Functionalization of *trans*-Decalin. III. A Stereospecific Preparation of Vicinal *cis* Two Methyl Groups of Eremophilane Skeleton, Leading to *dl*-Dehydrofukinone

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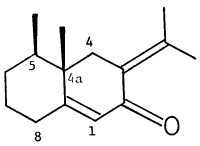
A procedure for the preparation of *dl*-dehydrofukinone (**1**), an eremophilane type sesquiterpene, from the diene adducts (**3**), prepared from the reaction of 4-methyl-3-methoxycarbonyl-2-cyclohexen-1-one with butadiene, is described. Acetalization-reduction ($LiAlH_4$) of **3** followed by treatment of the corresponding mesylate with base provided 5,6-*cis*-5-methyltricyclo[4.4.1.$0^{1,6}$]undec-8-en-2-one (**7**) in 69% overall yields. Reductive cleavage of **7** with lithium metal afforded *trans*-4β,4aβ-dimethyl-$\Delta^{6,7}$-octalin-1-one (**8**), bearing a set of vicinal *cis* two methyl groups on the C-4 and C-4a carbons in an 83% yield. Functionalization of the double bond of **8** involves (1) reduction of carbonyl group and following tetrahydropyranylation, (2) epoxidation followed by regiospecific reduction of the oxirane ring at the C-6 position, and (3) subsequent oxidation of the hydroxyl group, giving *trans*-4aβ,5β-dimethyl-8β-tetrahydropyranyloxydecalin-2-one (**14b**) in good yields. The conversion of **14b** into the desired **1** was achieved smoothly by (1) hydrolysis of tetrahydropyranyl ether, (2) pyrolysis of its mesylate, and (3) subsequent aldol reaction with acetone followed with dehydration and isomerization of the double bond.

As a part of our studies aimed to develop the stereocontrolled construction of a set of vicinal *cis* two methyl groups at the C-4a and C-5 carbons on eremophilane skeleton,[1] we investigated a different approach for the preparation of *dl*-dehydrofukinone (**1**), isolated from the leaves of Gobō (*Arctium lappa* L.).[2] Reported



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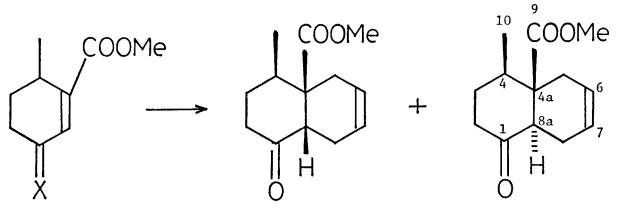
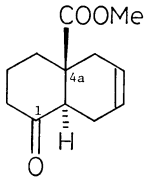
synthetic procedures to eremophilanes involve Robinson annelation reaction,[3] being associated with the inevitable epimerization at the C-4a carbon. With respect to stereochemical control of A, B ring junction, the *endo* rule of Diels-Alder reaction[4] is considered to be promising for the present requirement. In this paper, we record Diels-Alder reaction of 4-methyl-3-methoxycarbonyl-2-cyclohexen-1-one (**2b**) with butadiene as well as the transformation of the adducts (**3**) into *dl*-dehydrofukinone (**1**).

The diene addition of **2b**, prepared from methyl 6-methyl-1-cyclohexene-1-carboxylate (**2a**), with butadiene did take place at 150—160 °C in a sealed tube to give the adducts **3a** (11%) and **3b** (45%). Treatment of **3a** with base led to **3b** in a quantitative yield. The cis configuration of the C-4 methyl and C-4a ester groups of the adduct **3b** can be assigned based on their NMR data. The tentative assignment of



2a: X = H_2
2b: X = O

3a 3b



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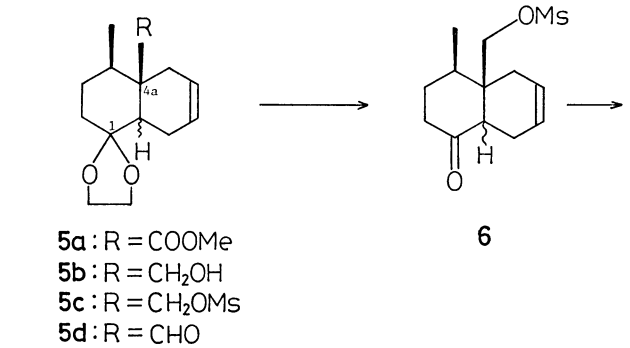
the C-4 methyl group of **3b** was carried out by comparison of ^{13}C NMR results of **3b** with methyl *trans*-1-oxo-$\Delta^{6,7}$-octalin-4a-carboxylate (**4**),[5] which lacks the C-4 methyl group. The chemical shift values of the C-2 (δ 40.0) and C-8a (δ 50.5) carbons (Table 1) of **3b** are close to the C-2 (δ 40.0) and C-8a (δ 50.9) of **4**, suggesting absence of the γ-effect[6] between the C-4 methyl and the C-2 and C-8a carbons of **3b**, due to the equatorial conformation of the C-4 methyl group. On the other hand, the steric compression shift of the C-9 carbon (δ 173.1) of **3b** appears at 2.0 ppm higher field than the value (δ 175.1) of **4**.

