Easy Access to Cyclopentanoid Structures. 1. Preparation and Transposition of Tricyclo[$m.n.0.0^{2,m+1}$]alca-2,3,m + 2-triol Derivatives

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Methylenecyclobutanols 1, conveniently obtained by 1,2-cycladiene condensation of ketone enolates, were used as starting materials for the easy preparation of polycyclic cyclopentane derivatives. Thus, the transposition and transposition–elimination of triol derivatives 3, 5, and 6 led to the synthesis of a series of polycyclic cyclopentan- or cyclopentenones. The stereochemistries of the transpositions were studied and mechanisms were proposed.

Introduction

The ubiquity of carbocyclic five-membered rings[1] justifies the very active current interest of organic chemists in the synthesis of mono- as well as polycyclic cyclopentanoid derivatives. Obviously, a strategy using easily obtained and inexpensive starting materials would be particularly appreciated if, however, they would lead to structures containing functional groups allowing further derivatizations if needed.

On the other hand, among the large variety of pathways leading to cyclopentane derivatives, one-carbon ring expansion of cyclobutanes is particularly attractive. A number of years ago,[2] we showed for the first time that appropriate cyclanones could be used as very simple starting materials to easily construct methylene cyclobutanols 1 according to the general pathway reported in Scheme I for unsubstituted substrates.

We demonstrated that ketone enolates activated[3] $NaNH_2$ giving nucleophilic complex bases[4] able to generate 1,2-cycladienes from the corresponding 1-chlorocycloalkenes.

Taking the above observations into account, we decided to investigate the use of alcohols 1 as starting material in the synthesis of cyclopentanoid structures. In the present paper we would like to report the results obtained in this area using the bishydroxylated derivatives of 1 as starting substrates. A few preliminary experiments have been reported elsewhere.[5]

Bishydroxylation of Alcohol 1 Derivatives. Exploratory study dealing with the bishydroxylation of 1 led to the following conclusions: (i) the sensitive hydroxy group must be protected as easily obtained (see Experimental Section) ether or ester derivatives, and (ii) the best bishydroxylation yields were obtained with the reaction developed by Tsuji et al.[6] The results are reported in Tables I and II.

The structure and stereochemistry of 3 (R = Me, m = 1, n = 2) were deduced from the X-ray diffraction analysis[7a] performed on the corresponding triol 3 (R = H, m = 1, n = 2) prepared elsewhere.[5] Compounds 3 (R = Ac, m = 2, n = 2), 5 (R = Me, m = 1, n = 1), and 5 (R = Ac, m = 2, n = 3) were identified by X-ray diffraction analysis.[7]

Scheme I

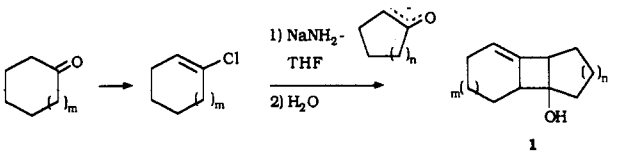
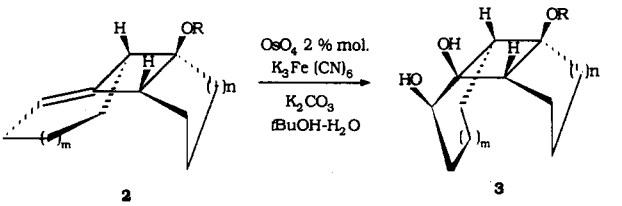


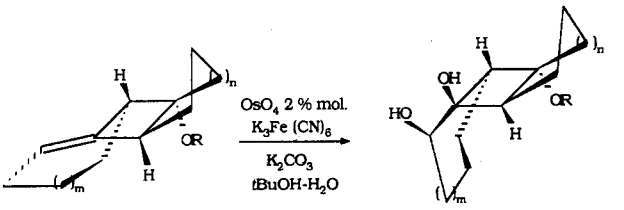
Table I



entry	R	m	n	% yield of 3[a]
1	$COCH_3$	1	1	95
2	CH_3	1	1	76
3	$COCH_3$	1	2	72
4	CH_3	1	2	60
5	$COCH_3$	1	3	65
6	$COCH_3$	2	1	100
7	$COCH_3$	2	2	71
8	$COCH_3$	2	3	69

[a] Isolated yield.

Table II



entry	R	m	n	% yield of 5[a]
1	$COCH_3$	1	1	95
2	CH_3	1	1	78
3	$COCH_3$	2	1	95[b]
4	$COCH_3$	2	2	65
5	$COCH_3$	2	3	71

[a] Isolated yield. [b] Formation of 5% of the isomer 6 which comes from a cis hydroxylation relative to acetate group.

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(1) Trost, B. *Chem. Soc. Rev.* **1982**, *11*, 141.
(2) (a) Caubère, P.; Brunet, J. J. *Tetrahedron* **1972**, *28*, 4835. (b) Brunet, J. J.; Fixari, B.; Caubère, P. *Tetrahedron* **1974**, *30*, 1237.
(3) Caubère, P. *Rev. Heteroatom Chem.* **1991**, *4*, 78.
(4) Caubère, P. *Top. Curr. Chem.* **1978**, *73*, 49.
(5) Jamart-Grégoire, B.; Brosse, N.; Ianelli, S.; Nardelli, M.; Caubère, P. *Tetrahedron Lett.* **1991**, *32*, 3069.
(6) Minato, M.; Yamamoto, K.; Tsuji, J. *J. Org. Chem.* **1990**, *55*, 766.

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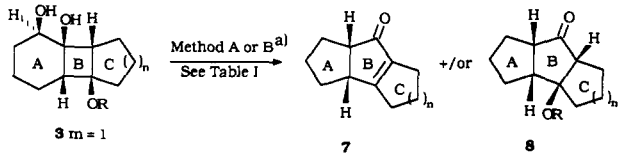
Table III



entry	n	R	method[a]	t (h)	% yield of 7[b]	% yield of 8[b]
1	1	Me	A	60	7	60
2	1	Me	B	10	15[c]	30[c]
3	1	Ac	A	36	56	
4	1	Ac	B	36	64	
5	2	Me	A	24	65	
6	2	Ac	A	20	75	
7	2	Ac	B	25	62	
8	3	Ac	A	72	65	

[a] Method A: MsCl, 1.2 equiv; pyridine, 100 equiv; CH_2Cl_2, 44 °C. Method B: MsCl, 1.2 equiv; triethylamine, 2 equiv; CH_2Cl_2, 42 °C. [b] Isolated yields. [c] Formation of 23% of a compound corresponding to a bismesylation of **3** (m = 1).

The stereochemistry of compound **3** (R = Me, m = 1, n = 1) was established by X-ray diffraction data[7a] of the corresponding bismesylate[5] obtained elsewhere (see Table I). The structures of the remaining compounds were deduced by comparison of their ^{13}C NMR data (see Experimental Section) with those of compounds which structures were established by X ray diffraction.

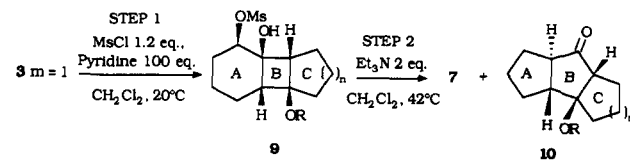
The OsO_4 hydroxylation mechanism has been extensively described and is well known as proceeding from a syn addition.[8] The reaction was directed by steric hindrance and took place highly regioselectively on the less hindered faces of **2** and **4**. Such a pathway also led to the less strained compounds **5** possessing an A/B cis junction. Note that starting from **4** (m = 2, n = 1) we once observed the formation of 5% of **6** possessing a A/B trans junction.

