Me). Treatment of **10** with $Co_2(CO)_8$ must have produced the labile cobalt complex **14** (R^1 = H, R^2 = Me) which would spontaneously collapse to the stable cation intermediate **C** (R^1 = H, R^2 = Me). The significant stability of the tertiary carbocation at the propynyl position of the intermediate **C** (R^1 = H, R^2 = Me) compared to that of the secondary carbocation at the homopropynyl position of another

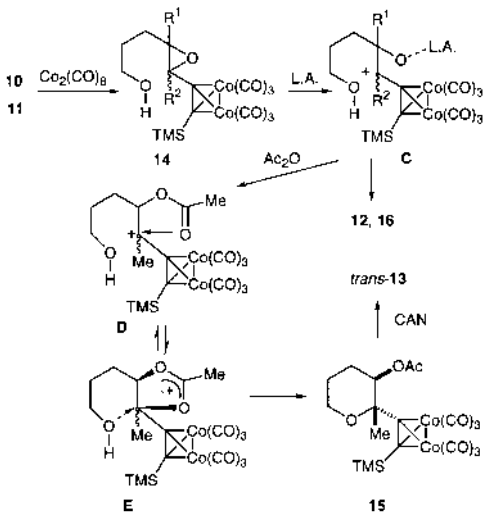

Chart 4

possible intermediate would control the regiochemical outcome.[7] The common cationic species **C** (R^1=H, R^2=Me), thus derived from both the *trans*-**14** and *cis*-**14**, should be further stabilized by the neighboring group participation of the cobalt-complexed alkyne moiety.[8] Therefore, the intermediate **C** (R^1=H, R^2=Me) seemed to be stable enough, thereby the ring closure would nonstereoselectively proceed under the reaction conditions (a catalytic amount of $BF_3 \cdot OEt_2$ at −78 °C). Easy isomerization of the *cis* isomer to the *trans* one in the presence of a stoichiometric amount of Lewis acid, especially under the acetylation conditions, might be understood by consideration of the intermediacy of the cationic intermediates **D** and **E** leading to *trans*-**13** *via* its cobalt-complexed form **15** as depicted in Chart 4. The exclusive production of *trans*-**15** under the thermodynamically controlled conditions would reflect its great stability over that of the corresponding *cis* one.

We next investigated the ring closure of the epoxy-alcohol **11**. Treatment of *trans*-**11** with $Co_2(CO)_8$ and a catalytic amount of $BF_3 \cdot OEt_2$ at −78 °C effected the *endo* mode cyclization to provide *trans*-**16** and *cis*-**16** in 90% yield in a *cis* selective manner (*trans*-**16**:*cis*-**16**=31:69). The *cis*-epoxy derivative, *cis*-**11**, also stereoselectively underwent *endo* mode cyclization to furnish *trans*-**16** as the major product (94% yield; *trans*-**16**:*cis*-**16**=72:28). No trace of the tetrahydrofuran derivatives resulting from the *exo* mode cyclization could be detected in the reaction mixture. The stereochemistry of these cyclized products was established by an NOE experiment (2.6% enhancement between the C-3 methyl group and the C-2 proton of *cis*-**16** was detected, while no enhancement was recorded when the C-3 methyl group or the C-2 proton of *trans*-**16** was irradiated). The tetrahydropyran derivatives **16** thus obtained were then transformed into the corresponding acetyl derivatives **17** by a standard method (see Experimental). It should be stated that the stereocomplementary construction of the tetrahydropyran framework was achieved. Namely, not only the *trans*-**11** stereoselectively afforded *cis*-**16**, but also *cis*-**11** produced *trans*-**16** in a stereoselective manner, although the stereoselectivity was fairly low compared to those obtained in previous studies (Chart 1, n=1,2; R^1=H).[1] The exclusive formation of the *endo* mode cyclized products **16** would tentatively be rationalized by consideration of the stability of the propynyl cation **C** (Chart 4, R^1=Me, R^2=H) in comparison with that of another possible secondary cation species at the homopropynyl position. The powerful propynyl cation stabilizing ability of the alkyne-cobalt complex[8] would again play a significant role in controlling the regioselectivity.

