[Chem. Pharm. Bull. 36(2) 542—550 (1988)]

Antiproliferating Polyquinanes. VI.[1] Synthesis of 2-Methylene[3.3.3]propellan-3-one Derivatives with Hydrophilic Groups

KIYOMI KAKIUCHI,* MASAKI UE, TERUHISA NAGASHIMA, MASAHIKO KINUGAWA, KAZUYA KOBIRO, YOSHITO TOBE, and YOSHINOBU ODAIRA.

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

(Received June 27, 1987)

New analogues related to 2-methylenetricyclo[3.3.3.0]undecan-3-one (**4**), which shows potent antiproliferating activity, *i.e.*, 2-(methoxymethoxy)-4-methylenetricyclo[3.3.3.0]undecan-3-one (**5**), (1*S**,5*R**,7*S**)-7-(methoxymethoxy)- and hydroxy-2-methylenetricyclo[3.3.3.0]undecan-3-ones (**6** and **7**), and (1*S**,5*R**,8*S**)-8-(methoxymethoxy)- and hydroxy-2-methylenetricyclo[3.3.3.0]-undecan-3-ones (**8** and **9**), were readily synthesized through skeletal transformations of derivatives of tricyclo[4.3.2.0]undecan-2-one (**2**).

Keywords——[3.3.3]propellane; α-methylene cyclopentanone; hydrophilic group; skeletal transformation

Skeletal transformation is a convenient method for construction of complex polycarbocyclic skeletons from available compounds. We have recently reported the highly selective and stepwise acid-catalyzed rearrangements of [4.3.2]propellan-2-one (**2**), readily derived by photocycloaddition of bicyclo[4.3.0]non-1(6)-en-2-one (**1**) to ethylene, to give polyquinane derivatives, [3.3.3]propellan-2-one (**3**), and tricyclo[4.3.2.$0^{1,5}$]- and [6.3.0.$0^{1,5}$]undecanes, which have the basic skeletons of natural polyquinane-type compounds.[2] On the other hand, it is well-known that many natural and/or artificial products involving an α-methylene γ-butyrolactone or α-methylene cyclopentanone moiety show a wide range of biological activities attributable to the moiety.[3] From this point of view, we have synthesized a variety of polyquinanes containing the above moiety by chemical modification of the rearrangement products and have found intriguing antiproliferating activity against typical tumor cells.[1] In particular, 2-methylene[3.3.3]propellan-3-one (**4**) was the most active of the polyquinanes presented.

From the standpoint of enhancement of hydrophilicity as well as further lowering of the toxicity, we describe herein the synthesis of the following five analogues **5**—**9**, having hydrophilic groups in the lead compound **4**, by application of our skeletal-transformation strategy to the derivatives of **2**. The analogue **5** possesses a methoxymethyl ether group in the α-methylene cyclopentanone ring of **4**, and should be obtainable by chemical modification of [3.3.3]propell-3-en-2-one (**10**), which can be prepared from 11-acetoxy[4.3.2]propellan-2-one (**11**) by means of acid-catalyzed rearrangement, as shown in Chart 1. To introduce a methoxymethyl ether or hydroxyl group into a different cyclopentane ring from the α-methylene cyclopentanone ring of **4**, *i.e.*, to synthesize the analogues **6**—**9**, the common intermediate, [3.3.3]propell-7-en-2-one (**12**), may be essential, and the skeletal transformation of [4.3.2]propell-3-en-2-one (**13**) would lead to the intermediate **12** (Chart 1).

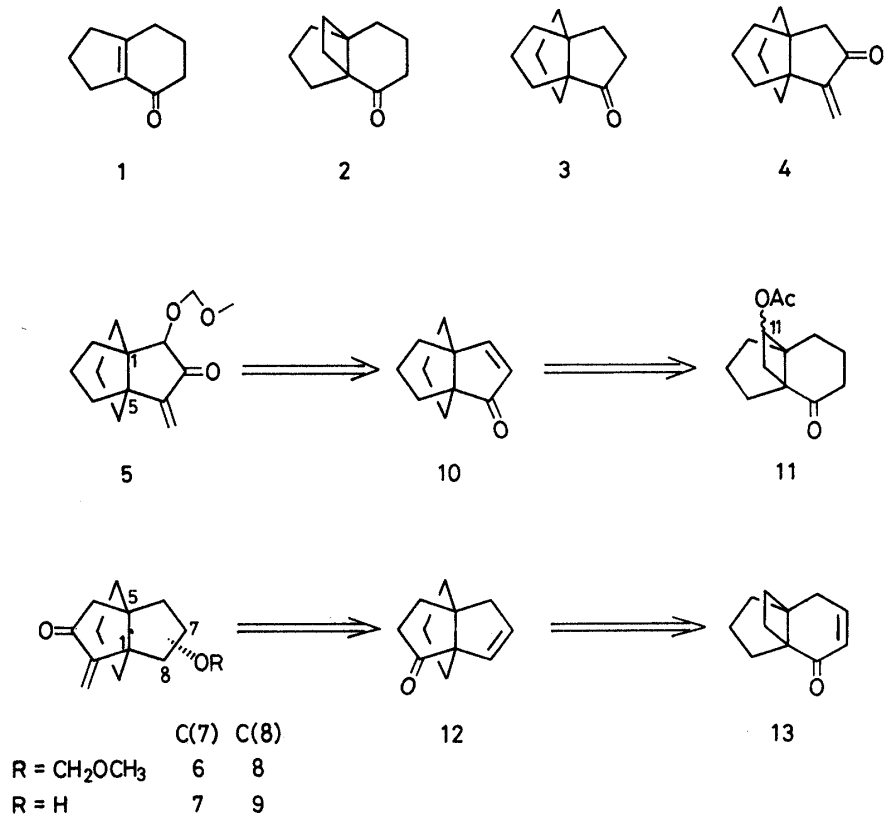

Chart 1

Results and Discussion

Synthesis of the Analogue 5

In order to introduce a methoxymethyl ether group into the α-methylene cyclopentanone ring (Chart 2), a convenient synthesis of the key intermediate **10** was required. Although Cargill and Crawford reported its preparation in 52% overall yield by photoaddition of **1** to dichloroethylene followed by metal reduction and then acid-catalyzed rearrangement,[4] we developed a modified and more efficient route to **10**. On the basis of the rearrangement mechanism of [4.3.2]propellanones, the substituent in the cyclobutane ring should be located in the cyclopentanone one after the rearrangement. As expected, treatment of the propellanone **11** involving an acetoxyl group at C(11) with concentrated sulfuric acid (concd. H_2SO_4) in benzene (PhH) at room temperature for 6 h resulted in rearrangement with elimination of acetic acid, to give **10** in 83% yield. Since the propellanone **11** was obtained in 91% yield by photoreaction of **1** and vinyl acetate as described previously,[5] the preparation of **10** could be achieved in two steps and 76% overall yield.