Transposition of 3 (m = 1, n = 1–3). We first intended to prepare a potentially easily solvolized derivative and turned toward the mesylation of the secondary hydroxy group of **3** (m = 1, n = 1–3). In fact, under the conditions used we were unable to isolate any mesylate and observed only the formation of transposed derivatives in good to very good yields (Table III). Curiously, in one case (entry 2), we observed the unexpected formation of 23% of the corresponding bismesylate whose structure was established from X-ray diffraction data.[7a]

The above results showed that these reactions, which may be easily performed on a large scale, constituted a good access to cyclopentanoid structures **7** and in one case to **8**.

In order to elucidate the mechanism of these transpositions we first tried to prepare the monomesylates suspected of being the transient intermediates. Under careful conditions we were able to obtain a number of monomesylates **9** which, warmed in the presence of triethylamine, led to **10**, isomers of **8**, where the stereochemistry of the starting materials was preserved. In two cases the formation of **7** was also observed. The results obtained are gathered in Table IV. The structures of compounds **7**, **8**, and **10** were established by ^1H and ^{13}C NMR (see Experimental Section).

Table IV



			step 1		step 2		
entry	n	R	t (h)	yield[a] (%) of **9** (m = 1)	t (h)	yield[a] (%) of **7** (m = 1)	yield[a] (%) of **10** (m = 1)
1	1	Me	72	69	22	0	61
2	1	Ac	15	85	40	81	0
3	2	Ac	24	75	80	5	74
4	3	Ac	48	52	92	0	80

[a] Isolated yields.

Table V

9 (n = 2, R = Ac) $\xrightarrow[CH_2Cl_2, 42\ °C]{\text{reactants (see Table IV)}}$ **7** (n = 2) + **10** (n = 2, R = Ac)

condns	t (h)	yield (%) of **7** (n = 2)[a]	yield (%) of **10** (n = 2)[a]
none	3	70	
Et_3N, 2 equiv	80	5	75
Et_3N, HCl, 1 equiv			
Et_3N, 1 equiv	5	75	
pyridine, 2 equiv	8	80	
pyridine, 1 equiv	3,5	80	
pyridine, HCl, 1 equiv			
pyridine 100 equiv	80	70	5
pyridine, 100 equiv			
pyridine, HCl, 1 equiv	20	80	

[a] Isolated yields.

Study of the thermal behavior of **9** (n = 2, R = Ac) as well as in the presence of amines and ammonium chlorohydrates (which is the salt formed during the intermediate step of mesylation of **3** and **5**) brought some interesting clues on the mechanism of the transposition step. Thus, from the data reported in Table V it appeared that simple warming of **9** (n = 2, R = Ac) at 42 °C led rapidly to **7** (n = 2). Two equiv of triethylamine decreased the rate of the transposition–elimination of **9** (n = 2, R = Ac) and led to **10** as main product. This base effect was nearly completely reversed in the presence of Et_3N, HCl. Interestingly enough, in the presence of 2 equiv of pyridine the reaction was much faster than in the presence of Et_3N and led to **7**. A large excess of pyridine was necessary to strongly postpone the transposition–elimination and to allow the formation of a small amount of **10**. As observed with Et_3N, addition of pyridine hydrochloride partly compensated the inhibiting pyridine effect.

Keeping in mind that with no amine added free MsOH was formed in the reaction medium, it clearly appeared from these data that these rearrangements were electrophilically catalyzed and that the very first step was the formation of **10** with retention of configuration of the mesylated carbon.

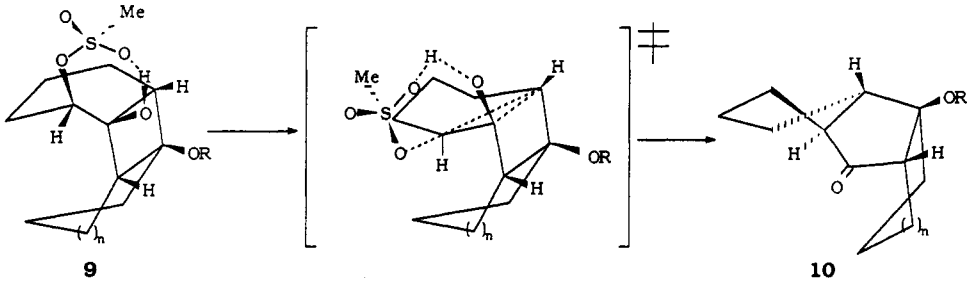
On the other hand it is well known[9] that internal electrophilic assistance may take place during a number of rearrangements implicating two vicinal functions. From Sybyl analysis it appeared that a hydrogen bond could be easily established between the hydroxy and mesyl groups (Scheme II), and we thus suspected such a structure as

(7) (a) Ianelli, S.; Nardelli, M.; Belletti, D.; Jamart-Grégoire, B.; Brosse, N.; Caubère, P. *Acta Crystallogr.*, in press. (b) Ianelli, S.; Nardelli, M.; Belletti, D.; Jamart-Grégoire, B.; Brosse, N.; Caubère, P. *Acta Crystallogr.*, in press. (c) To be published.

(8) Lohray, B. B. *Tetrahedron Asymmetry* **1992**, *3*, 1317 and references cited therein.

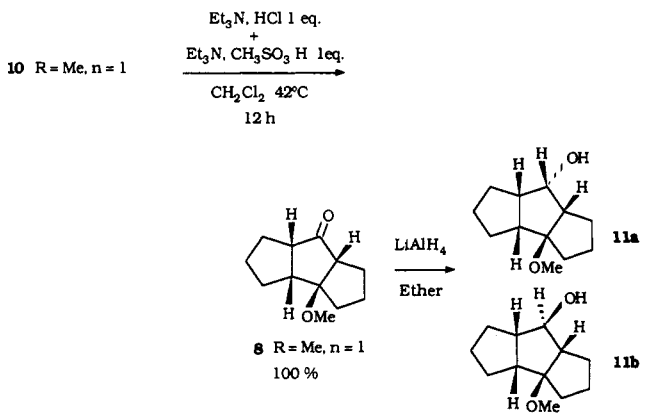
(9) Tsuchihashi, G.; Tomooka, K.; Suzuki, K. *Tetrahedron Lett.* **1984**, *25*, 4253.

Scheme II



9 10

Scheme III



playing an important part in the first step of the transposition. This hypothesis was completely confirmed. Indeed, warming the acetate of **9** (n = 2, R = Ac) (preparation given in the Experimental Section), in which such hydrogen bonding was suppressed, led to no rearrangement after 24 h.

Thus, we concluded that the first step of the rearrangements took place according to the mechanism reported in Scheme II. The transition state proposed looks like the one described in the literature[10] to explain such a kind of transposition taking place with a so-called "formal inversion".[10a] In the presence of Et_3N or pyridine a competition between the mesyl group and the nitrogen of the amines for the formation of a hydrogen bond with the hydroxyl group had as a consequence a decrease of the transposition rate.

Concerning the transformation of **10** (n = 2) into **7** (n = 2) a number of experiments, not presently reported, showed that the reaction was very slow in the absence of a proton source, such as ammonium salts. Moreover, in one case, reported in Scheme III, we were able to epimerize the keto ether **10** (R = Me, n = 1) into the more stable isomer **8** (R = Me, n = 1). The stereochemistry of **8** (R = Me, n = 1) was established by X-ray diffraction analysis performed on the corresponding alcohol **11a** obtained by reduction with $LiAlH_4$.