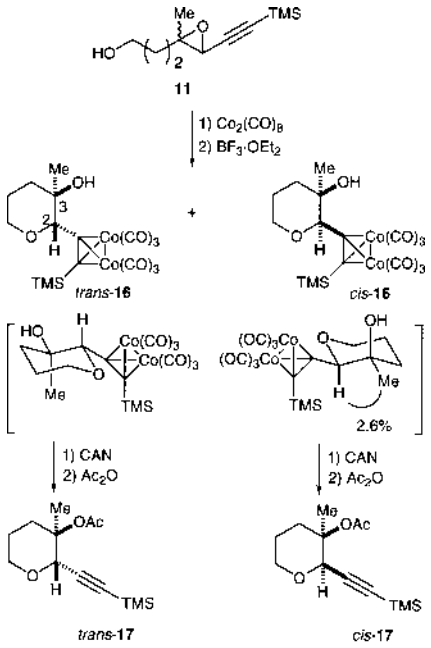

Chart 5

Upon direct treatment with a catalytic amount of $BF_3 \cdot OEt_2$ (0.10 eq) in methylene chloride at −78 °C, *trans*-**10** undertook ring closure to afford, after acetylation, *trans*-**13** with the inverted stereochemistry at the propynyl position in 68% yield. A similar *endo* mode cyclization of *cis*-**10** gave *cis*-**13** in 90% yield as the sole product. These results are of great interest because *trans*-**1** (Chart 1; n=2, R^1=H, R^2=TMS)[1b] produced a mixture of the *endo* mode cyclized products **2** and the corresponding *exo* mode ones in a ratio of 62 to 38, while a ratio of 20 to 80 between the *endo* mode cyclized products **2** and the *exo* mode ones from the *cis*-**1** (n=2, R^1=H, R^2=TMS) was recorded. This would reasonably explain that introduction of a substituent at the propynyl position of **1** (*e.g.* R^1=Me) would accelerate the generation of a fairly stable tertiary cation under acidic conditions in contrast to the case of the unsubstituted **1** (n=2, R^1=H). As a result, a methyl substituent at the propynyl position of the epoxy-alkyne **10** would govern the regiochemical outcomes ending up with the exclusive formation of the *endo* mode cyclized products. On the other hand, when the epoxy-alkynes **11** were reacted under direct ring closure conditions with a catalytic amount of $BF_3 \cdot OEt_2$ (0.10 eq), the reaction predominantly proceeded in an *exo* mode fashion to furnish the tetrahydrofuran derivative with inversion of the configuration at the homopropynyl position. Thus *trans*-**11** yielded, upon successive treatment with a catalytic amount of Lewis acid and acetylating reagents, a mixture of *anti*-**18** and *trans*-**17** in 84% yield in a ratio of 88 to 12. In addition, the exclusive formation of *syn*-**18** in 83% from *cis*-**11** was observed where no *endo* mode cyclized products were detected as antici-

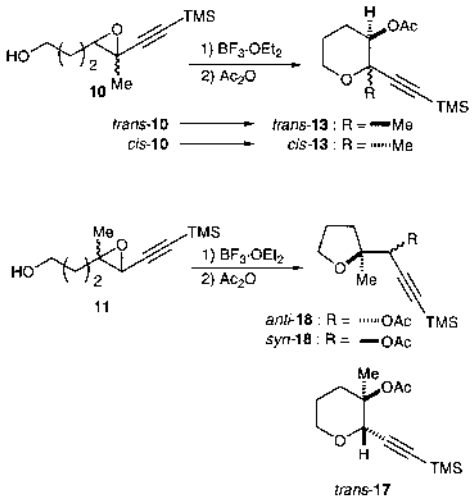

Chart 6

pated. These results are in accordance with the previous results.[1,2)]

In summary, we have disclosed that a recently developed novel $Co_2(CO)_8$-mediated *endo* mode cyclization of the epoxy-alkyne derivatives can be applicable to the substrates possessing the methyl group at the propynyl or homopropynyl position. Although the stereoselectivity observed was not satisfactory, the complete control of the regiochemistry was thus realized. This result in combination with the previous studies obviously demonstrates that the $Co_2(CO)_8$-mediated *endo* mode cyclization can be employed regardless of the substituent at the propynyl or homopropynyl position of the starting epoxy-alkyne derivatives.

Experimental

IR spectra were measured with a Shimazu IR-460 spectrometer in $CHCl_3$ and mass spectra with a Hitachi M-89 and JEOL JMS-SX 102A mass spectrometers. ^{1}H-NMR spectra were recorded on JEOL EX-270 and JEOL JNM-GX 500 spectrometers, using $CDCl_3$ as solvent and either tetramethylsilane as internal standard for compounds that have no silyl group, or $CDCl_3$ (7.26 ppm) for compounds possessing the silyl group. ^{13}C-NMR spectra were recorded on JEOL EX-270 and JEOL JNM-GX 500 spectrometers in $CDCl_3$ with $CDCl_3$ (77.0 ppm) as an internal reference. CH_2Cl_2 was freshly distilled from P_2O_5, and THF and Et_2O from sodium-benzophenone prior to use. All reactions were carried out under a nitrogen atmosphere. Silica gel (Silica gel 60, 230—400 mesh, Merck) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

(2*E*)-6-(*tert*-Butyldimethylsiloxy)-2-methyl-2-hexen-1-ol [(E)-4] A solution of DMSO (3.80 ml, 53.8 mmol) in CH_2Cl_2 (10.0 ml) was gradually added to a solution of oxalyl chloride (2.30 ml, 26.9 mmol) in CH_2Cl_2 (100 ml) at −78 °C. After stirring of the CH_2Cl_2 solution for 15 min, a solution of **3** (5.00 g, 24.5 mmol) in CH_2Cl_2 (20.0 ml) was added and the reaction was stirred at −78 °C for 1 h. Et_3N (17.0 ml, 122 mmol) was added to the reaction mixture, which was then gradually warmed to room temperature and quenched by addition of water and extracted with CH_2Cl_2. The extract was washed with water and brine, dried and concentrated to leave the crude aldehyde. To a solution of NaH (60% dispersion in oil, 1.10 g, 26.9 mmol) in THF (100 ml) was added 2-(diethylphosphono)propionate (5.80 ml, 26.9 mmol) at 0 °C. The mixture was stirred for 1 h and a solution of the crude aldehyde prepared from **3** in THF (10.0 ml) was added at the same temperature. The reaction mixture was stirred for 1 h at room temperature, quenched by addition of saturated aq. NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. To a solution of the crude α,β-unsaturated ester in hexane (100 ml) was added at −78 °C a solution of DIBAL-H in hexane (0.95 mol sol'n; 57.0 ml, 53.8 mmol). The reaction mixture was kept for 1 h at the same temperature and quenched by addition of water. The resulting precipitates were filtered off and the filtrate was extracted with AcOEt, which was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10 : 1) gave (*E*)-**4** (3.94 g, 74%) as a colorless oil. IR cm^{-1}: 3609, 3407 (OH). ^{1}H-NMR δ: 5.41 (1H, t, J=7.3 Hz, 3-H), 4.00 (2H, s, 1-H), 3.61 (2H, t, J=6.3 Hz, 6-H), 2.09 (2H, q, J=7.3 Hz, 4-H), 1.67 (3H, s, Me), 1.57 (2H, quin, J=7.3 Hz, 5-H), 1.42 (1H, s, OH), 0.90 (9H, s, SiBu^t) and 0.05 (6H, s, SiMe). ^{13}C-NMR δ: 135.0, 125.9, 68.9, 62.3, 32.6, 25.9, 23.9, 18.3, 13.6, −5.3. MS *m/z* (%): 244 (M$^+$, 8.9%), 216 (47), 112 (100), 104 (60), 73 (80). *Anal*. Calcd for $C_{13}H_{28}O_2Si$: C, 63.9; H, 11.55. Found: C, 63.7; H, 11.4.