The conversion of the ester group of **3b** into the corresponding methyl group was explored. By the reported procedure for the preparation of methyl group from ester function by (1) reduction of COOR with $LiAlH_4$, (2) following oxidation of CH_2OH to CHO, and (3) subsequent Wolf-Kishner reduction,[7] we have examined the conversion of **3b** into **8**. But, difficulties were encountered in the attempted reduction of the hindered formyl group of **5d**. Instead, in the preceding paper[1] we described a preparative procedure of the vicinal *cis* two methyl groups *via* methylation of the enolate anion generated by the reduction of cyclopropyl ketone. The promising procedure prompted us to examine reduction of the cyclopropane ring fused on the C-1, C-6 carbon of **7**, prepared by treatment of the mesylate **6** with base[1,8] (Scheme 1). Thus, reduction of **5a**, after acetalization of **3b**,[9] with $LiAlH_4$ provided **5b** in 86% yield (from **3b**). Mesylation of **5b**, giving the corresponding mesylate **5c**, followed with hydrolysis with $HClO_4$ afforded the mesylated ketone **6** in 95% yield (from **5b**). Cyclization of **6** with sodium methoxide in methanol resulted in the

Table 1. The ^{13}C chemical shifts[a] of substituted decalin derivatives

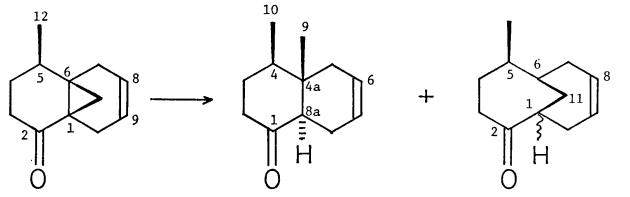
Compound[b]	Carbon No.														
	1	2	3	4	4a	5	6	7	8	8a	9	10	OMe	$-(OCH_2)_2-$	
3a	210.5	36.0	30.1	33.6	52.7	30.1	125.5*	123.3*	22.8	45.7	174.8	15.7	51.9		
3b	208.7	40.0	30.9	40.2	53.8	34.6	125.6*	124.6*	23.2	50.6	173.1	16.0	51.6		
4	208.5	40.4	22.2	36.1	50.6	36.2	126.8*	124.4*	23.2	50.9	175.1		52.0		
8	212.0	41.5	31.2	42.2	39.8	39.5	124.9*	124.3*	21.7	53.1	11.9	14.6			
10	110.0	35.7	28.3	42.8	36.1	41.3	125.7*	124.6*	21.4	47.8	11.9	15.0		64.0	65.4
11	110.0	35.9	19.5	40.7	33.6	43.4	126.1*	124.7*	21.4	47.0	18.2			64.0	65.5
12	70.5	35.0	25.5	43.3	35.0	41.5	125.7*	125.5*	25.5	44.2	13.5	15.3			
13a	70.5	35.3	24.4	43.2	34.0	39.9	53.0*	51.6*	25.4	39.2	14.7	15.3			

a) The chemical shifts are shown in δ values (ppm) relative to internal Me_4Si. b) For the numbering systems, see numbers on the structures. * Theses pairs of shifts may be interchanged since the assignments are ambiguous.



5a : R = COOMe
5b : R = CH_2OH
5c : R = CH_2OMs
5d : R = CHO

6



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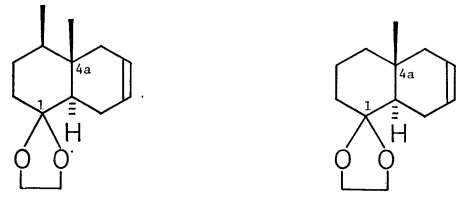

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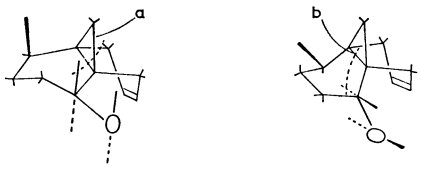
Scheme 1.