With the desired intermediate **10** in hand, chemical modification to the target compound **5** was undertaken as follows. Reaction of **10** with methyllithium (MeLi) followed by Jones oxidation of the resulting tertiary alcohol gave the enone **14** in 80% overall yield.[6] After reduction of **14** with lithium aluminum hydride ($LiAlH_4$) and subsequent conversion of the hydroxyl group of **15** into the methoxymethyl ether group in 84% overall yield, oxidation of the ether **16** with *m*-chloroperbenzoic acid (MCPBA) in the presence of disodium hydrogen phosphate (Na_2HPO_4) afforded two epoxides, **17a** and **17b**, in 47% and 48% yields, respectively. The stereochemistry of the epoxides was suggested on the basis of the coupling constants between the C(4) and C(5) hydrogens in the proton nuclear magnetic resonance (^{1}H-NMR) spectra and those of the following two allylic alcohols **18a** and **18b**. Base-induced

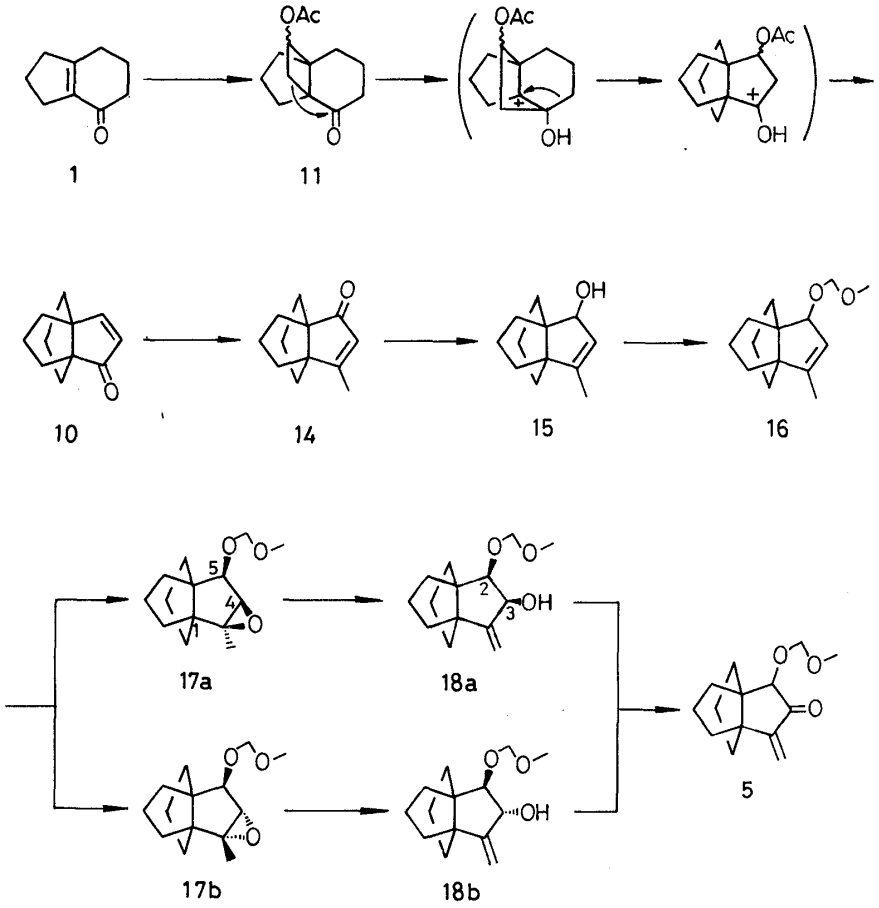

Chart 2

TABLE I. Acid-Catalyzed Rearrangement of [4.3.2]Propellenone **13** to [3.3.3]Propellenone **12**[a]

Run	Acid	Solv.	Time (h)	Yield (%)[b]
1	Concd. H_2SO_4 (cat.)	PhH	48	None[c]
2	CF_3SO_3H (2 eq)	CH_2Cl_2	24	22
3	$BF_3 \cdot OEt_2$ (2 eq)	CH_2Cl_2	3	None[d]
4	$BF_3 \cdot OEt_2$ (5 eq)	CH_3CN	3[e]	15
5	$FeCl_3$ (2 eq)	CH_2Cl_2	6	25
6	$FeCl_3$ (5 eq)	CH_3NO_2	24	39
7	$SnCl_4$ (5 eq)	CH_3NO_2	26	55
8	$AlCl_3$ (2 eq)	CH_2Cl_2	76	12

a) Reactions of **13** (100 mg) were continued at room temperature until **13** was consumed unless otherwise stated. *b*) Isolated yield after column chromatography. *c*) Polymeric unidentified products were obtained. *d*) Recovered **13** (91 mg). *e*) Reaction at reflux.

isomerization of **17a** and **17b** with lithium diethylamide ($LiNEt_2$) furnished the corresponding alcohols **18a** and **18b** in 51% and 92% yields. Finally, modified pyridinium-dichromate (PDC) oxidation[7] of **18a** or **18b** gave the analogue **5** in 75% or 72% yield, respectively.

Synthesis of the Analogues 6—9

In order to prepare the α-methylene cyclopentanones **6—9** (Chart 3), the accessibility of the key and common intermediate **12** was the crux of the synthetic route. Judging from the rearrangement behavior of **2**, the propellenone **13** was anticipated to be the most suitable