Thus, the mechanisms reported in Scheme IV appear reasonable.

Both pathways may take place simultaneously. However, due to the relief of ring strain, path A must be considered as strongly favored.

Extension to the Synthesis of New Cyclopentanoid Derivatives. Thanks to the reactions evidenced we were able to synthesize a palet of new polycyclopentane derivatives gathered in Table VI.

(10) (a) Cremlyn, R. J. W.; Garmaise, D. L.; Shoppee, C. W. *J. Chem. Soc.* **1953**, 1847. (b) Nussim, M.; Mazur, Y. *Tetrahedron* **1968**, *24*, 5337.

Formation of **12** (m = 1, n = 1) (H_1 and H_5 in α position) with no elimination product (entries 1 to 4) may be reasonably attributed to steric strain which after the transposition favored an epimerization to reach a cis junction but empeded elimination, whose consequence would be to increase the steric strain in the molecule. In fact, from the data of Table VI it appears that the five-membered ring (n = 1) empeded the elimination step.

It clearly appears that the performed reactions were run by the mechanism described above. However, it is difficult to enter into more details to seriously discuss the stereochemistry of the reaction which proceeds from a delicate balance between strain energy and experimental conditions.

Finally, in addition to the synthesis mentioned above, a number of polycyclic cyclopentenones **13** were obtained in excellent yields from the corresponding acetates **12** (R = Ac) by reaction with *t*BuOK in *t*BuOH (Table VII).

Starting from acetates **12** (R = Ac) with A/B trans junction an epimerization was, of course, observed during the elimination in order to reach the less strained A/B cis structure.

Conclusion

From this first paper in the series it appears that derivatives of methylene cyclobutanols **1** are interesting starting materials in the preparation of polycyclic cyclopentanoid structures. The mechanisms governing these transformations have been elucidated and are helpful in our current investigations.

Finally it must be kept in mind that methylene cyclobutanols **1** are very easily obtained from current starting material thanks to elimination–additions due to complex bases underlining the richness of these reactions and reagents.

Experimental Section

General Methods. Melting points were determined on a Totoli melting point apparatus and are uncorrected. ^{13}C NMR spectra were recorded with a Bruker AM 400 or a Bruker 300-MHz spectrometer (attached proton test method, APT). ^1H NMR spectra were recorded on a Jeol PMX 60 at 60 MHz or a Brucker AM 400 instrument at 400 MHz. Me_4Si was the internal standard. Infrared (IR) spectra of thin liquid films between NaCl plates or KBr pellets were recorded with a Perkin-Elmer 841 instrument. Elemental analyses were performed by CNRS Laboratory (Vernaison). Mass spectra were recorded on a Hewlett-Packard 5971A instrument or by the Laboratory of Mass Spectroscopy, Faculté de Pharmacie (Nancy). Thin-layer chromatography (TLC) was performed with plates coated with Kieselgel G (Merck). The plates were developed with petroleum ether/EtOAc. The silica gels used for column chromatography and flash chromatography were kieselgels of 0.063–0.2 mm and 0.04–0.063 mm particle size, respectively. High-pressure liquid

Scheme IV

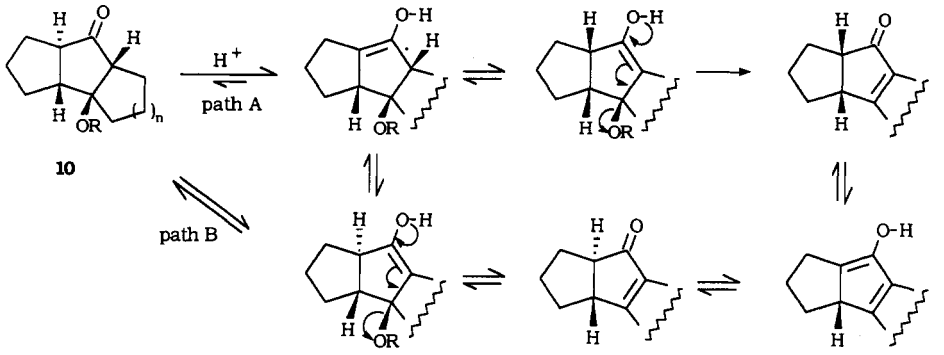
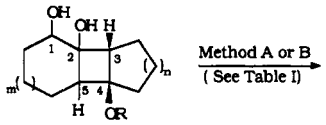
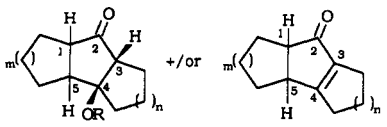


Table VI



3, 5 or 6

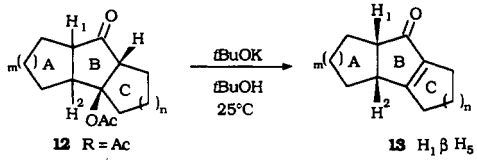


12 13

entry	compound	m	n	R	method	t (h)	12[a] H_1[b]	12[a] H_5[b]	12[a] %	13[a] H_1[b]	13[a] H_5[b]	13[a] %
1	5	1	1	Me	A	5	α	α	91			0
2		1	1	Me	B	3	α	α	90			0
3		1	1	Ac	A	5	α	α	90			0
4		1	1	Ac	B	5	α	α	96			0
5		2	1	Ac	A	13	β	α	100			0
6		2	1	Ac	B	7	β	α	78			0
7		2	2	Ac	A	20	β	α	76			0
8		2	2	Ac	B	72			0	β	β	70
9		2	3	Ac	A	40	β	β	35	β	α	36
10		2	3	Ac	B	34			0	β	β	61
11	3	2	1	Ac	A	9	α	β	97			0
12		2	1	Ac	B	9	α	β	97			0
13		2	2	Ac	A	18	α	β	68	α	β	25
14		2	2	Ac	B	5	α	β	35	β	β	35
15		2	3	Ac	A	18	α	β	58	α	β	15
16		2	3	Ac	B	8			0	β	β	60
17	6	2	1	Ac	A	3	β	β	90			0

[a] Isolated yields. [b] α down the plane; β up the plane.

Table VII



12 R = Ac 13 H_1 β H_5 β

m	n	12 H_1[b]	12 H_5[b]	t (h)	yield (%) of 13[a] (H_1β H_5β)
1	1	α	α	6	60
	1	α	β	6	75
2	2	α	β	0.5	95
	3	α	β	0.5	100
	1	β	α	4	75
2	2	β	α	0.5	90
	3	β	α	0.5	95

[a] Isolated yield. [b] α down the plane, β up the plane.

chromatography was performed with a Waters PREP 500 chromatograph equipped with a silica gel column.

Materials. Sodium amide powder was obtained commercially (Merck). Reagent-grade tetrahydrofuran (THF) (BASF) was distilled from sodium benzophenone ketyl. 1,2-Dimethoxyethane (DME) was distilled from sodium and was stored under sodium until used. The reaction of ketone enolates with 1,2-cycladienes leading to the formation of 1 has been previously described.[2]

Synthesis of 8-Acetoxytricyclo[6.3.0.0^{2,7}]-2-undecene (2, *m* = 1, *n* = 1, R = Ac). The typical procedure used a workup described in the literature.[11] A mixture of alcohol 1, (*m* = 1, *n* = 1) (5.0 g, 30 mM), triethylamine (35 mM, 3.6 g), acetic anhydride (35 mM, 3.6 g), and DMAP (5 mM, 610 mg) in CH_2Cl_2 (100 mL) was allowed to stand at 25 °C for 24 h. The solution was partitioned between ether and diluted HCl; the organic phase was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed through silica gel with 3% petroleum ether/EtOAc mixture to give 5.9 g (90%) of 2 (*m* = 1, *n* = 1, R = Ac): IR (NaCl) 1739 cm^{-1} (C=O); ^1H NMR (60 MHz, CCl_4) δ 5.7–5.3 (1 H, m =CH), 3.3–2.8 (2 H, m, CH), 2.5–1 (15 H, m, 6 CH_2 with s at 2, OAc); ^{13}C NMR ($CDCl_3$) δ 169.6 (C=O), 137.5 (C=), 117.0 (CH=), 89.4 (COAc), 55.1, 50.5 (2 CH), 32.3, 28.1, 26.4, 25.0, 22.1, 21.3 (6 CH_2), 21.3 (Me); MS *m/e* 206. Anal. Calcd for $C_{13}H_{18}O_2$ C, 75.70; H, 8.79. Found: C, 75.25; H, 8.49.