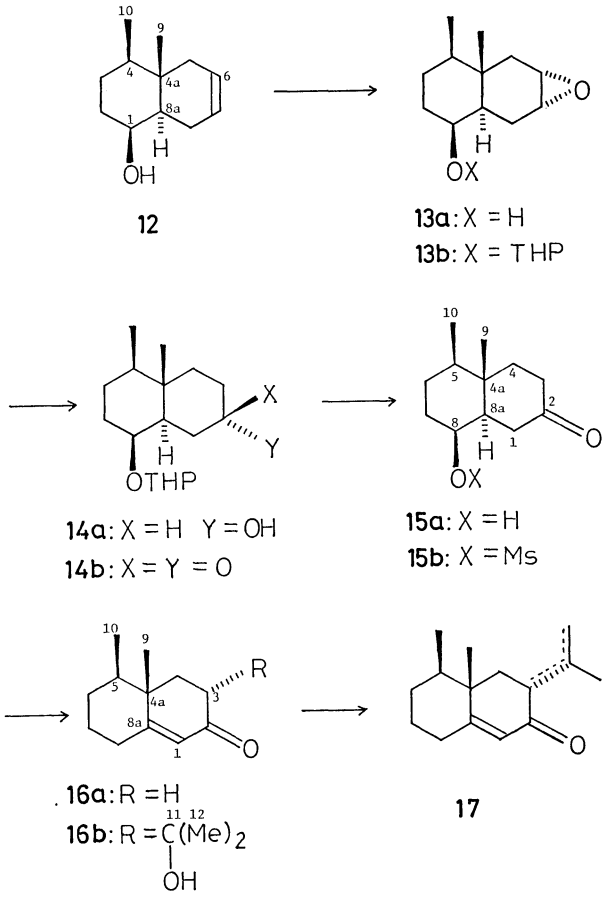
7a 7b

Scheme 2.

desired **7** in 84% yield.

Reductive cleavage of the cyclopropane ring of **7** with lithium metal in liquid ammonia gave a mixture of **8**[10] (83%) and **9** (10%). The product distribution of the reduction would depend on preferential conformations of the transition states **7a** and **7b** (Scheme 2). Either bond **a** or **b** of the cyclopropane ring of **7** being close to the carbonyl π-electron would be opened by electron transfer from metal lithium.[11] As the result, it appears that the present reduction does preferentially take place through the conformation **7a**. The marked upfield shift in ^{13}C NMR spectra of the C-9 methyl signal of **10** at δ 11.9, contrasting to that of **11**[12] at δ 18.2, can rationally interpret the assigned stereochemistry of **10**, compatible with the calculated values of Crews's substituents increment parameter.[13]

In pursuing the approach from **8** to the important intermediate **14b**, we examined the functionalization of the double bond of **8** by epoxidation followed with regiospecific reduction at the C-6 position and subsequent oxidation of hydroxyl group. Reduction of **8** with $LiAlH_4$ afforded the 1β-alcohol **12** in 90% yield. The structure of **12** can be interpreted on the basis of 1,3-diaxial downfield shift of ^1H NMR signal due to the C-4a methyl group of **12** (δ 0.88), comparing to the value of δ 0.63 of **8**. Epoxidation of **12** with *m*-chloroperbenzoic acid (*m*-CPBA) at 0—10 °C gave the 6α,7α-epoxide **13a** preferentially by attack of the bulky reagent from the less hindered α-face.[14] Assignment of the epoxy ring of **13a** can be made by analysis of the ^{13}C NMR spectra of the C-4a and C-8a carbons, appearing at 1.0 and 5.0 ppm higher fields than those of **12** (Table 1), due to the presence of the γ-effect[6] between either the C-4a or C-8a carbon and the ring of the 6α,7α-epoxide. After protection of the hydroxyl group of **13a** as a tetrahydropyranyl ether, **13b** was treated with lithium metal in liquid ammonia to give the alcohol **14a** (65% yield based on **12**). The reductive cleavage of the carbon–oxygen bond of **13b** can be expected to occur at the C-6 position based on the axial ring opening rule,[15] giving **14a** as a sole product. The structure of **14a** can be confirmed by further elaboration into the enone **16a**. Oxidation of **14a** with pyridinium chlorochromate[16] gave the desired ketone **14b** in 95% yield. The conversion of **14b** into **16a**[17] *via* **15a** and **15b** was carried out in 54% overall yields by hydrolysis of **14b** with pyridinium *p*-toluenesulfonate[18] at 60—63 °C in ethanol and subsequent pyrolysis of the mesylate **15b** at



Scheme 3.