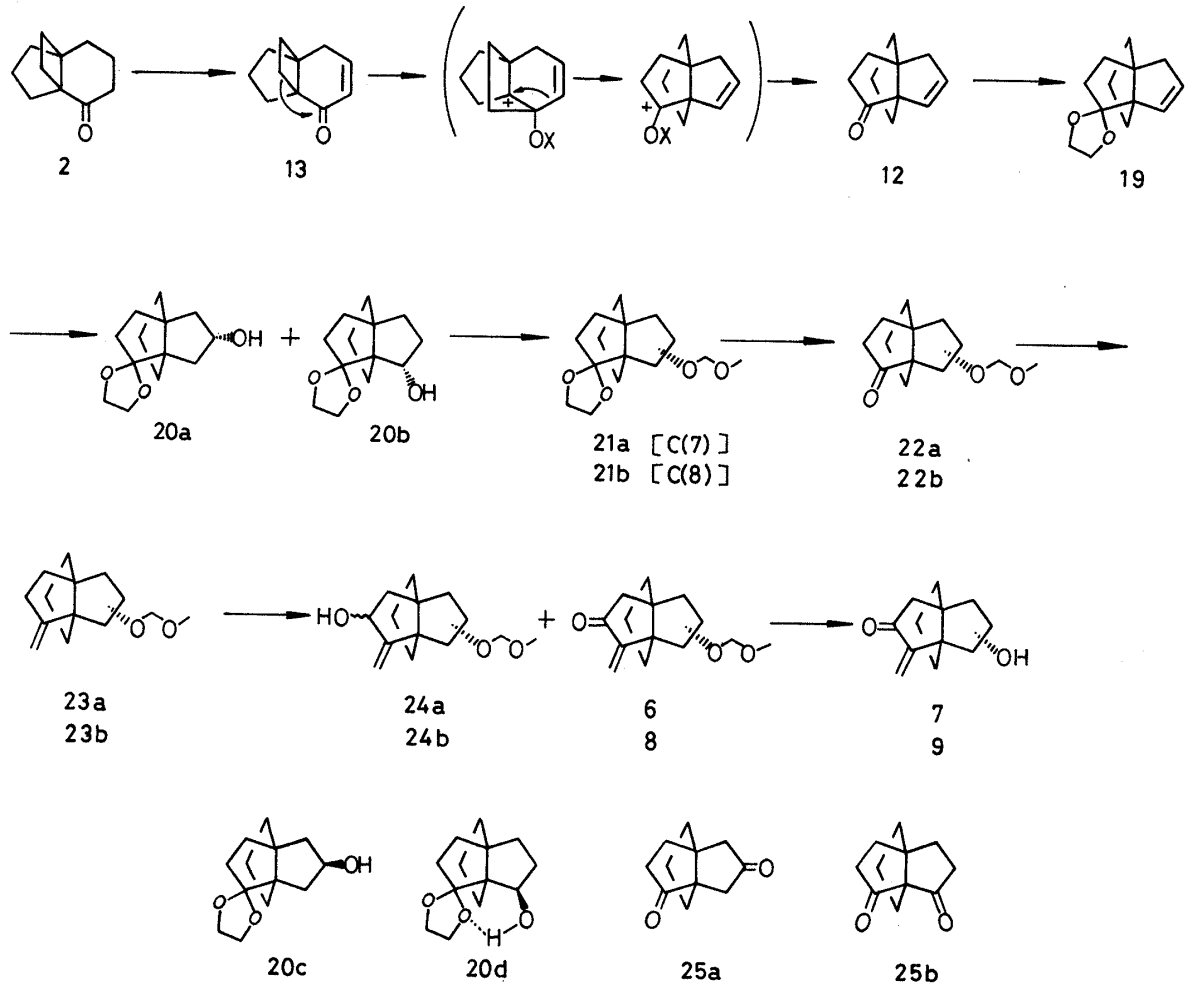

Chart 3

substrate to get **12** through the skeletal transformation. The enone **13** was easily available from **2** by bromination and then β-elimination in 76% overall yield. Reactions of **13** under a variety of acidic conditions were undertaken and the results are listed in Table I. From Table I, a tin(IV) chloride ($SnCl_4$)–nitromethane (CH_3NO_2) system was found to be the best way to **12**. The structure of **12** was determined on the basis of the spectral data, hydrogenation of **12** to **3**, and the results of the following hydroboration-oxidation.

With a viable approach to the common intermediate **12** assured, we turned next to chemical modification of **12** to the analogues **6**—**9** (Chart 3). After protection[8] (99% yield) of the carbonyl group of **12** as the acetal, hydroboration-oxidation of the acetal **19** with thexylborane gave two major alcohols **20a** and **20b** in 54% and 36% yields, respectively, along with a small amount of the epimeric alcohols **20c** (3%) and **20d** (4%). Regio- and stereochemistries of the four alcohols **20a**—**d** were elucidated as follows. Since oxidation of **20a** and **20c** gave the same ketone, which was subject to deketalization[9] to afford the unsymmetrical diketone **25a**, the two alcohols was proved to be C(7) epimers. Similarly, **20b** and **20d** were converted to the symmetrical diketone **25b** and, therefore, were concluded to have epimeric C(8) hydroxyl groups. A sharp hydroxyl stretching band at 3510 cm^{-1} in the infrared (IR) spectrum of **20d** due to intramolecular hydrogen bonding with the acetal oxygen atom and the directions[10] of the hydroboration indicate that the major alcohols involve *exo* hydroxyl groups and the minor ones have *endo* groups as shown in Chart 3.

With the *exo* alcohols **20a** and **20b** in hand, treatment of **20a** and **20b** with methoxymethyl chloride followed by deacetalization of the ethers **21a** and **21b** with pyridinium *p*-

toluenesulfonate (PPTS)[9] gave the keto ethers **22a** and **22b** in 87% and 86% overall yields, respectively. After Wittig olefination of **22a** and **22b** in 94% and 89% yields, allylic oxidation of the olefins **23a** and **23b** furnished the desired analogues **6** and **8** in 29% and 43% yields, together with the allylic alcohols **24a** and **24b** in 44% and 37% yields, respectively. The analogues **6** and **8** were also obtained by PDC oxidation of the respective allylic alcohols **24a** and **24b** in 78% and 70% yields. Finally, reactions of **6** and **8** with 6 M HCl gave the target α-methylene cyclopentanone derivatives **7** and **9** in 98% and 97% yields, respectively.

The bioassay of the α-methylene cyclopentanones obtained are now in preparation.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise stated. ^{1}H-NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer (100 MHz) in CCl_4 and ^{13}C-NMR spectra were taken on a JEOL JNM-FX-60 spectrometer in $CDCl_3$ unless otherwise stated. A JEOL JNM-FX-90Q spectrometer was also used for ^{1}H-NMR (90 MHz) and ^{13}C-NMR (22.5 MHz) spectra in $CDCl_3$. Chemical shifts are reported as δ-values in parts per million relative to Me_4Si (δ, 0.0) as the internal standard. Mass spectra (MS) were measured with a Hitachi RMU-6E spectrometer and are given in terms of *m/z* (relative intensity) compared with the base peak. Analytical gas liquid chromatography (GLC) was carried out on a Hitachi 163 gas chromatograph with a 10% FFAP column or a 30% SE-30 column. Preparative GLC was conducted on a Varian Aerograph 920 gas chromatograph for analytical samples unless recrystallization was carried out. Products were isolated by extraction of the aqueous layer with several portions of the indicated solvent. The combined organic extracts were washed with A: none (no washing), B: saturated brine, and C: saturated sodium hydrogen carbonate ($NaHCO_3$) solution and saturated brine. The organic layer was dried over anhydrous magnesium sulfate and the organic solvent was removed *in vacuo*. Column chromatography was performed with Wako C-200 silica gel and flash chromatography was carried out with Merck Silica gel 60 (No. 7729), using ether–petroleum ether as the eluent. Volume percent of ether in petroleum ether is shown in parentheses. Products (unless melting points are stated) were obtained as colorless oils and their boiling points were not determined. Yields were calculated based on the consumed starting materials.

[3.3.3]Propellenone 10——Concentrated H_2SO_4 (0.2 ml) was added to a stirred solution of the acetoxypropellanone **11**[5] (730 mg, 3.29 mmol) in PhH (20 ml) at room temperature. The mixture was stirred at room temperature for 6 h and water was added. The product was isolated by ether extraction (C) and the resulting crude material was chromatographed to give **10** (386 mg, 83% yield, 5% ether) and recovered **11** (90 mg, 20% ether). The IR and ^{1}H-NMR spectra of **10** were identical with those of an authentic sample which was prepared according to the literature[4] from tricyclo[4.3.2.0]undec-10-en-2-one.[1]

4-Methyltricyclo[3.3.3.0]undec-3-en-2-one (14)——A 1.2 M solution of MeLi (18.5 ml, 22.2 mmol) in ether was added to a stirred solution of **10** (1.05 g, 9.26 mmol) in dry ether (30 ml) *via* a syringe at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and then stirred for 2 h. Water was carefully added to the cooled mixture at 0 °C and the product was isolated by ether extraction (B). An analytical sample was obtained by flash chromatography (30% ether) of a small amount of the crude material. 2-Methyltricyclo-[3.3.3.0]undec-3-en-2-ol, mp 39—40 °C. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.83; H, 10.12. IR (KBr): 3300 (OH) cm^{-1}. ^{1}H-NMR: 0.9—1.9 (15H, m, containing s at 1.29 (CH_3)), 2.10 (1H, m), 5.31 (1H, d, J=6 Hz, CH=CH), 5.53 (1H, d, J=6 Hz, CH=CH). MS *m/z*: 178 (M^+, 26), 135 (53), 121 (100).