Synthesis of 8-Methoxytricyclo[6.3.0.0^{2,7}]-2-undecene (2, *m* = 1, *n* = 1, R = CH_3). A typical procedure used a workup described in the literature.[12] To a mixture of alcohol 1 (*m* = 1, *n* = 1) (8.7 g, 53 mM), CH_2Cl_2 (100 mL), 50% NaOH (150 mL), and NBu_4Br (3 mM, 1.0 g) was added 2 equiv of Me_2SO_4 (110 mM, 10 mL). The solution mixture was vigorously stirred during 48 h at room temperature. An excess of 32% ammonia solution was added, and the stirring was continued for about 10 min. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with diluted HCl, dried ($MgSO_4$), and concentrated at reduced pressure. The crude product was chromatographed through silica gel with a 2% petroleum ether/EtOAc mixture to give 8.4 g (82%) of 2 (*m* = 1, *n* = 1, R = Me): IR (NaCl) 1690 cm^{-1} (C=C); ^1H NMR (60 MHz, CCl_4) δ 5.3–5.1 (1 H, m, =CH), 3.3–2.6 (5H, m, 2CH with s at 3.1, OCH_3), 2.2–1.0 (12H, m, 6 CH_2); ^{13}C NMR ($CDCl_3$) δ 137.5 (C=), 116.2 (CH=), 89.8 (C-OMe) 54.1, 51.6, 48.1 (2 CH, OMe); 30.1, 28.5, 26.3, 24.9, 22.5, 21.5 (6 CH_2); MS *m/e* 178. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 80.42; H 9.97.

Synthesis of *cis,syn,cis*-8-Acetoxytricyclo[6.3.0.0^{2,7}]-undecane-2,3-diol (3, *m* = 1, *n* = 1, R = Me) or of *cis,anti,cis*-8-Acetoxytricyclo[6.3.0.0^{2,7}]undecane-2,3-diol (5, *m* = 1, *n* = 1, R = Ac) (Tables I and II). A typical procedure used a workup described in the literature.[6] Preparation of the OsO_4 solution: a solution of OsO_4 was prepared by dissolving OsO_4 (1 g) in tert-butyl alcohol (80 mL) followed by addition of several drops of 70% *t*BuOOH. Each milliliter should contain 0.05 mmol of OsO_4.

To a solution of the olefin 2 (*m* = 1, *n* = 1, R = Me) (3.55 g, 20 mM) in *tert*-butyl alcohol (100 mL) and water (100 mL) were added $K_3Fe(CN)_6$ (60 mM, 19.8 g), K_2CO_3 (60 mM, 8.3 g), and the OsO_4 solution previously prepared (1.2 mM, 8 mL). The mixture was stirred for 48 h at room temperature. To this solution was then added a proper quantity of $Na_2S_2O_5$, and stirring was continued for an additional hour. The solution was concentrated under reduced pressure, and the residue was extracted with three portions of ether. The combinated extracts were dried ($MgSO_4$)

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(12) Ogawa, H.; Ichimura, Y.; Chihara, T.; Teratani, S.; Taya, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2481.

and evaporated. The residual oil was purified by chromatography to give 3.0 g (70%) of **3** (m = 1, n = 1, R = Me): IR (KBr) 3600–3100 cm^{-1} (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 4.12–3.80 (1 H, m, OH exchanged with D_2O), 4.62 (1 H, dd, (CHOH), 3.44–3.20 (1 H, m, OH exchanged with D_2O), 3.14 (3 H, s, OMe), 2.56–2.44 (2 H, m, 2 CH), 1.89–1.35 (12 H, m, 6 CH_2); ^{13}C NMR ($CDCl_3$) δ 86.2 (C-OMe), 70.0 (COH), 67.3 (CHOH), 57.0 (CH A/B ring junction), 51.1 (OMe), 48.0 (CH B/C ring junction), 30.4, 27.8, 27.1, 26.2, 20.9, 20.0 (6CH_2); MS m/e 262. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 67.78; H, 9.62. X-ray diffraction data were also collected on the corresponding bis-mesylated compounds (*vide infra*).

Starting from **4** (m = 1, n = 1, R = Me) (2.1 g, 12 mM), 2.0 g (80%) of **5** (m = 1, n = 1, R = Me) was obtained: IR (KBr) 3600–3100 cm^{-1} (OH); ^1H NMR (400 MHz, $CDCl_3$) δ 4.87 (1 H, dd, CHOH) 3.23 (3 H, s, OMe), 2.44 (1 H, d, CH), 2.23 (1 H, dd, CH), 3.14 (1 H, s, OMe), 2.56–2.44 (1 H, m, 2 CH), 1.90–1.40 (14 H, m, 6 CH_2 and 2 OH exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 86.6 (C-OMe), 74.2 (CHOH), 69.4 (C-OH), 51.6 (OMe), 49.1 (CH A/B ring junction), 47.7 (CH B/C ring junction), 33.4, 27.6, 25.2, 24.8, 21.4, 16.7 (6 CH_2); mp (petroleum ether–AcOEt) 124 °C. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 67.71; H, 9.52. X-ray diffraction data were also collected. Note that for compound **3** (m = 1, n = 1, R = Me) the underlined chemical shift of (CH A/B ring junction) 57.0 ppm is higher than for compounds **5** (m = 1, n = 1, R = Me) at 49.1 ppm; on the contrary, the chemical shift of the (CHOH) is higher for compound **5** (m = 1, n = 1, R = Me) at 74.2 ppm than for the compound **3** (m = 1, n = 1, R = Me) at 67.3 ppm. These observations led us to attribute the stereochemistry of all the other products to these two series.

Synthesis of 7 (n = 1) and 8 (n = 1) (Table III). Method A. To a solution of diol **3** or **5** (2 mM) in CH_2Cl_2 (80 mL) and pyridine (16 mL) was added the mesyl chloride (2.4 mM, 280 mg). The solution was heated to reflux for the time indicated in Tables III and VI. After the mixture was poured into ice–diluted HCl, the organic layer was separated and water layer was extracted with CH_2Cl_2. The combinated organic extract was washed with diluted HCl, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by liquid chromatography.

Method B (using a procedure described in the literature[13]). To a solution of diol **3** or **5** (2 mM) in Et_3N (4 mM, 400 mg) in CH_2Cl_2 (100 mL) was added the mesyl chloride (2.4 mM, 280 mg). The solution was heated to reflux for the time indicated in Tables III and VI. After the mixture was poured into ice–water, the organic layer was separated, and water layer was extracted with CH_2Cl_2. The combinated organic extract was washed with diluted HCl, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by liquid chromatography.