(4*E*)-5-Methyl-7-trimethylsilyl-4-heptene-6-yn-1-ol [(*E*)-5] According to the procedure described for the preparation of (*E*)-**4** from **3**, (*E*)-**4** (2.50 g, 10.2 mmol) was treated with DMSO (1.60 ml, 22.5 mmol), oxalyl chloride (0.98 ml, 11.2 mmol) and Et_3N (7.10 ml, 51.1 mmol) to afford the crude aldehyde. To a solution of CBr_4 (7.50 g, 225 mmol) in CH_2Cl_2 (50.0 ml) was added PPh_3 (11.8 g, 45.0 mmol) at 0 °C and the solution was stirred for 10 min. A solution of the crude aldehyde derivative in CH_2Cl_2 (5.00 ml) was then added to a solution of the ylide in CH_2Cl_2 solution at −78 °C. The reaction mixture was gradually warmed to room temperature and stirring was continued for 2 h. The reaction was quenched by addition of saturated aq. Na_2SO_4 and filtered. The filtrate was passed through a short pad of silica gel with CH_2Cl_2 in order to remove triphenylphosphine oxide. The residue was dissolved in THF (50.0 ml), to which *n*-BuLi in hexane (1.44 mol sol'n; 15.5 ml, 22.5 mmol) was added at −78 °C. After stirring for 1 h, the resulting acetylide was quenched by addition of TMSCl (3.90 ml, 30.7 mmol) and the mixture was warmed to room temperature. The reaction mixture was diluted with saturated aq. NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to leave the crude oil. The residual oil was then dissolved in EtOH (1% HCl containing solution, 50.0 ml) and the mixture was allowed to stand at room temperature for 1 h. EtOH was evaporated off and the residue was taken up in AcOEt, which was washed with water several times, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (4 : 1) gave (*E*)-**5** (998 mg, 50%) as a colorless oil. IR cm^{-1}: 3629 (OH), 2139 (CC). ^{1}H-NMR δ: 5.93 (1H, tq, J=7.3 and 1.5 Hz, 4-H), 3.65 (2H, t, J=6.3 Hz, 1-H), 2.17 (2H, q, J=7.3 Hz, 3-H), 1.79 (3H, d, J=1.5 Hz, Me), 1.65 (2H, quin, J=6.3 Hz, 2-H), 0.18 (9H, s, SiMe). ^{13}C-NMR δ: 138.5, 118.5, 108.4, 90.1, 62.3, 31.8, 24.8, 17.0 and 0.0. MS *m/z* (%): 196 (M$^+$, 42%), 181 (30), 163 (32), 135 (39) and 73 (97). *Anal*. Calcd for $C_{11}H_{20}OSi$: C, 67.3; H, 10.3. Found: C, 67.5; H, 10.3.

7-(*tert*-Butyldimethylsiloxy)-3-methyl-1-trimethysilylhept-1-yn-3-ol (7) According to the procedure described for the preparation of (*E*)-**4** from **3**, **6** (5.00 g, 22.9 mmol) was treated with DMSO (3.60 ml, 50.4 mmol), oxalyl chloride (2.20 ml, 25.2 mmol), and Et_3N (16.0 ml, 114 mmol) to afford the crude aldehyde. To a solution of the crude aldehyde in THF (100 ml) was added MeLi in Et_2O (1.14 mol sol'n; 20.0 ml, 22.9 mmol) was added at −78 °C. The reaction mixture was stirred for 10 min at the same temperature, quenched by addition of water and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short column with hexane–AcOEt (7 : 1) to afford 6-(*tert*-butyldimethylsiloxy)hexane-2-ol (3.43 g, 64%) [^{1}H-NMR δ: 3.80 (1H, sex, J=6.4 Hz, 2-H), 3.62 (2H, t, J=6.4 Hz, 6-H), 1.57—1.35 (6H, m, CH_2), 1.19 (3H, d, J=6.4 Hz, Me), 0.89 (9H, s, SiBu^t), 0.05 (6H, s, SiMe)]. The alcohol (3.43 g, 14.8 mmol), prepared from **6**, was then exposed to Swern conditions [DMSO (2.31 ml, 32.5 mmol), oxalyl chloride (1.39 ml, 16.3 mmol and Et_3N (10.3 ml, 32.5 mmol)] according to the procedure described above to provide the aldehyde. To a solution of trimethylsilylacetylene (2.50 ml, 15.0 mmol) in THF (70.0 ml) was added *n*-BuLi in hexane (1.42 mol sol'n; 10.6 ml, 15.0 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and a solution of the crude aldehyde in THF (30.0 ml) added to the reaction mixture at the same temperature. After stirring for 10 min, the reaction was quenched by addition of saturated aq. NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10 : 1) gave **7** (3.82 g, 86%) as a colorless oil. IR cm^{-1}: 3587 (OH), 2165 (CC). ^{1}H-NMR δ: 3.64 (2H, t, J=5.9 Hz, 7-H), 1.67—1.64 (2H, m, CH_2), 1.58—1.54 (4H, m, CH_2), 1.46 (3H, s, Me) 0.90 (9H, s, SiBu^t), 0.15 (9H, s, SiMe), 0.05 (6H, s, SiMe). ^{13}C-NMR δ: 109.6, 87.3, 68.4, 63.1, 43.3, 32.8, 29.8, 26.0, 21.1, 18.4, −0.05, −5.3. MS(CI) *m/z* (%): 329 (M$^+$+1, 28%), 311 (100), 271 (82), 231 (6.5) and 179 (9.5). *Anal*. Calcd for $C_{17}H_{36}O_2Si_2$: C, 62.1; H, 11.0. Found: C, 61.9; H, 11.1.