Jones reagent (CrO_3–H_2SO_4) was added to a stirred solution of the crude alcohol in acetone (30 ml) at 0 °C until the orange color of the mixture was maintained. The mixture was stirred at 0 °C for 3 h and then 2-propanol was added until the color turned green. The solvent was removed *in vacuo* and water was added to the residue. The product was isolated by ether extraction (B) and the crude material was chromatographed to give **14** (1.32 g, 80% yield from **10**, 10% ether). *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.48; H, 9.22. IR: 3050 (C=C), 1700 (C=O), 1615 (C=C) cm^{-1}. ^{1}H-NMR: 1.4—2.0 (12H, m), 2.04 (3H, s, CH_3), 5.60 (1H, s, CHC=O). ^{13}C-NMR: 15.6 (q, CH_3), 27.0 (2C, t, 7-C and 10-C), 35.2 (4C, t, 6-C, 8-C, 9-C, and 11-C), 67.7 (2C, s, 1-C and 5-C), 129.8 (d, 3-C), 181.0 (s, 4-C), 213.6 (s, 2-C). MS *m/z*: 176 (M^+, 41), 161 (100).

4-Methyltricyclo[3.3.3.0]undecan-3-en-2-ol (15)——A solution of **14** (595 mg, 3.38 mmol) in dry ether (7 ml) was added to a stirred solution of $LiAlH_4$ (64 mg, 1.69 mmol) in dry ether (10 ml) at 0 °C. The mixture was stirred at room temperature for 2 h. Water was carefully added to the cooled mixture at 0 °C and then 5% HCl was added. The product was isolated by ether extraction (C) and flash chromatography of the crude material gave **15** (531 mg, 89% yield, 10% ether), mp 38—40 °C. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.51; H, 10.18. IR (KBr): 3300 (OH), 3030, 1650 (C=C), 1030 (C–O) cm^{-1}. ^{1}H-NMR: 1.0—1.8 (14H, m, containing d at 1.64, J=1.5 Hz (CH_3)), 1.98 (1H, m), 2.70 (1H, s, OH), 4.17 (1H, m, CHOH), 5.09 (1H, m, CH=CCH_3). MS *m/z*: 178 (M^+, 17), 163 (100), 28 (40), 18 (41).

2-(Methoxymethoxy)-4-methyltricyclo[3.3.3.0]undec-3-ene (16)——*N*,*N*-Diisopropylethylamine (1.22 ml, 7.00 mmol) was added *via* a syringe to a stirred solution of **15** (832 mg, 4.67 mmol) in CH_2Cl_2 (13 ml) at room temperature under a nitrogen atmosphere, and then chloromethyl methyl ether (MOMCl, 0.54 ml, 7.11 mmol) was added *via* a syringe to the stirred mixture. The mixture was stirred at room temperature for 1.5 h and water was added to the cooled mixture. The product was isolated by CH_2Cl_2 extraction (B) and flash chromatography of the crude material gave **16** (974 mg, 94% yield, 7% ether). *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.85; H, 10.06. IR: 3030, 1650 (C=C), 1145, 1100, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.0—1.8 (14H, m, containing d at 1.64, J=1.5 Hz (CH_3)), 1.92 (1H, m), 3.28 (3H, s, OCH_3), 4.10 (1H, m, C<u>H</u>OCH_2O), 4.54 (2H, s, OCH_2O), 5.12 (1H, m, C<u>H</u>=CCH_3). MS m/z: 222 (M^+, 12), 135 (100), 45 (55).

(2*S,4*R**,5*R**)- and (2*R**,4*S**,5*R**)-5-(Methoxymethoxy)-2-methyl-3-oxatetracyclo[4.3.3.0.0^{2,4}]dodecanes (17a and 17b)**——MCPBA (1.58 g, 70%, 6.39 mmol) was added to a stirred mixture of **16** (946 mg, 4.26 mmol) and Na_2HPO_4 (1.82 g, 12.8 mmol) in CH_2Cl_2 (23 ml) at 0 °C. The mixture was stirred at 0 °C for 5 h. A saturated sodium sulfite solution (100 ml) was added and the products were isolated by CH_2Cl_2 extraction (C). Flash chromatography of the crude material gave **17b** (483 mg, 48% yield, 5% ether) and **17a** (475 mg, 47% yield, 10% ether).

17a: *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.42; H, 9.35. IR: 1145, 1100, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.0—2.2 (15H, m, containing s at 1.28 (CH_3)), 3.31 (1H, d, J=2 Hz, OCHCHO), 3.36 (3H, s, OCH_3), 3.68 (1H, d, J=2 Hz, OCHCHO), 4.61 (2H, s, OCH_2O). MS m/z: 238 (M^+, trace), 178 (44), 135 (44), 108 (71), 45 (100).

17b: *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.74; H, 9.33. IR: 1145, 1100, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.1—2.2 (15H, m, containing s at 1.31 (CH_3)), 3.21 (1H, s, OCHCHO), 3.33 (3H, s, OCH_3), 3.65 (1H, s, OCHCHO), 4.68 (2H, ABq, J=7 Hz, ν_{AB}=6 Hz, OCH_2O). MS m/z: 238 (M^+, 6), 135 (39), 45 (100).

(2*R,3*S**)-2-(Methoxymethoxy)-4-methylenetricyclo[3.3.3.0]undecan-3-ol (18a)**——A 1.5 M solution of butyllithium (1.7 ml, 2.75 mmol) in hexane was added to a stirred solution of diethylamine (0.34 ml, 2.50 mmol) in dry tetrahydrofuran (THF, 6 ml) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 15 min and then a solution of **17a** (119 mg, 0.5 mmol) in THF (7 ml) was added *via* a syringe to the $LiNEt_2$ solution. The mixture was stirred at 0 °C for 5 h. Water was added and the products were isolated by ether extraction (the extracts were washed with cold 1% HCl and then C). Flash chromatography of the crude material gave **4** (25 mg, 48% yield, 10% ether), recovered **17a** (49 mg, 10% ether), and **18a** (36 mg, 51% yield, 15% ether). IR: 3400 (OH), 1660 (C=C), 1145, 1100, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.1—1.7 (10H, m), 1.8—2.2 (2H, m), 2.42 (1H, br s, OH), 3.36 (3H, s, OCH_3), 3.54 (1H, d, J=5 Hz, OC<u>H</u>CHOH), 4.29 (1H, m, OCHC<u>H</u>OH), 4.64 (2H, s, OCH_2O), 4.88 (1H, d, J=1 Hz, C=CH_2), 4.96 (1H, d, J=1 Hz, C=CH_2). MS m/z: 176 (M^+ −62, 100), 132 (52), 45 (56).