***cis*-Tricyclo[6.3.0.0^{2,7}]undec-1(8)-en-2-one (7, m = 1, n = 1)**: IR (NaCl) 1695 cm^{-1} (C=O), 1633 cm^{-1} (C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 3.19–3.07 (2 H, m, 2 CH), 2.58–2.27 (6 H, m), 1.97–1.87 (1 H, m), 1.71–1.53 (4 H, m), and 1.34–1.22 (1 H, m) (6 CH_2); ^{13}C NMR ($CDCl_3$) δ 206.6 (C=O), 188.9, 149.3 (C=C), 57.4, 44.7 (2 CH), 30.3, 29.3, 27.8, 27.6, 24.5, 24.3 (6 CH_2); MS calcd for $C_{11}H_{14}O$ m/e 162. Its spectroscopic data (IR, NMR) were identical with those described in the literature.[14]

***cis*-Tricyclo[6.4.0.0^{2,7}]dodec-1(8)-en-2-one (7, m = 1, n = 2)**: IR (NaCl) 1695 (C=O), 1645 cm^{-1} (C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 3.04–2.97 (1 H, m, CH), 2.66 (1 H, dd, J_1 = 10 Hz, J_2 = 6 Hz, CH), 2.38–2.28 (1 H, m), 2.21–2.11 (1 H, m), 2.08–2.02 (2 H, m), 1.84–1.78 (1 H, m), and 1.70–1.42 (9 H, m) (7 CH_2); ^{13}C NMR ($CDCl_3$) δ 208.0 (C=O), 174.9, 138.8 (C=C), 50.7, 47.0 (2 CH), 28.7, 28.0, 26.4, 23.6, 22.0, 21.5, 19.7 (7 CH_2); UV (MeOH) λ (log ϵ) 243 (4.1); MS calcd for $C_{12}H_{16}O$ m/e 176.

***cis*-Tricyclo[6.5.0.0^{2,7}]tridec-1(8)-en-2-one (7, m = 1, n = 3)**: IR (NaCl) 1694 (C=O), 1645 cm^{-1} (C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 3.19–3.07 (1 H, m, 2 CH), 2.71 (1 H, dd, J_1 = 10 Hz, J_2 = 5.5 Hz, CH), 2.57–2.43 (2 H, m), 2.38–2.21 (2 H, m), 1.93–1.39 (10 H, m), and 1.24–1.11 (2 H, m) (8 CH_2); ^{13}C NMR ($CDCl_3$) δ 210.1 (C=O), 177.7, 142.3 (C=C), 49.4, 47.8 (2 CH), 31.5, 31.0, 29.2, 29.1, 27.5, 26.1, 26.0, 22.7 (8 CH_2). Anal. Calcd for $C_{13}H_{19}ON$: C, 76.05; H, 9.27; N, 6.81. Found: C, 75.90; H, 9.29; N, 6.65.

***cis,syn,cis*-7-Methoxytricyclo[6.4.0.0^{2,6}]undecan-2-one (8, m = 1, n = 1)**: IR (NaCl) 1738 cm^{-1} (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (3 H, s, OMe), 3.06 (1 H, dddd, J_1 = 10 Hz, J_2 = 10 Hz, J_3 = 5 Hz, J_4 = 2 Hz, CH), 2.86 (1 H, m, CH), 2.78 (1 H, ddd, J_1 = 9 Hz, J_2 = 4 Hz, J_3 = 2 Hz, CH), 1.84–1.58 (6 H, m) and 1.51–1.24 (6 H, m), (6 CH_2); ^{13}C NMR ($CDCl_3$) δ 220.0 (C=O), 89.0 (COMe), 55.6, 55.1, 52.0 (3 CH), 49.5 (OMe), 37.0, 35.9, 33.9, 33.1, 24.2, 18.4 (6 CH_2); MS calcd for $C_{12}H_{18}O_2$ m/e 194. X-ray diffraction data have been collected on the corresponding alcohol (**11a**) (*vide infra*).

***cis,syn,cis*-8-Methoxy-2,3-bis[(methanesulfonyl)oxy]-tricyclo[6.3.0.0^{2,7}]undecane** (see footnote b in Table III): ^1H NMR 60 MHz (CCl_4) δ 4.8 (1 H, dd, J_1 = 10 Hz, J_2 = 7 Hz, CHOMs), 3.5–2.8 (11 H, m with 3s at 3.2, 3.1, 3.0, 2 SO_2CH_3, OCH_3, 2 CH), 2.2–1.3 (12 H, m, 6 CH_2); ^{13}C NMR ($CDCl_3$) δ 86.6, 85.3 (COMs, COMe), 77.7 (CHOMs), 54.7, 51.3, 49.5 (3 OCH_3), 41.0, 39.7 (2 CH), 30.2, 27.5, 25.6, 24.6, 19.8, 19.2 (6 CH_2); mp 112 °C. X-ray diffraction data were collected.

Synthesis of *cis,syn,cis*-8-Acetoxy-3-[(methanesulfonyl)-oxy]tricyclo[6.4.0.0^{2,7}]dodecan-2-ol (9, n = 2) (Table IV). A typical procedure: To a solution of diol **3** (m = 1, n = 2, R = Ac) (510 mg, 2 mM) in CH_2Cl_2 (80 mL) and pyridine (16 mL) was added mesyl chloride (2.4 mM, 280 mg). The solution was stirred for the appropriate time (see Table IV) at room temperature. After the usual workup, the crude product was purified by column chromatography on silica gel to give 500 mg (75%) of **9** (n = 2, R = Ac): IR (KBr) 3528 (OH), 1737 cm^{-1} (OAc); ^1H NMR 60 MHz ($CHCl_3$) δ 5.4–5.1 (1 H, m, OH exchanged with D_2O), 5.0–4.5 (1 H, m, CHOMs), 3.0 (3 H, s, OSO_2Me), 2.9–1.1 (19 H, m, 7 CH_2, 2 CH with s at 1.9, OAc); ^{13}C NMR ($CDCl_3$) δ 169.8 (OAc), 82.0 (CHOMs), 75.9, 70.3 (COAc and COH), 53.5, 50.0, 40.0 (2 CH and SO_2CH_3), 26.5, 25.6, 21.4, 21.3 (OCOMe), 20.8, 18.7, 18.6, 18.5 (7 CH_2); mp 106 °C. Anal. Calcd for $C_{15}H_{28}SO_6$: C, 54.38; H, 7.29; S, 9.68. Found: C, 54.43; H, 7.19; S. 9.60.

Synthesis of *cis,syn,cis*-2,8-Diacetoxy-3-[(methanesulfonyl)oxy]tricyclo[6.4.0.0^{2,7}]dodecane (the Acetate of 9 (m = 1, n = 2, R = Ac). A mixture of **9** (m = 1, n = 2, R = Ac) (1.0 g, 3 mM), acetic anhydride (3.5 mM, 200 mg), triethylamine (3.5 mM, 350 mg), and DMAP (0.5 mM, 60 mg) in CH_2Cl_2 (25 mL) was heated to reflux during 24 h. The mixture was poured into 30 mL of ice–water and extracted with CH_2Cl_2. The combined organic layers were washed with diluted HCl and dried over $MgSO_4$. The residue after evaporation was purified by chromatography to give 220 mg (20%) of acetate: IR (KBr) 1741 cm^{-1} (OAc); ^1H NMR 400 MHz ($CHCl_3$) δ 5.07 (1 H, dd, J_1 = 5 Hz, J_2 = 16 Hz, CHOMs), 3.02 (3 H, s, OSO_2Me), 2.90–2.80 (2 H, m, 2 CH), 2.26–2.19 (1 H, m) and 2.07–1.94 (7 H, m with 2 s at 2.06 and 2.00) (3 CH_2, 2 OAc), 1.90–1.23 (13 H, m); ^{13}C NMR ($CDCl_3$) δ 169.6, 169.2 (2 OAc), 79.1 (CHOMs), 77.5, 77.3 (2 COAc), 53.1, 48.5 (2 CH), 39.4 (SO_2CH_3), 27.3, 25.8, 21.6, 21.5 (2 OCOMe), 21.3, 20.5, 19.7, 18.6, 18.2 (7 CH_2); mp 100 °C. Anal. Calcd for $C_{17}H_{28}O_7S$ C, 54.89; H, 7.11; S, 8.49. Found: C, 54.75; H, 6.94; S, 8.60.