(4*Z*)-5-Methyl-7-trimethylsilyl-4-heptene-6-yn-1-ol [(*Z*)-5] $SOCl_2$ (0.55 ml, 7.49 mmol) was added dropwise to a solution of **7** (1.50 g, 4.99 mmol) in pyridine (25.0 ml) at room temperature. The reaction mixture was stirred for 1 h, diluted with water and extracted with AcOEt. The extract was

washed with water several times, dried and concentrated to leave the crude dehydrated products. The residual oil was dissolved in EtOH (1% HCl containing solution, 30.0 ml) and the mixture was allowed to stand at room temperature for 1 h. EtOH was evaporated off and the residue was taken up in AcOEt, which was washed with water several times, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (4 : 1) gave (*Z*)-**5** (509 mg, 52%) along with (*E*)-**5** (147 mg, 15%). (*Z*)-**5** was a colorless oil. IR cm^{-1}: 3635 (OH), 2133 (CC). ^{1}H-NMR δ: 5.68 (1H, tq, J=7.8 and 1.5 Hz, 4-H), 3.61 (2H, t, J=6.4 Hz, 1-H), 2.34 (2H, qq, J=7.8 and 1.0 Hz, 3-H), 1.83 (3H, d, J=1.0 Hz, Me), 1.63 (2H, quin, J=6.8 Hz, 2-H), 0.19 (9H, s, SiMe). ^{13}C-NMR δ: 138.3, 119.0, 104.6, 97.8, 61.8, 31.5, 26.6, 22.7 and 0.0. MS *m/z* (%): 196 (M^+, 42%), 181 (30), 163 (32), 135 (39), 123 (15), 91 (66) and 73 (97). HR-MS Calcd for $C_{11}H_{20}OSi$: 196.1284. Found: 196.1293.

(4*R,5*R**)-4,5-Epoxy-5-methyl-7-trimethylsilylhept-6-yn-1-ol (*tans*-10)** To a solution of (*E*)-**5** (500 mg, 2.55 mmol) in CH_2Cl_2 (25.0 ml) were added Na_2HPO_4 (3.60 g, 25.5 mmol) and *m*CPBA (80% purity, 815 mg, 3.80 mmol) at room temperature. The suspension was stirred at room temperature for 3 h and filtered. The filtrate was washed with saturated aq. Na_2SO_3, water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (3 : 1) gave *trans*-**10** (403 mg, 74%) as a colorless oil. IR cm^{-1}: 3629 (OH), 2171 (CC). ^{1}H-NMR δ: 3.72 (2H, t, J=6.4 Hz, 1-H), 3.17 (1H, dd, J=7.8, 4.9 Hz, 4-H), 1.80—1.70 (3H, m, CH_2), 1.55 (1H, m, CH_2), 1.43 (3H, s, Me), 0.16 (9H, s, SiMe). ^{13}C-NMR δ: 105.8, 86.7, 64.7, 62.0, 51.2, 29.2, 24.6, 18.2, −0.3. MS(FAB) *m/z* (%): 213 (M^++1, 23%), 195 (61), 154 (18), 136 (31), 123 (64), 97 (45), 73 (100). HR-MS Calcd for $C_{11}H_{21}O_2Si$(M+1): 213.1311. Found: M^++1, 213.1311.

(4*R, 5*S**)-4,5-Epoxy-5-methyl-7-trimethylsilylhept-6-yn-1-ol (*cis*-10)** According to the procedure described for the preparation of *trans*-**10**, *cis*-**10** (203 mg, 75%) was obtained from (*Z*)-**5** (250 mg, 1.27 mmol), *m*CPBA (80% purity, 301 mg, 1.40 mmol) and Na_2HPO_4 (1.80 g, 12.7 mmol). Compound *cis*-**10** was a colorless oil. IR cm^{-1}: 3619 (OH), 2174 (CC). ^{1}H-NMR δ: 3.70 (2H, m, 1-H), 2.86 (1H, t, J=5.9 Hz, 4-H), 1.83—1.72 (4H, m, CH_2), 1.61 (1H, s, OH), 1.53 (3H, s, Me), 0.17 (9H, s, SiMe). ^{13}C-NMR δ: 103.15, 89.7, 64.8, 62.1, 52.7, 28.9, 24.45, 23.1, −0.3. MS(FAB) *m/z* (%): 213 (M^++1, 13%), 195 (32), 154 (21), 136 (30), 123 (40), 73 (100). HR-MS Calcd for $C_{11}H_{21}O_2Si$ (M+1) 213.1311. Found: M^++1, 213.1318.

5-(*tert*-Butyldimethylsiloxy)-2-pentanone (8) According to the Swern oxidation described for the preparation of (*E*)-**4**, compound **3** (5.00 g, 24.5 mmol) was converted into the crude aldehyde. To a solution of the crude aldehyde in THF (100 ml) was added MeMgBr in THF (0.93 mol sol'n; 27.0 ml, 24.9 mmol) at −78 °C. The mixture was stirred for 10 min, quenched by addition of saturated aq. NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was oxidized under Swern conditions and the residual oil was chromatographed with hexane–AcOEt (15 : 1) to afford **8** (3.81 g, 72%) as a colorless oil. IR cm^{-1}: 1711(CO). ^{1}H-NMR δ: 3.60 (2H, t, J=6.4 Hz, 5-H), 2.50 (2H, t, J=7.3 Hz, 3-H), 2.14 (3H, s, Me), 1.77 (2H, quin, J=6.4 Hz, 4-H), 0.88 (9H, s, SiBu^t), 0.03 (6H, s, SiMe). ^{13}C-NMR δ: 208.75, 128.25, 62.05, 40.0, 29.85, 26.8, 25.8, 18.2, −5.5. MS *m/z* (%): 216 (M^+, 40%), 173 (100), 159 (22), 43 (80). *Anal*. Calcd for $C_{11}H_{24}O_2Si$: C, 61.05; H, 11.2. Found: C, 61.3; H, 11.2.