130—140 °C in DMSO.

Kinetically controlled aldol reaction[1] of **16a** with acetone in the presence of zinc chloride was allowed to lead to **16b** in 79% yield. The compound **16b** was dehydrated by warming the mesylate of **16b** at 40—50 °C in pyridine and the resulting *exo* and *endo* double bond isomers **17** were converted into the desired *dl*-dehydrofukinone (**1**) either by passing an activated alumina column or by treatment with $RhCl_3 \cdot 2H_2O$ (72% yield). The desired product **1** was shown to be identical by IR and ^1H NMR spectral comparison with those of authentic specimen.[19]

Experimental

The melting points and boiling points are uncorrected. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were determined at 60 MHz with a Hitachi R-24 instrument and at 100 MHz with a JEOL MH-100 spectrometer. ^{13}C NMR spectra were determined at 25.05 MHz with a JEOL pulsed Fourier transform spectrometer, Model FX-100. Samples were dissolved in $CDCl_3$ and the chemical shift values were expressed in δ values (ppm) relative to Me_4Si as an internal standard Elemental analyses were performed in our laboratory.

*Methyl 6-Methyl-1-cyclohexene-1-carboxylate (**2a**).* A solution of 6-methyl-1-cyclohexene-1-carboxylic acid[20] (18.1 g, 129 mmol) in MeOH (40 ml, 989 mmol) and 1,2-dichloroethane (300 ml) containing concd H_2SO_4 (10 ml) was refluxed for 24 h and worked up in the usual manner to give 18.5 g (93%) of **2a**: bp 85.0—90.0 °C/25 Torr; IR (neat) 1712 (ester C=O), 1641 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 1.05 (d, 3, J=6.5 Hz, CH_3), 1.44—2.73 (m, 4, CH_2), 1.98—2.32 (m, 2, CH_2), 2.42—2.91 (m, 1, CH), 3.66 (s, 3, OCH_3), 6.83 (t, 1, J=4 Hz, HC=C). Found: C, 70.22; H, 9.31%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

*4-Methyl-3-methoxycarbonyl-2-cyclohexen-1-one (**2b**).* A mixture of **2a** (1.79 g, 12 mmol) and SeO_2 (1.92 g, 17 mmol) in dioxane (10 ml) was heated at 85 °C for 20 h and at reflux for 3 h. The precipitate was filtered and washed with benzene. The combined filtrates were concentrated and the residue was dissolved in CH_2Cl_2 (20 ml). To this solution was added dropwise a chromium trioxide solution[21] with vigorous stirring for 30 min under N_2 at 0 °C. The mixture was worked up in the usual manner and the crude product was chromatographed (SiO_2, hexane–ether 2:1) to give 928 mg (46%) of **2b** as an oil: bp 132.0—133.0 °C/9 Torr; IR (neat) 1722 (ester C=O), 1683 (C=O), 1620 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 1.23 (d, 3, J=7 Hz, CH_3), 1.63—2.27 (m, 2, CH_2), 2.35 (t, 2, J=2 Hz, $COCH_2$), 2.65—3.20 (m, 1, CH), 3.76 (s, 3, OCH_3), 6.42 (s, 1, HC=C); ^{13}C NMR δ 18.0 (q, C_4–Me), 28.8 (d, C-4), 29.1 (t, C-5), 33.4 (t, C-6), 52.4 (q, OMe), 131.8 (d, C-2), 153.2 (s, C-3), 166.7 (s, ester C=O), 199.6 (s, C-1). Found: C, 64.13; H, 7.35%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