Transformation of 9 to 7 and 10 (Tables IV and V). To a solution of **9** (2 mM) in CH_2Cl_2 was added Et_3N (2 equiv, 400 mg). The mixture was heated to reflux during the appropriate time (see Table IV). After the usual workup, the residue was purified by chromatography.

To a solution of **9** (0.5 mM, 170 mg) in CH_2Cl_2 (20 mL) was added Et_3N (1 equiv, 50 mg) and freshly prepared Et_3N–HCl (1 equiv, 70 mg). The mixture was heated to reflux during 5 h. After the usual workup, the crude product was purified by liquid chromatography.

To a solution of **9** (0.5 mM) in CH_2Cl_2 (20 mL) was added pyridine (2 equiv, 80 mg). The mixture was heated to reflux during 8 h. After the usual workup, **7** was purified by liquid chromatography.

To a solution of **9** (0.5 mM, 170 mg) in CH_2Cl_2 (20 mL) was added pyridine (100 equiv, 4 mL). The solution was heated to reflux during 80 h and then poured into ice–diluted HCl. The organic layer was separated, and the water layer was extracted with CH_2Cl_2. The combinated organic extract was washed with

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diluted HCl, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by liquid chromatography.

To a solution of **9** (0.5 mM, 170 mg) in CH_2Cl_2 was added 100 equiv of pyridine (4 mL) and 1 equiv of freshly prepared pyridine, HCl (60 mg). The mixture was refluxed during 20 h. After the usual workup, **6** was purified by chromatography.

To a solution of **9** (0.5 mM, 170 mg) in CH_2Cl_2 (20 mL) was added pyridine (100 equiv, 4 mL) and freshly prepared pyridine, HCl (1 equiv, 60 mg). The mixture is heated to reflux during 20 h. After the usual workup, **7** was purified by liquid chromatography.

Compounds **7** were described above. The A/B trans junction of all compounds **10** was assigned by measuring the coupling constant between the hydrogens of the A/B ring junction: J = 16–17 Hz.

(1*SR*,2*RS*, 6*RS*,8*RS*)-7-Methoxytricyclo[6.4.0.0^{2,6}]undecan-2-one 10 (m = 1, n = 1, R = Me): IR (NaCl) 1743 cm^{-1}; ^{1}H NMR 400 MHz ($CDCl_3$) δ 3.26 (3 H, s, OMe), 2.79 (1 H, dd, J_1 = 6 Hz, J_2 = 10 Hz, CH, COC*H*COMe); 2.53 (1 H, ddd, J_1 = 7 Hz, J_2 = 11 Hz, J_3 = 16 Hz) and 2.33 (1 H, ddd, J_1 = 6 Hz, J_2 = 12 Hz, J_3 = 16 Hz) (2 CH), 2.16–1.35 (12 H, m, 6 CH_2); ^{13}C NMR ($CDCl_3$) δ 211.5 (C=O), 89.5 (COMe), 66.3, 58.7, 53.5 (3 CH), 51.5 (OMe), 29.6, 28.3, 27.2, 27.1, 24.2, 18.2 (6 CH_2). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.62. Found: C, 68.42; H, 8.57.

(1*SR*,2*RS*,6*RS*,8*RS*)-8-Acetoxytricyclo[6.4.0.0^{2,6}]dodecan-2-one 10, m = 1, n = 2, R = Ac): IR (NaCl) 1741 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (1 H, pd), 2.57–2.51 (1 H, m, 1/2 CH_2), 2.44 (1 H, ddd, J_1 = 8 Hz, J_2 = 10 Hz, J_3 = 16 Hz) and 2.38 (1 H, ddd, J_1 = 5 Hz, J_2 = 12 Hz, J_3 = 16 Hz) (2 CH), 2.11–1.85 (8 H, m, 6.5 CH_2 with s at 2.04, OAc), 1.80–1.30 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 211.1 (C=O), 169.9 (OAc), 81.4 (COAc), 62.1, 60.2, 55.8 (3 CH), 26.3, 24.6, 23.8, 23.0, 22.1 (5 CH_2), 21.9 (Me), 20.2, 19.7 (2 CH_2); mp 55 °C. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.71; H, 8.49.

(1*SR*,2*RS*,6*RS*,8*RS*)-9-Acetoxytricyclo[6.4.0.0^{2,6}]tridecan-2-one (10, m = 1, n = 3, R = Ac): IR (NaCl) 1741 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84–2.74 (2 H, m, COC*H*COAc, 1/2 CH_2), 2.79 (1 H, ddd, J_1 = 7 Hz, J_2 = 11 Hz, J_3 = 17 Hz) and 2.59 (1 H, ddd, J_1 = 7 Hz, J_2 = 12 Hz, J_3 = 17 Hz) (2 CH_2), 2.16–1.21 (18 H, m, 7.5 CH_2 with s at 2.06, OAc); ^{13}C NMR ($CDCl_3$) δ 211.5 (C=O), 169.7 (OAc), 86.6 (C-OAc), 67.5, 58.2, 57.6 (3 CH), 31.3, 29.8, 26.6, 26.4, 26.2, 24.7, 23.0 (7 CH_2), 21.8 (Me), 18.9 (1 CH_2); mp 68 °C. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86. Found: C, 71.21; H, 8.56.

Alcohols **11a** and **11b** were prepared by treatment of **8** (m = 1, n = 1) with 6 equiv of $LiAlH_4$ in anhydrous ether. **11a**: IR (KBr) 3600–3200 cm^{-1} (OH); ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.95 (1 H, dd, J_1 = J_2 = 6 Hz, C*H*OH), 3.19 (3 H, s, OMe), 2.88–2.79 (1 H, m) and 2.57–2.49 (2 H, m) (3 CH), 1.86–1.45 (13 H, m, 6 CH_2, OH exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 98.6 (COMe), 74.2 (CHOH), 59.11, 51.3, 50.6, 49.6 (3 CH and OCH_3), 29.6, 29.5, 28.6, 26.2, 25.4, 23.3 (6 CH_2); mp 56 °C. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.63; H, 10.27. X-ray diffraction data were also collected. **11b**: IR (KBr) 3600–3100 cm^{-1} (OH); ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.25–3.11 (1 H, m, OH exchanged with D_2O), 3.15 (3 H, s, OMe), 3.13 (1 H, dd, CHOH), 2.62–2.53 (1 H, m), 2.52–2.40 (1 H, m), and 2.31–2.27 (1 H, m) (3 CH), 1.82–1.32 (12 H, m, 6 CH_2); ^{13}C NMR ($CDCl_3$) δ 98.6 COMe), 74.2 (CHOH), 59.11, 51.3, 50.6, 49.6 (3 CH and OCH_3), 30.7, 29.7, 28.8, 27.1, 26.8, 24.7 (6 CH_2); MS calcd for $C_{12}H_{20}O_2$ m/e 196.