(*E*)-and (*Z*)-4-Methyl-7-trimethylsilyl-4-hepten-6-yn-1-ol [(*E*)-and (*Z*)-9] To a solution of (3-trimethylsilyl-2-propynyl)triphenylphosphonium bromide (11.8 g, 25.9 mmol) in THF (100 ml) was added *n*-BuLi in hexane (1.54 mol sol'n; 17.0 ml, 25.9 mmol) at −78 °C and the mixture was stirred for 1 h. A solution of **8** (3.74 g, 173 mmol) in THF (15.0 ml) was added to a solution of the ylide thus adjusted in THF at −78 °C and the mixture was stirred for 14 h at the same temperature. The reaction mixture was warmed to room temperature and the solvent was evaporated off. The residue was passed through a short pad of silica gel with hexane–AcOEt (20 : 1) in order to remove triphenylphosphine oxide. The resulting crude enyne was dissolved in EtOH (1% HCl containing solution, 50.0 ml) and the mixture was allowed to stand at room temperature for 1 h. EtOH was evaporated off and the residue was taken up in AcOEt, which was washed with water several times, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10 : 1) gave (*E*)-**9** (1.41 g, 45%) and (*Z*)-**9** (331 mg, 11%). Compound (*E*)-**9** was a colorless oil. IR cm^{-1}: 3624 (OH), 3448 (OH), 2130(CC) and 1623 (C=C). ^{1}H-NMR δ: 5.43 (1H, s, 4-H), 3.64 (2H, t, J=6.4 Hz, 1-H), 2.17 (2H, t, J=7.8 Hz, 3-H), 1.92 (3H, s, Me), 1.70 (2H, tt, J=7.8 and 6.4 Hz, 2-H), 1.44 (1H, s, OH), 0.19 (9H, s, SiMe). ^{13}C-NMR δ: 153.3, 105.2, 96.7, 62.1, 34.8, 30.3, 19.3, 0.0. MS *m/z* (%): 196 (M^+, 14%), 181 (6.6), 163 (14), 135 (8.5), 73 (22). *Anal*. Calcd for $C_{11}H_{20}OSi$: C, 67.3; H, 10.3. Found: C, 67.6; H, 10.0. Compound (*Z*)-**9** was a colorless oil. IR cm^{-1}: 3622 (OH), 3540 (OH), 2124(CC), 1623 (C=C). ^{1}H-NMR δ: 5.34 (1H, q, J=1.5 Hz, 4-H), 3.59 (2H, t, J=6.4 Hz, 1-H), 2.42 (2H, t, J=7.3 Hz, 3-H), 1.95 (1H, s, OH), 1.77 (3H, d, J=1.5 Hz, Me), 1.70 (2H, tt, J=7.3, 6.4 Hz, 2-H), 0.17 (9H, s, SiMe). ^{13}C-NMR δ: 153.3, 106.2, 103.4, 96.6, 61.35, 30.5, 29.7, 22.3, −0.05. MS *m/z* (%): 196 (M^+, 20%), 181 (6.8), 163 (24), 135 (16), 73 (68). *Anal*. Calcd for $C_{11}H_{20}OSi$: C, 67.3; H, 10.3. Found: C, 67.0; H, 10.1.

(4*R,5*R**)-4,5-Epoxy-4-methyl-7-trimethylsilylhept-6-yn-1-ol (*trans*-11)** According to the procedure described for the preparation of *trans*-**10**, *trans*-**11** (220 mg, 41%) was obtained from (*E*)-**9** (500 mg, 2.55 mmol), *m*CPBA (80% purity, 1.65 g, 7.68 mmol) and Na_2HPO_4 (3.60 g, 25.5 mmol). Compound *trans*-**11** was a colorless oil. IR cm^{-1}: 3623 (OH), 2178 (CC). ^{1}H-NMR δ: 3.65 (2H, m, 1-H), 3.24 (1H, s, 5-H), 1.72—1.58 (4H, m, CH_2), 1.43 (3H, s, Me) and 0.17 (9H, s, SiMe). ^{13}C-NMR δ: 100.85, 91.2, 62.9, 62.1, 51.25, 33.3, 27.8, 17.7, −0.4. MS(FAB) *m/z* (%): 213 (M^++1, 5.5%), 195 (38), 154 (29), 136 (37), 123 (12), 73 (100). HR-MS Calcd for $C_{11}H_{21}O_2Si$ (M+1), 213.1311. Found: M^++1, 213.1309.

(4*R,5*S**)-4,5-Epoxy-4-methyl-7-trimethylsilylhept-6-yn-1-ol (*cis*-11)** According to the procedure described for the preparation of *trans*-**10**, *cis*-**11** (85.8 mg, 35%) was obtained from (*Z*)-**9** (230 mg, 1.17 mmol), *m*CPBA (80% purity, 755 mg, 3.51 mmol) and Na_2HPO_4 (1.70 g, 11.7 mmol). Compound *cis*-**11** was a colorless oil. IR cm^{-1}: 3613 (OH), 2178 (CC). ^{1}H-NMR δ: 3.70 (2H, m, 1-H), 3.23 (1H, s, 5-H), 1.84—1.59 (4H, m, CH_2), 1.33 (3H, s, Me) and 0.18 (9H, s, SiMe). ^{13}C-NMR δ: 101.0, 91.45, 62.8, 62.3, 52.1, 30.3, 28.2, 20.6, −0.4. MS *m/z* (%): 212 (M^+, 0.7%), 196 (4.1), 95 (16) and 73 (18). *Anal*. Calcd for $C_{11}H_{20}OSi$: C, 62.2; H, 9.5. Found: C, 61.85; H, 9.6.