(2*R,3*R**)-2-(Methoxymethoxy)-4-methylenetricyclo[3.3.3.0]undecan-3-ol (18b)**——Reaction of **17b** (100 mg, 0.42 mmol) with 10 eq of $LiNEt_2$ as described above gave **4** (5 mg, 8% yield, 7% ether), recovered **17b** (17 mg, 7% ether), and **18b** (76 mg, 92% yield, 25% ether) after flash chromatography. IR: 3400 (OH), 1660 (C=C), 1145, 1100, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.1—2.2 (12H, m), 3.02 (1H, d, J=9 Hz, OC<u>H</u>CHOH), 3.32 (1H, br s, OH), 3.45 (3H, s, OCH_3), 4.20 (1H, ddd, J=9, 3, 3 Hz, OCHC<u>H</u>OH), 4.73 (2H, s, OCH_2O), 4.91 (1H, d, J=3 Hz, C=CH_2), 5.02 (1H, d, J=3 Hz, C=CH_2). MS m/z: 238 (M^+, trace), 176 (100), 45 (50).

Analogue 5——A reaction mixture of **18a** (57 mg, 0.24 mmol), 4 Å molecular sieves (MS, 200 mg), and PDC[7] (136 mg, 0.36 mmol) in CH_2Cl_2 (1.4 ml) was stirred at room temperature for 2.5 h.[7] Hyflo Super-Cel (Johns-Manville Sales Corp., 200 mg) was added and the resulting mixture was stirred for 20 min. The mixture was filtered and the residue was washed with CH_2Cl_2. The combined filtrates were concentrated *in vacuo* and flash chromatography of the crude material gave **5** (43 mg, 75% yield, 15% ether). Similarly, reaction of **18b** (77 mg, 0.32 mmol) gave **5** (54 mg, 72% yield). *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.31; H, 8.60. IR: 1715 (C=O), 1625 (C=C), 1145, 1090, 1040 (C–O) cm^{-1}. ^{1}H-NMR (90 MHz): 1.3—2.0 (12H, m), 3.40 (3H, s, OCH_3), 4.02 (1H, s, CHC=O), 4.80 (2H, ABq, J=8 Hz, ν_{AB}=7 Hz, OCH_2O), 5.29 (1H, d, J=1 Hz, C=CH_2), 5.96 (1H, d, J=1 Hz, C=CH_2). ^{13}C-NMR (22.5 MHz): 25.9 (t, 7-C or 10-C), 26.9 (t, 7-C or 10-C), 34.1, 41.0, 43.6 (t, 2t, t, 6-C, 8-C, 9-C, and 11-C), 55.7 (d, 2-C), 58.4 (s, 1-C), 60.6 (s, 5-C), 85.4 (q, OCH_3), 96.3 (t, OCH_2O), 118.6 (t, C=<u>C</u>H_2), 153.3 (s, 4-C), 206.1 (s, 3-C). MS m/z: 236 (M^+, 17), 176 (70), 45 (100).

[4.3.2]Propellenone 13——Trimethylphenylammonium tribromide (18.8 g, 50 mmol) was added at once to a stirred solution of the propellanone **2**[1] (8.20 g, 50 mmol) in dry THF (250 ml) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 1 h and poured into a mixture of saturated $NaHCO_3$ solution (250 ml), 1 M solution of sodium thiosulfate (250 ml), and saturated brine (250 ml). The products were isolated by ethyl acetate extraction (B). The crude material was roughly separated by flash chromatography to give recovered **2** (0.42 g, 10% ether) and a mixture of the epimeric monobromo derivatives in a ratio of *ca.* 6:4 (11.5 g, 10% ether). IR: 1690 (C=O) cm^{-1}.

A mixture of the above bromides, lithium carbonate (50 g, 0.68 mol), and lithium bromide (50 g, 0.67 mol) in freshly distilled dimethylformamide (400 ml) was stirred at 110—120 °C (bath temperature) for 1.5 h. The mixture was poured into a mixture of saturated $NaHCO_3$ solution (500 ml), 1 M solution of sodium thiosulfate (250 ml), and saturated brine (500 ml). The white solid was filtered off and the solid was washed with ether. The product was isolated by ether extraction (B) of the combined filtrates. Chromatography of the crude material gave **13** (5.86 g, 76% yield from **2**, 5% ether). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.12; H, 8.80. IR: 3030 (C=C), 1670

(C=O) cm^{-1}. ^{1}H-NMR: 1.2—2.4 (12H, m), 6.01 (1H, dt, J=10, 2 Hz, CH=CHC=O), 6.69 (1H, m, CH=CHC=O). MS m/z: 162 (M^+, 44), 134 (100), 133 (60), 106 (63), 91 (70).

[3.3.3]Propellenone 12——A mixture of **13** (100 mg, 0.62 mmol) and an acid indicated in Table I in an appropriate solvent (5 ml) was stirred under the conditions shown in Table I. Water was added and the product was isolated by ether extraction (C). The results after flash chromatography (10% ether) are summarized in Table I. Reactions of **13** (1.0—5.0 g) using the $SnCl_4$–CH_3NO_2 system gave **12** (38—55% yields), mp 54—56 °C. *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.16; H, 8.66. IR (KBr): 3050 (C=C), 1735 (C=O), 720 (C=C) cm^{-1}. ^{1}H-NMR: 1.4—2.0 (8H, m), 2.1—2.3 (2H, m, CH_2C=O), 2.43 (2H, t, J=1.5 Hz, CH_2CH=CH), 5.43 (1H, dt, J=6, 1.5 Hz, CH=CH), 5.59 (1H, dt, J=6, 1.5 Hz, CH=CH). MS m/z: 162 (M^+, 38), 107 (55), 106 (100), 91 (51).

2,2-(Ethylenedioxy)tricyclo[3.3.3.0]undecan-7-ene (19)——1,2-Bis(trimethylsiloxy)ethane (2.95 ml, 12.0 mmol) was added *via* a syringe to a stirred solution of trimethylsilyl trifluoromethanesulfonate (a catalytic amount) in CH_2Cl_2 (10 ml) at −10 °C under a nitrogen atmosphere and then a solution of **12** (1.62 g, 10 mmol) in CH_2Cl_2 (2 ml) was added *via* a syringe.[8] The violet solution was stirred at −10 °C for 2 h. Pyridine (0.18 ml, 2.24 mmol) and then saturated $NaHCO_3$ solution were added. The product was isolated by ether extraction (A), and flash chromatography of the crude material gave **19** (2.04 g, 99% yield, 8% ether). *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.48; H, 8.78. IR: 3040, 1610 (C=C), 1170, 1070, 1030 (C–O), 715 (C=C) cm^{-1}. ^{1}H-NMR: 1.0—2.0 (10H, m), 2.28 (2H, t, J=1.5 Hz, CH_2CH=CH), 3.8—4.0 (4H, m, OCH_2CH_2O), 5.40 (1H, dt, J=4, 1.5 Hz, CH=CH), 5.28 (1H, dt, J=4, 1.5 Hz, CH=CH). MS m/z: 206 (M^+, 4), 99 (100).