Synthesis of 12 and 13 (Table VI). See methods A and B described for the preparation of **7** and **8**. The stereochemistry of compounds **12** was assigned by measuring the coupling constant of the hydrogens of the A/B ring junction (J = 12–13 Hz for a trans junction and J = 8 Hz for a cis junction) or by comparison of the ^{13}C resonance of the carbonyl group. In fact, as it has been described in the literature[15] δ (C=O) for a cis junction is higher than for a trans junction (δ (C=O) = 215.5 ppm for **12** (m = 2, n = 1, $H_1\alpha H_5\beta$ or $H_1\beta H_5\alpha$) and δ (C=O) = 218 ppm for **12** (m = 2, n = 1 $H_1\beta H_5\beta$).

(1*SR*,2*RS*,7*RS*,9*RS*)-7-Acetoxytricyclo[7.4.0.0^{2,7}]dodecan-2-one (12, $H_1\alpha$ $H_5\beta$ m = 2, n = 1, R = Ac): IR (NaCl) 1739 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (1 H, dd, J_1 = 10 Hz, J_2 = 4 Hz, COC*H*COAc), 2.30–1.95 (8 H, m with s at 2.0, OAc), 1.90–1.72 (4 H, m), 1.67–1.55 (2 H, m), and 1.39–1.01 (5 H, m) (OAc, 2 CH, 7 CH_2); ^{13}C NMR ($CDCl_3$) δ 215.5 (C=O), 169.9 (OAc), 94.8 (COAc), 57.9, 51.9, 47.8 (3 CH), 32.8, 29.7, 27.6, 26.4, 25.4, 24.9 (6 CH_2), 21.6 (OMe); mp 170–175 °C. Anal. Calcd for the corresponding oxime $C_{14}H_{21}O_3N$: C, 66.90; H, 8.42; N, 5.57. Found: C, 66.56; H, 8.66; N, 5.24.

(1*SR*,2*RS*,7*RS*,9*RS*)-8-Acetoxytricyclo[7.4.0.0^{2,7}]tridecan-2-one (12, $H_1\alpha$ $H_5\beta$ m = 2, n = 2, R = OAc): IR (NaCl) 1743 cm^{-1} (C=O) with sh at 1740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (1 H, d, J = 7 Hz, COC*H*COAc), 2.45–2.38 (1 H, ddd, J_1 = 12 Hz, J_2 = 12 Hz, J_3 = 2 Hz, H_1), 2.05–2.30 (8 H, m with s at 2.06, OAc), 1.75–1.90 (2 H, m), and 1.10–1.06 (10 H, m) (CH, OAc, 8 CH_2); ^{13}C NMR ($CDCl_3$) δ 214.0 (C=O), 170.3 (OAc), 85.8 (COAc), 53.0, 52.9, 47.3 (3 CH), 27.6, 25.8, 25.7, 25.6, 22.5 (5 CH_2), 22.0 (COAc), 21.7, 20.6, 20.0 (3 CH_2); mp 170–175 °C. Anal. Calcd for the corresponding oxime $C_{15}H_{23}O_3N$: C, 67.89; H, 8.73; N, 5.27. Found: C, 67.48; H, 8.59; N, 4.88.

(1*SR*,2*RS*,7*RS*,9*RS*)-9-Acetoxytricyclo[7.4.0.0^{2,7}]tetradecan-2-one (12, $H_1\alpha$ $H_5\beta$ m = 2, n = 3, R = Ac): IR (NaCl) 1742 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94–2.81 (1 H, m, COC*H*COAc), 2.32 (1 H, dd, J_1 = J_2 = 12 Hz, H_1), 2.21–1.05 (22 H, m, (H_5, 9 CH_2) with s at 2.04, OAc); ^{13}C NMR ($CDCl_3$) δ 214.8 (C=O), 169.3 ($COCH_3$), 90.6 (COAc), 59.6 (O=CCOAc), 52.0, 50.0 (2 CH), 30.0, 28.6, 28.1, 27.7, 25.7, 25.6, 25.3, 24.8, 22.5 (9 CH_2), 21.6 (OAc). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.41; H, 9.05.

(1*SR*,2*SR*,6*RS*,8*RS*)-7-Acetoxytricyclo[7.4.0.0^{2,7}]dodecan-2-one (12, $H_1\beta$ $H_5\alpha$ m = 2, n = 1, R = Ac): IR (NaCl) 1740 cm^{-1} (C=O); ^{1}H NMR 400 MHz ($CDCl_3$) δ 3.09 (1 H, dd, J_1 = 11 Hz, J_2 = 2 Hz, COC*H*COAc), 2.33 (1 H, ddd, J_1 = 14 Hz, J_2 = 11 Hz, J_3 = 4 Hz, H_1), 2.26–2.16 (1 H, m), 2.11–1.78 (11 H, m with s at 2.07 OAc), and 1.53–1.01 (6 H, m) (OAc, H_5, 7 CH_2); ^{13}C NMR ($CDCl_3$) δ 215.2 (C=O), 169.7 ($COCH_3$), 92.9 (COAc), 56.3 (OC*C*HCOAc), 50.4, 49.1 (2 CH), 34.0, 25.7, 25.6, 25.4, 25.1, 24.7, 24.5 (7 CH_2), 21.2 (OAc); mp 65 °C. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.15; H, 8.53. Found: C, 71.14; H, 8.59.

(1*SR*,2*SR*,7*RS*,8*RS*)-8-Acetoxytricyclo[7.4.0.0^{2,7}]tridecan-2-one (12, $H_1\beta$ $H_5\alpha$ m = 2, n = 2, R = Ac): IR (NaCl) 1743 cm^{-1} with sh at 1740 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.11 (1 H, dd, J_1 = 12 Hz, J_2 = 8 Hz, COC*H*COAc), 2.40 (1 H, ddd, J_1 = 13 Hz, J_2 = 13 Hz, J_3 = 5 Hz, H_1), 2.24–1.63 (13 H, m, with s at 2, OAc) and 1.50–1 (7 H, m) (OAc, H_5, 8CH_2); ^{13}C NMR ($CDCl_3$) δ 217.1 (C=O), 170.2 ($COCH_3$), 86.8 (C-OAc), 50.9, 50.1, 45.3 (3 CH), 26.8, 26.0, 25.9, 25.7, 25.6, 24.6, 23.0, 22.7 (8 CH_2), 22.0 (OAc); mp 104–106 °C. X-ray diffraction data were also collected.

(1*SR*,2*SR*,7*RS*,8*RS*)-9-Acetoxytricyclo[7.4.0.0^{2,7}]tetradecan-2-one (12, $H_1\beta$ $H_5\alpha$ m = 2, n = 3, R = Ac): IR (NaCl) 1738 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97–2.84 (1 H, m, COC*H*COAc), 2.29 (1 H, dd, J_1 = J_2 = 12 Hz, H_1), 2.14–1.43 (16 H, m with s at 2.04, OAc) and 1.33–1.03 (6 H, m) (OAc, H_5, 9CH_2); ^{13}C ($CDCl_3$) δ 216.9 (C=O), 170.5 (OAc), 91.3 (COAc), 58.1 (OC*C*HOAc), 49.21, 48.8 (2 CH), 32.4, 31.0, 27.26, 26.55, 25.9, 25.3, 25.1, 23.7 (8 CH_2); mp 83 °C. Anal. Calcd for $C_{14}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.37; H, 9.27.