$Co_2(CO)_8$-Mediated Ring Closure of Epoxide 10 with a Catalytic Amount of $BF_3\cdot OEt_2$ To a solution of *trans*-**10** (23.8 mg, 0.11 mmol) in CH_2Cl_2 (3.00 ml) was added $Co_2(CO)_8$ (51.5 mg, 0.15 mmol) at room temperature. After being stirred for 30 min (consumption of the starting material was monitored by TLC), the reaction mixture was cooled to −78 °C and held at the same temperature for 30 min. $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.1 mol sol'n; 0.11 ml, 0.01 mmol) was added to the reaction mixture, which was further stirred for 10 min. The reaction was quenched by addition of water, diluted with CH_2Cl_2. The CH_2Cl_2 was separated, washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–CH_2Cl_2 (1 : 1) gave hexacarbonyl-μ-[η^4-(2*R**,3*R**)-3-hydroxy-2-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran]dicobalt(Co-Co)(*trans*-**12**; 22.3 mg, 41%) and hexacarbonyl-μ-[η^4-(2*R**,3*S**)-3-hydroxy-2-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran]dicobalt(Co-Co)(*cis*-**12**; 26.6 mg, 49%). Compound *trans*-**12** was a reddish brown oil. IR cm^{-1}: 2087 (CO), 2047 (CO), 2024 (CO). ^{1}H-NMR δ: 4.01 (1H, d, J=5.4 Hz, OH), 3.69—3.66 (2H, m, 6-H), 3.49 (1H, m, 3-H), 1.98 (1H, m, CH_2), 1.78 (1H, m, CH_2), 1.71—1.67 (2H, m, CH_2), 1.51 (3H, s, Me), 0.34 (9H, s, SiMe). ^{13}C-NMR δ: 200.8, 118.9, 78.2, 77.2, 75.3, 61.1, 28.9, 25.6, 19.4 and 1.0. MS *m/z* (%): 499 (M^++1, 1.4%), 470 (5.4), 442 (47), 414 (80), 386 (63), 358 (25), 330 (12). *Anal*. Calcd for $C_{17}H_{20}Co_2O_8Si$: C, 41.0; H, 4.05. Found: C, 40.8; H, 4.1. Compound *cis*-**12** was a reddish brown oil. IR cm^{-1}: 2087 (CO), 2050 (CO), 2021 (CO). ^{1}H-NMR δ: 3.89 (1H, d, J=3.9 Hz, OH), 3.69—3.65 (3H, m, 3-H and 6-H), 1.90—1.79 (3H, m, CH_2), 1.61 (3H, s, Me), 1.47 (1H, m, CH_2), 0.33 (9H, s, SiMe). ^{13}C-NMR δ: 200.5, 81.9, 79.2, 77.2, 71.1, 62.0, 27.8, 25.5, 20.3, 1.2. MS(FAB) *m/z* (%): 499 (M^++1, 1.2%), 470 (10), 442 (69), 414 (91), 386 (65), 358 (36), 330 (8.1). *Anal*. Calcd for $C_{17}H_{20}Co_2O_8Si$: C, 41.0; H, 4.05. Found: C, 41.3; H, 4.15. Similar treatment of *cis*-**10** (22.2 mg, 0.10 mmol) with $BF_3\cdot OEt_2$ afforded *trans*-**12** (24.1 mg, 48%) and *cis*-**12** (19.7 mg, 40%).

(2*R,3*S**)-3-Acetoxy-2-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran (*trans*-13)** To a solution of *trans*-**12** (22.3 mg, 0.04 mmol) in acetone (1.00 ml) was added CAN (98.0 mg, 0.18 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and the solvent was evaporated off. The residue was taken up in AcOEt, which was washed with water and brine, dried and concentrated to dryness. The residual oil was dissolved in CH_2Cl_2 (1.00 ml) to which Et_3N (0.01 ml, 0.07 mmol), Ac_2O (one drop) and DMAP (8.00 mg, 0.07 mmol) were successively added. The reaction mixture was allowed to stand for 1 h, washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10 : 1) gave *trans*-**13** (8.40 mg, 74%) as a colorless oil. IR cm^{-1}: 2170(CC), 1734 (CO). ^{1}H-NMR δ: 4.87 (1H, t, J=2.4 Hz, 3-H), 4.01 (1H, td, J=11.7, 2.4 Hz, 6-H), 3.81 (1H, dd, J=11.7, 4.9 Hz, 6-H), 2.22—2.17 (2H, m, CH2), 2.12 (3H, s, Ac), 1.99—1.78 (2H, m, CH_2), 1.59 (3H, s, Me) and 0.18 (9H, s, SiMe). ^{13}C-NMR δ: 170.4, 104.1, 92.5, 71.8, 71.6, 63.6, 25.1, 25.0, 21.1, 19.8, −0.2. MS *m/z* (%): 254 (M^+, 1.5%), 153 (2.2), 239 (10), 211 (23), 184 (23). *Anal*. Calcd for $C_{13}H_{22}O_3Si$: C, 61.4; H, 8.7. Found: C, 61.1; H, 8.8.

(2*R,3*R**)-3-Acetoxy-2-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran (*cis*-13)** According to the procedure described for the preparation of *trans*-**13**, *cis*-**13** (8.70 mg, 64%) was obtained from *cis*-**12** (26.6 mg, 0.05 mmol). Compound *cis*-**13** was a colorless oil. IR cm^{-1}: 2171(CC), 1736 (CO). ^{1}H-NMR δ: 4.55 (1H, dd, J=11.7, 2.9 Hz, 3-H), 3.86 (1H, td, J=11.7, 2.9 Hz, 6-H), 3.70 (1H, ddd, J=11.7, 2.9, 1.5 Hz, 6-H), 2.08 (3H, s, Ac), 1.93 (1H, m, CH_2), 1.82—1.64 (3H, m, CH_2), 1.42 (3H, s, Me), 0.21 (9H, s, SiMe). ^{13}C-NMR δ: 170.3, 103.4, 92.4, 74.6, 73.2, 63.0, 26.3, 26.1, 24.9, 21.2, 0.0. MS *m/z* (%): 254 (M^+, 1.8%), 153 (2.8), 239 (14), 211 (29), 184 (31). *Anal*. Calcd for $C_{13}H_{22}O_3Si$: C, 61.4; H, 8.7. Found: C, 61.2; H, 8.9.