(1*R,5*S**,7*S**)- and (1*R**,5*S**,7*R**)-2,2-(Ethylenedioxy)tricyclo[3.3.3.0]undecan-7-ols (20a and 20c) and (1*S**,5*R**,8*S**)- and (1*S**,5*R**,8*R**)-2,2-(Ethylenedioxy)tricyclo[3.3.3.0]undecan-8-ols (20b and 20d)**——2,3-Dimethyl-2-butene (0.24 ml, 2.0 mmol) was added to a 1.5 M solution of borane (BH_3, 1.5 ml, 2.25 mmol) in THF at 0 °C for under a nitrogen atmosphere. The mixture was stirred at 0 °C for 1 h and then a solution of **19** (103 mg, 0.50 mmol) in dry THF (3.0 ml) was added to the thexylborane solution at −10 °C. The mixture was stirred at −10 °C for 5 h. Water (1 ml) was carefully added and then 10% sodium hydroxide solution (2.0 ml) and 30% hydrogen peroxide (2.0 ml) were added subsequently. The mixture was stirred at 40 °C for 1.5 h and water was added. The products were isolated by ether extraction (B) and flash chromatography (30% ether) of the crude material gave recovered **19** (10 mg), **20a** (55 mg, 54% yield), **20b** (36 mg, 36% yield), **20c** (3 mg, 3% yield based on GLC), and **20d** (4 mg, 4% yield). The alcohol **20c** was not characterized because of the difficulty of separation. However, since oxidation of a mixture of **20a** and **20c** gave the single ketone (*vide infra*), **20c** should be the epimeric alcohol of **20a**. Scale-up of the reaction (**19**, 1.0—2.0 g) gave them in almost the same yields.

20a: *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.55; H, 9.02. IR: 3350 (OH), 1160, 1080, 1050 (C–O) cm^{-1}. ^{1}H-NMR: 1.01 (1H, dd, J=13, 6 Hz), 1.1—2.1 (13H, m), 2.37 (1H, br s, OH), 3.8—4.3 (5H, m, OCH_2CH_2O and CHOH). MS m/z: 224 (M^+, 8), 99 (100).

20b: mp 50—52 °C. *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.65; H, 9.00. IR (KBr): 3420 (OH), 1140, 1075, 1020 (C–O) cm^{-1}. ^{1}H-NMR: 1.0—2.9 (15H, m), 3.8—4.1 (5H, m, OCH_2CH_2O and CHOH). MS m/z: 224 (M^+, 7), 99 (100).

20d: *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.89; H, 9.05. IR: 3510 (OH), 1170, 1090, 1060 (C–O) cm^{-1}. ^{1}H-NMR: 0.8—2.0 (14H, m), 3.14 (1H, br s, OH), 3.70 (1H, m, CHOH), 3.8—4.0 (4H, m, OCH_2CH_2O). MS m/z: 224 (M^+, 3), 99 (100).

(1*R,5*S**,7*S**)-2,2-(Ethylenedioxy)-7-(methoxymethoxy)tricyclo[3.3.3.0]undecane (21a)**——Reaction of **20a** (224 mg, 1.00 mmol) with MOMCl as described above gave **21a** (237 mg, 88% yield, 20% ether) after flash chromatography. *Anal.* Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.08; H, 9.08. IR: 1145, 1100, 1080, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.06 (1H, dd, J=13, 10 Hz), 1.2—2.2 (13H, m), 3.26 (3H, s, OCH_3), 3.8—4.1 (5H, m, OCH_2CH_2O and $CHOCH_2$), 4.50 (2H, s, OCH_2O). MS m/z: 268 (M^+, 14), 99 (100), 45 (56).

(1*S,5*R**,8*S**)-2,2-(Ethylenedioxy)-8-(methoxymethoxy)tricyclo[3.3.3.0]undecane (21b)**——Reaction of **20b** (1.50 g, 6.70 mmol) with MOMCl as described above gave **21b** (1.46 g, 89% yield, 25% ether) and recovered **20b** (135 mg, 25% ether) after flash chromatography. *Anal.* Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.75; H, 9.11. IR: 1170, 1140, 1080, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.2—2.0 (14H, m), 3.28 (3H, s, OCH_3), 3.8—4.0 (5H, m, OCH_2CH_2O and $CHOCH_2$), 4.52 (2H, ABq, J=6 Hz, ν_{AB}=10 Hz, OCH_2O). MS m/z: 268 (M^+, 3), 99 (100).

(1*R,5*S**,7*S**)-7-(Methoxymethoxy)tricyclo[3.3.3.0]undecan-2-one (22a)**——PPTS (63 mg, 0.25 mmol) was added to a stirred solution of **21a** (200 mg, 0.75 mmol) in acetone (10 ml) and water (0.75 ml) at room temperature.[9] The mixture was stirred at reflux for 3 h and the solvent was removed *in vacuo*. Water was added to the residue and the product was isolated by ether extraction (C). Flash chromatography of the crude material gave **22a** (166 mg, 99% yield, 30% ether). *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.55; H, 9.03. IR: 1735 (C=O), 1145, 1115, 1090, 1040 (C–O), 870 (C=C) cm^{-1}. ^{1}H-NMR: 1.3—2.5 (14H, m), 3.26 (3H, s, OCH_3), 3.78 (1H, m, $CHOCH_2$), 4.48 (2H, s, OCH_2O). MS m/z: 224 (M^+, 20), 123 (57), 45 (100).

(1*S,5*R**,8*S**)-8-(Methoxymethoxy)tricyclo[3.3.3.0]undecan-2-one (22b)**——Reaction of **21b** (1.41 g, 5.26 mmol) with PPTS as described above gave **22b** (1.14 g, 97% yield, 40% ether) after flash chromatography. *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.32; H, 9.06. IR: 1735 (C=O), 1045, 1110, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.3—2.1 (12H, m), 2.2—2.4 (2H, m, CH_2C=O), 3.28 (3H, s, OCH_3), 3.84 (1H, dd, J=6, 5 Hz, $CHOCH_2$), 4.53 (2H,

ABq, $J=6$ Hz, $\nu_{AB}=12$ Hz, OCH_2O). MS *m/z*: 224 (M^+, trace), 45 (100).

(1*S,3*S**,5*S**)-3-(Methoxymethoxy)-6-methylenetricyclo[3.3.3.0]undecane (23a)**——A 2 M solution of sodium *tert*-amylate (1.50 ml, 3.00 mmol) in toluene was added to a stirred mixture of triphenylmethylphosphonium bromide (1.07 g, 3.00 mmol) in dry toluene (2 ml) at room temperature under a nitrogen atmosphere. A solution of **22a** (224 mg, 1.00 mmol) in dry toluene (3 ml) was further added. The mixture was heated at reflux with stirring for 1.5 h and then water was added to the cooled mixture at 0 °C. The product was isolated by ether extraction (B), and flash chromatography of the crude material gave **23a** (208 mg, 94% yield, 5% ether). *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.59; H, 10.00. IR: 3050, 1645 (C=C), 1140, 1110, 1040 (C–O), 870 (C=C) cm^{-1}. ^{1}H-NMR: 1.2—2.4 (14H, m), 3.26 (3H, s, OCH_3), 3.78 (1H, m, C<u>H</u>OCH_2), 4.48 (2H, s, OCH_2O), 4.72 (1H, s, C=C<u>H</u>$_2$), 4.74 (1H, s, C=C<u>H</u>$_2$). MS *m/z*: 222 (M^+, 8), 121 (87), 45 (100).