***cis,anti,cis*-7-Methoxytricyclo[6.4.0.0^{2,6}]undecan-2-one (12, $H_1\beta$ $H_5\beta$ m = 1, n = 1, R = Me)**: IR (NaCl) 1749 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (3 H, s, OMe), 2.42–2.38 (1 H, m, COC*H*COMe), 2.24 (1 H, dd, J_1 = 8 Hz, J_2 = 5.5 Hz, H_1), 1.17–1.74 (7 H, m), 1.58–1.36 (3 H, m), and 1.23–1.13 (3 H, m) (H_5, 6CH_2); ^{13}C NMR ($CDCl_3$) δ 219.5 (C=O), 93.2 (COMe), 61.0, 54.9 (2 CH), 50.5 (OMe), 45.7 (CH), 31.4, 29.7, 27.2, 27.0, 25.2, 25.1 (6 CH_2); MS calcd for $C_{12}H_{18}O_2$ m/e 194.

***cis,anti,cis*-7-Acetoxytricyclo[6.4.0.0^{2,6}]undecan-2-one (12, $H_1\beta$ $H_5\beta$ m = 1, n = 1, R = Ac)**: IR (NaCl) 1740 cm^{-1} (C=O) (with sh at 1740); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96–2.88 (1 H, m, COC*H*COAc), 2.56 (1 H, dd, J_1 = 8 Hz, J_2 = 5 Hz, H_1), 2.33–1.46 (15 H, m) and 1.33–1.21 (1 H, m) (OAc, H_5, 6CH_2); ^{13}C NMR ($CDCl_3$) δ 218.4 (C=O), 169.6 (OCOMe), 90.4 (COAc), 56.2, 53.3, 48.8 (3 CH), 39.4, 36.5, 33.3, 33.0, 24.1 (5 CH_2), 20.6 (Me), 18.1 (CH_2); mp 135 °C. Anal. Calcd for the corresponding oxime $C_{13}H_{19}O_3N$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.85; H, 7.85; N, 5.96.

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***cis,anti,cis*-7-Acetoxytricyclo[7.4.0.0^{2,7}]dodecan-2-one (12, $H_1\beta$ $H_8\beta$ $m = 2$, $n = 1$, R = Ac)**: IR (NaCl) 1738 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (1 H, ddd, J_1 = 13 Hz, J_2 = 8 Hz, J_3 = 8 Hz, H_1), 2.71 (1 H, pd, COC*H*COAc), 2.47–2.3 (2 H, m), 2.24–2 (6 H, m with s at 2.05), 1.87–1.77 (2 H, m), 1.71–1.49 (4 H, m), 1.43–1.31 (1 H, m), and 1.20–0.83 (3 H, m), (OAc, H_5, 7 CH_2); ^{13}C NMR ($CDCl_3$) δ 217.6 (C=O), 170.2 ($COCH_3$), 94.3 (COAc), 56.8 (OC*C*HCOAc), 49.3, 42.8 (2 CH), 38.8, 29.8, 26.4, 26.3, 24.0, 22.3, 21.9 (7 CH_2), 21.3 (OAc); mp 86 °C. X-ray diffraction data were also collected.

***trans*-Tricyclo[7.3.0.0^{3,8}]dodec-1(9)-en-2-one (13, $H_1\alpha$ $H_8\beta$ $m = 2$, $n = 1$)**: IR (NaCl) 1703 (C=O), 1619 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 2.8–1.0 (m); ^{13}C NMR ($CDCl_3$) δ 202.1 (C=O), 182.2, 145.9 (C=C), 60.5, 45.2 (2 CH), 29.2, 28.0, 26.5, 26.1, 25.7, 24.3, 23.9 (7 CH_2). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.58; H, 9.13.

***trans*-Tricyclo[7.4.0.0^{3,8}]tridec-1(9)-en-2-one (13, $H_1\alpha$ $H_8\beta$ $m = 2$, $n = 2$)**: IR (NaCl) 1703 (C=O), 1634 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 2.5–1.0 (m); ^{13}C NMR ($CDCl_3$) δ 206.9 (C=O), 169.5, 136.5 (C=C), 55.9, 48.5 (2 CH), 27.8, 26.5, 26.2, 24.9, 24.0, 21.8, 21.7, 19.6 (8 CH_2). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.85; H, 9.45.

***trans*-Tricyclo[7.5.0.0^{3,8}]tetradec-1(9)-en-2-one (13, $H_1\alpha$ $H_8\beta$ $m = 2$, $n = 3$)**: IR (NaCl) 1705 (C=O), 1628 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 2.7–1.0 (m); ^{13}C NMR ($CDCl_3$) δ 206.4 (C=O), 171.6, 139.9 (C=C), 55.25, 48.5 (2 CH), 30.6, 28.6, 27.9, 26.6, 26.4, 26.1, 25.9, 23.9, 22.4 (9 CH_2). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.04; H, 9.51.

Transformation of 12 (R = Ac) to 13 ($H_1\beta$ $H_8\beta$). To a solution of 12 (R = Ac) (1 mM) in *t*BuOH (20 mL) was added 2 equiv of *t*BuOK (2 mM, 220 mg). The mixture was stirred at 25 °C during the time indicated in Table VII. Water (50 mL) was added, and the mixture was extracted with ether (2 × 30 mL). The combinated organic layer was dried over $MgSO_4$ and evaporated in vacuo. 13 ($H_1\beta$ and $H_2\beta$) was purified by chromatography.

***cis*-Tricyclo[7.3.0.0^{3,8}]dodec-1(9)-en-2-one (13, $H_1\beta$ $H_8\beta$ $m = 2$, $n = 1$)**: IR (NaCl) 1695 (C=O), 1634 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 3–0.9 (m); ^{13}C NMR ($CDCl_3$) δ 203.8 (C=O), 187.8, 145.5 (C=C), 50.6, 36.5 (2 CH), 29.0, 26.3, 25.6, 23.6, 21.8, 20.0, 19.9 (7 CH_2). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.44; H, 9.02.

***cis*-Tricyclo[7.4.0.0^{3,8}]tridec-1(9)-en-2-one (13, $H_1\beta$ $H_8\beta$ $m = 2$, $n = 2$)**: IR (NaCl) 1698 (C=O), 1645 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 3–1 (m); ^{13}C NMR ($CDCl_3$) δ 210.2 (C=O), 175.7, 136.5 (C=C), 45.4, 41.3 (2 CH), 26.6, 26.1, 22.4, 22.3, 22.1, 21.7, 20.9, 19.7 (8 CH_2). Anal. Calcd for the corresponding oxime $C_{13}H_{19}ON$: C, 76.05; H, 9.27; N, 6.81. Found: C, 75.83; H, 9.27; N, 6.61.

***cis*-Tricyclo[7.5.0.0^{3,8}]tetradec-1(9)-en-2-one (13, $H_1\beta$ $H_8\beta$ $m = 2$, $n = 3$)**: IR (NaCl) 1698 (C=O), 1643 cm^{-1} (C=C); ^{1}H NMR (60 MHz, CCl_4) δ 3–0.8 (m); ^{13}C NMR ($CDCl_3$) δ 209.8 (C=O), 178.7, 140.1 (C=C), 45.2, 42.8 (2 CH), 31.3, 31.1, 26.8, 26.5, 26.2, 23.1, 22.2, 21.0, 20.7 (9 CH_2). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.84 H, 9.59.

The structure of the enone 13 ($H_1\beta$ $H_5\beta$ $m = 2$, $n = 2$) was determined by the method described by Eaton et al.[15] for the determination of the structure of 7 ($m = 1$, $n = 1$). The structure of the remaining compounds 13 was deduced by comparison of their ^{13}C NMR and IR data.

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Supplementary Material Available: Additional compound characterization data and ORTEP representations (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.