Isomerization of Cobalt Complex 12 $BF_3\cdot OEt_2$ in CH_2Cl_2 (1.00 mol sol'n; 0.05 ml, 0.05 mmol) was added to a mixture of *trans*-**12** and *cis*-**12** (23.4 mg, 0.05 mmol, 46 : 54) in CH_2Cl_2 (1.55 ml) at 0 °C. The reaction mixture was stirred for 3 h, washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1 : 1) gave *trans*-**12** (15.9 mg, 68%) and *cis*-**12** (2.34 mg, 10%). Similar treatment of a mixture of *trans*-**12** and *cis*-**12** (23.4 mg, 0.05 mmol, 55 : 45) in CH_2Cl_2 (1.55 ml) with $BF_3\cdot OEt_2$ in CH_2Cl_2 (1.00 mol sol'n; 0.05 ml, 0.05 mmol) afforded *trans*-**12** (14.7 mg, 63%) and *cis*-**12** (1.40 mg, 6%).

Treatment of Cobalt Complex 12 with $BF_3\cdot OEt_2$ in the Presence of Acetic Anhydride To a solution of *cis*-**10** (21.2 mg, 0.10 mmol) in CH_2Cl_2 (3.00 ml) was added $Co_2(CO)_8$ (51.3 mg, 0.15 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was cooled to −78 °C and held at the same temperature for 30 min. $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.10 mol/l; 0.10 ml, 0.01 mmol) was then added to the reaction mixture, which was further stirred for 10 min. Acetic anhydride (two drops) and $BF_3\cdot OEt_2$ in CH_2Cl_2 (1.00 mol/l; 0.10 ml, 0.10 mmol) was successively added to the reaction mixture at −78 °C and the mixture was stirred for an additional hour at the same temperature. The reaction was quenched by addition of water, diluted with CH_2Cl_2, which was washed with brine, dried and concentrated to dryness. The residue was dissolved in acetone (0.80 ml) to which CAN (164 mg, 0.30 mmol) was added at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and the solvent was evaporated off. The residue was taken up in CH_2Cl_2 which was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10 : 1) gave *trans*-**13** (15.5 mg, 61%). Similar treatment of *trans*-**10** (20.0 mg, 0.09 mmol) produced *trans*-**13** (15.3 mg, 64%).

$Co_2(CO)_8$-Mediated Ring Closure of Epoxide 11 with a Catalytic Amount of $BF_3\cdot OEt_2$ According to the procedure described for ring closure of epoxide 10, *trans*-**11** (21.2 mg, 0.10 mmol) in CH_2Cl_2 (3.00 ml) was treated with $Co_2(CO)_8$ (49.5 mg, 0.15 mmol) and $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.10 mol sol'n; 0.10 ml, 0.01 mmol) to afford hexacarbonyl-μ-[η^4-(2*R**,3*R**)-3-hydroxy-3-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran]-dicobalt(Co–Co) (*trans*-**16**; 14.0 mg, 28%) and hexacarbonyl-μ-[η^4-(2*R**,3*S**)-3-hydroxy-3-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran]dicobalt(Co–Co) (*cis*-**16**; 30.7 mg, 62%). Compound *trans*-**16** was a reddish brown oil. IR cm^{-1}: 2088 (CO), 2049 (CO), 2023 (CO). ^{1}H-NMR δ: 4.39 (1H, s, 2-H), 4.05 (1H, m, 6-H), 3.54 (1H, m, 6-H), 1.87 (1H, m, CH_2), 1.77—1.67 (2H, m, CH_2), 1.58 (1H, m, CH_2), 1.19 (3H, s, Me), 0.30 (9H, s, SiMe). ^{13}C-NMR δ: 200.6, 104.9, 87.2, 78.9, 71.1, 68.9, 40.2, 24.9, 21.5, 1.0. MS(FAB) *m/z* (%): 499 (M^++1, 1.7%), 470 (7.4), 442 (76), 414 (100), 386 (77), 358 (38), 330 (14). *Anal*. Calcd for $C_{17}H_{20}Co_2O_8Si$: C, 41.0; H, 4.05. Found: C, 41.2; H, 4.1. Compound *cis*-**16** was a reddish brown oil. IR cm^{-1}: 2089 (CO), 2049 (CO), 2024 (CO). ^{1}H-NMR δ: 4.32 (1H, s, 2-H), 4.03 (1H, ddd, J=11.2, 4.9, and 1.5 Hz, 6-H), 3.59 (1H, td, J=11.2, 2.5 Hz, 6-H), 1.76—1.66 (3H, m, CH_2), 1.45 (1H, m, CH_2), 1.25 (3H, s, Me), 0.31 (9H, s, SiMe). ^{13}C-NMR δ: 200.4, 105.0, 84.8, 69.4, 69.0, 37.9, 29.7, 25.2, 22.2, 1.2. MS(FAB) *m/z* (%): 499 (M^++1, 1.6%), 470 (6.3), 442 (49), 414 (98), 386 (85), 358 (40), 330 (21). *Anal*. Calcd for $C_{17}H_{20}Co_2O_8Si$: C, 41.0; H, 4.05. Found: C, 41.3; H, 4.2. Similar treatment of *cis*-**11** (21.2 mg, 0.10 mmol) with $BF_3\cdot OEt_2$ afforded *trans*-**16** (33.9 mg, 68%) and *cis*-**16** (12.9 mg, 26%).