(1*S,2*S**,5*S**)-2-(Methoxymethoxy)-8-methylenetricyclo[3.3.3.0]undecane (23b)**——Wittig reaction of **22b** (1.10 g, 4.93 mmol) as described above gave **23b** (0.97 g, 89% yield, 5% ether) after flash chromatography. IR: 3050, 1645 (C=C), 1145, 1130, 1110, 1040 (C–O), 870 (C=C) cm^{-1}. ^{1}H-NMR: 1.1—2.0 (12H, m), 2.2—2.4 (2H, m, C<u>H</u>$_2$C=CH_2), 3.28 (3H, s, OCH_3), 3.58 (1H, dd, $J=8$, 6 Hz, C<u>H</u>OCH_2), 4.53 (2H, s, OCH_2O), 4.72 (1H, s, C=C<u>H</u>$_2$), 4.74 (1H, s, C=C<u>H</u>$_2$). MS *m/z*: 222 (M^+, trace), 45 (100).

(1*S,5*R**,7*S**)-7-(Methoxymethoxy)-2-methylenetricyclo[3.3.3.0]undecan-3-ols (24a) and Analogue 6**——A mixture of selenium (IV) oxide (125 mg, 1.12 mmol) and 80% *tert*-butyl hydroperoxide (0.44 ml, 4.46 mmol) in CH_2Cl_2 (1 ml) was stirred at 25 °C for 30 min. The mixture was cooled to 0 °C and a solution of **23a** (482 mg, 2.17 mmol) in CH_2Cl_2 (2 ml) was added *via* a syringe. The mixture was stirred at 25 °C for 2 h and then saturated sodium hydrogen sulfite solution and water were added successively. The product was isolated by ether extraction (B) and flash chromatography of the crude material gave **6** (147 mg, 29% yield, 20% ether) and **24a** (225 mg, 44% yield, 50% ether) as a mixture of two epimeric alcohols in a ratio of *ca.* 1 : 1.

24a: IR: 3380 (OH), 3050, 1655 (C=C), 1145, 1110, 1090, 1040 (C–O), 890 (C=C) cm^{-1}.

6: mp 35—36 °C, recrystallized from ether–pentane. *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.02; H, 8.58. IR (KBr): 1715 (C=O), 1625 (C=C), 1145, 1110, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.1—2.2 (10H, m), 2.33 (2H, s, CH_2C=O), 3.27 (3H, s, OCH_3), 3.84 (1H, m, C<u>H</u>OCH_2), 4.52 (2H, s, OCH_2O), 5.22 (1H, s, C=C<u>H</u>$_2$), 5.88 (1H, s, C=C<u>H</u>$_2$). ^{13}C-NMR: 25.4 (t, 10-C), 42.1 (t, 9-C or 11-C), 42.2 (t, 9-C or 11-C), 47.0 (t, 8-C), 48.0 (t, 6-C), 50.9 (s, 5-C), 52.2 (t, 4-C), 54.5 (q, OCH_3), 58.8 (s, 1-C), 77.2 (d, 7-C), 95.1 (t, OCH_2O), 117.4 (t, C=<u>C</u>H_2), 155.3 (s, 2-C), 207.2 (s, 3-C). MS *m/z*: 236 (M^+, 8), 45 (100).

Reaction of **24a** (555 mg, 2.33 mmol) with PDC (no MS) as described above gave **6** (355 mg, 78% yield, 25% ether) and recovered **24a** (97 mg) after flash chromatography.

(1*S,5*R**,8*S**)-8-(Methoxymethoxy)-2-methylenetricyclo[3.3.3.0]undecan-3-ols (24b) and Analogue 8**——Reaction of **23b** (423 mg, 1.89 mmol) with selenium (IV) oxide as described above gave **8** (191 mg, 43% yield, 20% ether) and **24b** (168 mg, 37% yield, 50% ether) as a mixture of two epimeric alcohols in a ratio of *ca.* 6 : 4, after flash chromatography.

24b: IR: 3050, 1655 (C=C), 1145, 1110, 1040 (C–O), 890 (C=C) cm^{-1}.

8: *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.86; H, 8.55. IR: 3050 (C=C), 1715 (C=O), 1625 (C=C), 1145, 1110, 1040 (C–O) cm^{-1}. ^{1}H-NMR: 1.3—2.3 (10H, m), 2.42 (2H, s, C<u>H</u>$_2$C=O), 3.39 (3H, s, OCH_3), 3.78 (1H, dd, $J=7$, 5 Hz, C<u>H</u>OCH_2), 4.68 (2H, ABq, $J=6$ Hz, $\nu_{AB}=5$ Hz, OCH_2O), 5.44 (1H, s, C=C<u>H</u>$_2$), 6.00 (1H, s, C=C<u>H</u>$_2$). ^{13}C-NMR: 26.6 (t, 10-C), 31.8 (t, 7-C), 36.9 (2C, t, 6-C and 9-C), 42.8 (t, 11-C), 52.5 (t, 4-C), 53.3 (s, 5-C), 55.4 (q, OCH_3), 64.3 (s, 1-C), 86.4 (d, 8-C), 96.1 (t, OCH_2O), 118.7 (t, C=<u>C</u>H_2), 154.8 (s, 2-C), 208.8 (s, 3-C). MS *m/z*: 236 (M^+, trace), 45 (100).

Reaction of **24b** (279 mg, 1.17 mmol) with PDC (no MS) as described above gave **8** (192 mg, 70% yield, 20% ether) after flash chromatography.

Analogue 7——A solution of **6** (100 mg, 0.49 mmol) in 6 M HCl (2 ml) and THF (5 ml) was stirred at 50 °C for 1 h and saturated brine was added to the cooled mixture. The product was isolated by ether extraction (B) and flash chromatography of the crude material gave **7** (79 mg, 98% yield, 50% ether), mp 58—62 °C, recrystallized from ether–pentane. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.82; H, 8.42. IR (KBr): 3270 (OH), 1715 (C=O), 1625 (C=C) cm^{-1}. ^{1}H-NMR (90 MHz): 1.2—2.3 (10H, m), 2.40 (2H, ABq, $J=12$ Hz, $\nu_{AB}=10$ Hz, CH_2C=O), 2.48 (1H, br s, OH), 4.03 (1H, m, C<u>H</u>OH), 5.24 (1H, d, $J=1$ Hz, C=C<u>H</u>$_2$), 5.92 (1H, d, $J=1$ Hz, C=C<u>H</u>$_2$). ^{13}C-NMR (22.5 MHz): 26.0 (t, 10-C), 42.7 (2C, t, 9-C and 11-C), 49.9 (t, 8-C), 50.9 (t, 6-C), 51.9 (s, 5-C), 52.9 (t, 4-C), 59.8 (s, 1-C), 72.4 (d, 7-C), 118.4 (t, C=<u>C</u>H_2), 155.8 (s, 2-C), 200.8 (s, 3-C). MS *m/z*: 192 (M^+, 7), 150 (100).