(2*R,3*S**)-3-Acetoxy-3-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran (*trans*-17)** According to the procedure described for the preparation of *trans*-**13**, *trans*-**17** (17.7 mg, 78%) was obtained from *trans*-**16** (44.5 mg, 0.09 mmol). Compound *trans*-**17** was a colorless oil. IR cm^{-1}: 2172(CC), 1729 (CO). ^{1}H-NMR δ: 4.79 (1H, s, 2-H), 3.95 (1H, ddd, J=11.7, 9.8, 2.9 Hz, 6-H), 3.63 (1H, dt, J=11.7, 4.4 Hz, 6-H), 2.13 (1H, m, CH_2), 2.04 (3H, s, Ac), 1.79 (1H, m, CH_2), 1.56 (3H, s, Me), 1.53—1.47 (2H, m, CH_2), 0.19 (9H, s, SiMe). ^{13}C-NMR δ: 170.4, 101.0, 93.2, 80.1, 71.45, 63.4, 30.8, 22.3, 21.8, 21.3, −0.25. MS *m/z* (%): 254 (M^+, 0.6%), 194 (18), 170 (13). HR-MS Calcd for $C_{13}H_{22}O_3Si$: 254.1338. Found: 254.1341.

(2*R,3*R**)-3-Acetoxy-3-methyl-2-(2-trimethylsilyl)ethynyltetrahydropyran (*cis*-17)** According to the procedure described for the preparation of *trans*-**13**, *cis*-**17** (8.95 mg, 68%) was obtained from *cis*-**16** (25.8 mg, 0.05 mmol). Compound *cis*-**17** was a colorless oil. IR cm^{-1}: 2174 (CC), 1729 (CO). ^{1}H-NMR δ: 4.48 (1H, s, 2-H), 3.96 (1H, ddd, J=11.2, 7.3, 3.9 Hz, 6-H), 3.53 (1H, dd, J=11.2, 7.3, 3.9 Hz, 6-H), 2.46 (1H, m, CH_2), 2.04 (3H, s, Ac), 1.72—1.61 (3H, m, CH_2), 1.60 (3H, s, Me), 0.18 (9H, s, SiMe). ^{13}C-NMR δ: 170.3, 100.5, 92.45, 78.6, 73.8, 65.0, 31.1, 22.4, 22.1, 21.5, −0.1. MS *m/z* (%): 254 (M^+, 1.1%), 194 (4.7), 170 (12). HR-MS Calcd for $C_{13}H_{22}O_3Si$: 254.1338. Found: M^+, 254.1339.

Direct Ring Closure of Epoxide 10 with a Catalytic Amount of $BF_3\cdot OEt_2$ $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.1 mol sol'n; 0.10 ml, 0.01 mmol) was added to a solution of *trans*-**10** (21.2 mg, 0.10 mmol) in CH_2Cl_2 (3.00 ml) at −78 °C. The reaction mixture was stirred at the same temperature for 10 min, gradually warmed to 0 °C and quenched by addition of water. The CH_2Cl_2 layer was separated, washed with water and brine, dried and concentrated to dryness. The residual oil was dissolved in CH_2Cl_2 (2.00 ml) to which Et_3N (0.03 ml, 0.21 mmol), Ac_2O (one drop) and DMAP (24.0 mg, 0.21 mmol) were successively added. The reaction mixture was allowed to stand for 1 h, washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (8 : 1) gave *trans*-**13** (15.7 mg, 68%). Similar treatment of *cis*-**10** (21.2 mg, 0.10 mmol) afforded *cis*-**13** (21.7 mg, 90%).

Direct Ring Closure of Epoxide 11 with a Catalytic Amount of $BF_3\cdot OEt_2$ According to the procedure described for direct ring closure of epoxide **10**, *trans*-**11** (21.2 mg, 0.10 mmol) was treated with $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.1 mol sol'n; 0.10 ml, 0.01 mmol) to give the ring closed product, which was successively acetylated with Ac_2O to afford (1′*R**,2*S**)-2-(1′-acetoxy-3′-trimethylsilyl-2′-propyn-1′-yl)-2-methyltetrahydrofuran (*anti*-**18**; 17.9 mg, 74%) and *trans*-**17** (2.30 mg, 10%).Compound *anti*-**18** was a colorless oil. IR cm^{-1}: 2181 (CC), 1740 (CO). ^{1}H-NMR δ: 5.35 (1H, s, 1′-H), 3.93—3.85 (2H, m, 5-H), 2.17 (1H, m, CH_2), 2.11 (3H, s, Ac), 2.01—1.88 (2H, m, CH_2), 1.71 (1H, m, CH_2), 1.29 (3H, s, Me), 0.16 (9H, s, SiMe). ^{13}C-NMR δ: 169.7, 101.0, 90.9, 83.7, 69.5, 34.0, 26.2, 24.0, 21.0, −0.3. MS *m/z* (%): 254 (M^+, 12%), 212 (6.8), 194 (29), 127 (57), 85 (100), 73 (26). *Anal*. Calcd for $C_{13}H_{22}O_3Si$: C, 61.4; H, 8.7. Found: C, 61.2; H, 8.8. Similar treatment of *cis*-**11** (21.2 mg, 0.10 mmol) with $BF_3\cdot OEt_2$ in CH_2Cl_2 (0.1 mol sol'n; 0.10 ml, 0.01 mmol) and acetylation gave (1′*R**,2*R**)-2-(1′acetoxy-3′-trimethylsilyl-2′-propyn-1′-yl)-2-methyltetrahydrofuran (*syn*-**18**; 21.1 mg, 83%) as a colorless oil. IR cm^{-1}: 2180 (CC), 1739 (CO). ^{1}H-NMR δ: 5.36 (1H, s, 1′-H), 3.90 (1H, ddd, J=8.3, 6.8, 5.9 Hz, 5-H), 3.83 (1H, dt, J=8.3, 6.8 Hz, 5-H), 2.12 (3H, s, Ac), 2.07 (1H, m, CH_2), 1.98—1.92 (2H, m, CH_2), 1.73 (1H, m, CH_2), 1.34 (3H, s, Me), 0.16 (9H, s, SiMe). ^{13}C-NMR δ: 169.85, 101.15, 90.75, 83.9, 68.5, 34.9, 25.95, 22.1, 21,0, −0.3. MS(CI) *m/z* (%): 255 (M^++1, 100%), 195 (55). *Anal*. Calcd for $C_{13}H_{22}O_3Si$: C, 61.4; H, 8.7. Found: C, 61.1; H, 8.8.

References and Notes

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