Analogue 9——Reaction of **8** (96 mg, 0.41 mmol) with 6 M HCl as described above gave **9** (76 mg, 97% yield, 45% ether) after flash chromatography, mp 42—46 °C, recrystallized from ether–pentane. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.98; H, 8.40. IR (KBr): 3370 (OH), 1715 (C=O), 1625 (C=C) cm^{-1}. ^{1}H-NMR (90 MHz): 1.1—2.2 (10H, m), 2.40 (2H, s, CH_2C=O), 2.63 (1H, br s, OH), 3.83 (1H, dd, $J=7$, 5 Hz, C<u>H</u>OH), 5.37 (1H, d, $J=1$ Hz, C=C<u>H</u>$_2$), 5.92 (1H, d, $J=1$ Hz, C=C<u>H</u>$_2$). ^{13}C-NMR: 26.7 (t, 10-C), 34.3 (t, 7-C), 36.2 (t, 6-C or 9-C), 36.9 (t, 6-C or 9-C), 42.8 (t, 11-C), 52.7 (t, 4-C), 53.7 (s, 5-C), 65.1 (s, 1-C), 81.4 (d, 8-C), 118.6 (t, C=<u>C</u>H_2), 154.8 (s, 2-C), 209.4 (s, 3-C). MS *m/z*: 192 (M^+, 39), 149 (83), 136 (78), 135 (100), 91 (52).

Hydrogenation of 12 to 3——A mixture of **12** (35 mg, 0.21 mmol) and 10% palladized charcoal (a catalytic

amount) in ethyl acetate (10 ml) was stirred at room temperature for 4 h under atmospheric pressure of hydrogen. The mixture was filtered and the catalyst was washed with ether. The combined filtrates were concentrated *in vacuo* and flash chromatography of the residue gave **3**[1,2] (26 mg, 74% yield, 8% ether).

Tricyclo[3.3.3.0]undecane-2,7-dione (25a)——Reaction of **20a** (62 mg, 0.28 mmol) with PDC and pyridinium trifluoroacetate (PTA, 49 mg, 0.25 mmol)[7] as described above gave 2,2-(ethylenedioxy)tricyclo[3.3.3.0]undecan-7-one (53 mg, 86% yield, 30% ether) after flash chromatography. This ketone was also obtained in 75% yield by a similar oxidation of a mixture of **20a** and **20c** (49 mg, 0.22 mmol, 78 : 22). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.05; H, 8.19. IR: 1735 (C=O), 1160, 1065, 1020 (C–O) cm^{-1}. ^{1}H-NMR (90 MHz): 1.5—1.9 (10H, m), 1.93 (1H, d, J=21 Hz, $COCH_2CH_2OCC\underline{H}_2C=O$), 2.32 (2H, br s, $CH_2C=O$), 2.75 (1H, d, J=21 Hz, $COCH_2CH_2OCC\underline{H}_2C=O$), 3.90 (4H, br s, OCH_2CH_2O). MS *m/z*: 222 (M^+, 5), 99 (100).

Reaction of the above ketone (90 mg, 0.41 mmol) with PPTS as described above gave **25a** (44 mg, 63% yield, 50% ether) after flash chromatography, mp 128—130 °C, recrystallized from CH_2Cl_2. *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.85; H, 7.92. IR (KBr): 1735 (C=O) cm^{-1}. ^{1}H-NMR (100 MHz, $CDCl_3$): 1.6—2.3 (8H, m), 2.4—2.7 (6H, m). ^{13}C-NMR: 26.0 (t, 10-C), 31.8 (t, 3-C), 37.2 (t, 4-C or 9-C), 37.7 (t, 4-C or 9-C), 40.2 (t, 11-C), 47.0 (t, 8-C), 51.4 (t, 6-C), 54.9 (s, 5-C), 62.3 (s, 1-C), 216.5 (s, 7-C), 220.8 (s, 2-C). MS *m/z*: 178 (M^+, 100), 135 (50), 94 (67), 79 (50).

Tricyclo[3.3.3.0]undecane-2,8-dione (25b)——Reaction of **20b** (70 mg, 0.31 mmol) with PDC and PTA as described above gave 2,2-(ethylenedioxy)tricyclo[3.3.3.0]undecan-8-one (53 mg, 76% yield, 30% ether) after flash chromatography. This ketone was also obtained in 73% yield by a similar oxidation of **20d** (18 mg, 0.08 mmol). *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 70.24; H, 8.16. Found: C, 70.29; H, 8.21. IR: 1735 (C=O), 1170, 1070, 1015 (C–O) cm^{-1}. ^{1}H-NMR (90 MHz): 1.2—2.3 (13H, m), 2.65 (1H, ddd, J=17, 13, 9 Hz, $CH_2C=O$), 3.6—4.1 (4H, m, OCH_2CH_2O). MS *m/z*: 222 (M^+, 8), 99 (100).

Reaction of the above ketone (58 mg, 0.22 mmol) with PPTS as described above gave **25b** (33 mg, 85% yield, 50% ether) after flash chromatography, mp 149—153 °C, recrystallized from CH_2Cl_2. *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.90; H, 7.90. IR (KBr): 1735 (C=O) cm^{-1}. ^{1}H-NMR: 1.5—2.1 (10H, m), 2.2—2.5 (4H, m). ^{13}C-NMR: 27.1 (t, 10-C), 30.9 (2C, t, 3-C and 7-C), 36.7 (t, 9-C), 38.7 (3C, s+t, 5-C, 4-C, and 6-C), 40.0 (t, 11-C), 57.4 (s, 1-C), 211.7 (2C, s, 2-C and 8-C). MS *m/z*: 178 (M^+, 100), 123 (77), 121 (59), 79 (70).

References and Notes

1) Part V: K. Kakiuchi, M. Ue, M. Takeda, T. Tadaki, Y. Kato, T. Nagashima, Y. Tobe, H. Koike, N. Ida, and Y. Odaira, *Chem. Pharm. Bull.*, **35**, 617 (1987).
2) Y. Odaira and K. Kakiuchi, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 930 (1986) and references cited therein.
3) For recent reviews, see: S. Kano, S. Shibuya, and T. Ebata, *Heterocycles*, **14**, 661 (1980); H. M. R. Hoffmann and J. Rabe, *Angew. Chem. Int. Ed. Eng.*, **24**, 94 (1985).
4) R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970).
5) K. Kakiuchi, M. Ue, T. Tadaki, Y. Tobe, and Y. Odaira, *Chem. Lett.*, **1986**, 507.
6) For a review, see: T. Nakai and T. Mimura, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 964 (1977) and references cited therein.
7) For PDC oxidation, see: E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **1979**, 399. For the modified oxidation, see: S. Czernecki, C. Georgoulis, C. L. Stevens, and K. Vijayakumaran, *ibid.*, **26**, 1699 (1985).
8) T. Tsunoda, M. Suzuki, and R. Noyori, *Tetrahedron Lett.*, **21**, 1357 (1980).
9) R. Sterzycki, *Synthesis*, **1979**, 724.
10) Speculation based on a molecular model indicates that **20a** and **20b** arise by attack of the borane from the less-hindered side of **19**.