Methyl cis-*4β-Methyl-1-oxo-*$\Delta^{6,7}$*-octalin-4a-carboxylate (**3a**) and Methyl* trans-*4β-Methyl-1-oxo-*$\Delta^{6,7}$*-octalin-4a-carboxylate (**3b**).* A mixture of **2b** (2.95 g, 17.5 mmol), 1,3-butadiene (2.3 g, 41.0 mmol) and 2,5-di-*t*-butylhydroquinone (50 mg) in benzene (10 ml) was heated at 150—160 °C for 3 days in a sealed tube and extracted with hot MeOH. The extract was filtered and the filtrate was concentrated. Distillation at 80—90 °C/3 Torr afforded an unchanged **2b** (1.14 g) and the residue in the flask was chromatographed (SiO_2, hexane–AcOEt 2:1) to give 263 mg (11% based on recovered **2b**, R_f 0.75, hexane–AcOEt 2:1) of **3a** and 1.08 g (45%, R_f 0.68) of **3b**. The physical constants together with elemental analyses of **3a** and **3b** are as follows: **3a**, mp 84.0—85.0 °C (hexane); IR (Nujol) 3027, 1720 (ester C=O), 1714 (C=O), 1653 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 1.12 (d, 3, J=7 Hz, CH_3), 1.70—2.60 (m, 9, CH_2, CH), 3.00—3.40 (m, 1, COCH), 3.69 (s, 3, OCH_3), 5.55 (m, 2, HC=C). Found: C, 70.38; H, 8.32%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%. **3b**: mp 88.0—89.0 °C (hexane); IR (Nujol) 3018, 1721 (ester C=O), 1698 (C=O), 1655 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.94 (d, 3, J=6.5 Hz, CH_3), 1.68—2.50 (m, 9, CH_2, CH), 2.69—3.10 (m, 1, COCH), 3.59 (s, 3, OCH_3), 5.60 (m, 2, HC=C). Found: C, 70.36; H, 8.32%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

*Conversion of **3a** into **3b**.* A mixture of **3a** (32 mg, 0.14 mmol) and MeONa (10 mg, 0.19 mmol) in MeOH (0.5 ml) was stirred for 24 h at room temperature and worked up in the usual manner to give 32 mg (100%) of **3b** as a solid.

Methyl 1,1-Ethylenedioxy-4β-methyl-$\Delta^{6,7}$*-octalin-4a-carboxylate (**5a**).* A mixture of **3b** (420 mg, 1.89), ethylene glycol (2.3 g, 37.0 mmol), and *p*-toluenesulfonic acid (50 mg) in benzene (40 ml) was refluxed for 24 h in a Dean-Stark apparatus and worked up in the usual manner to give 466 mg (92%) of **5a** as an oil: bp 61.0—63.0 °C/0.01 Torr (Kugelrohr); IR (neat) 3022, 1727 (ester C=O), 1664 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.92—1.05 (m, 3, CH_3), 1.35—2.85 (m, 10, CH_2, CH), 3.62—3.80 (m, 3, OCH_3), 3.95 (br s, 4, CH_2O), 5.49—5.88 (m, 2, HC=C). Found: C, 67.57; H, 8.49%. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33%.

4aβ-Hydroxymethyl-4β-methyl-$\Delta^{6,7}$*-octalin-1-one Ethylene Acetal (**5b**).* To a suspension of $LiAlH_4$ (50 mg, 1.32 mmol)

in THF (2 ml) was added a solution of **5a** (115 mg, 0.43 mmol) in THF (2 ml) at 0 °C. The mixture was stirred for 10 h at room temperature, quenched with AcOEt (1 ml) and 5% aqueous $NaHCO_3$, and worked up in the usual manner to give 95 mg (93%) of **5b** as an oil: bp 57.0—59.5 °C/0.005 Torr (Kugelrohr); IR (neat) 3450 (OH), 3021, 1660 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.79—1.09 (m, 3, CH_3), 1.18—2.64 (m, 10, CH_2, CH), 3.59 (br s, 1, OH), 3.00—3.70 (m, 2, CH_2O), 3.78—4.10 (m, 4, CH_2O), 5.60 (br s, 2, HC=C). Found: C, 70.68; H, 9.41%. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30%.

4β-Methyl-4aβ-methylsulfonyloxymethyl-$\Delta^{6,7}$*-octalin-1-one Ethylene Acetal (**5c**).* A mixture of **5b** (386 mg, 1.62 mmol), $MeSO_2Cl$ (592 mg, 5.2 mmol), and pyridine (2.5 ml) was stirred for 2 h at 0 °C and for 3 h at room temperature, quenched with cold aqueous 5% $NaHCO_3$, and worked up in the usual manner to give 500 mg (97%) of **5c** as an oil: IR (neat) 3028, 1671 (C=C), 1175 cm^{-1} (SO_2); ^1H NMR (60 MHz) δ 0.92 (d, 3, J=7 Hz, CH_3), 1.40—2.59 (m, 10, CH_2, CH), 3.01 (s, 3, SO_2CH_3), 3.93 (s, 4, CH_2O), 4.29 (AB_q, 2, J=8 Hz, CH_2O), 5.63 (br s, 2, HC=C). Found: C, 57.11; H, 7.79%. Calcd for $C_{15}H_{24}O_5S$: C, 56.95; H, 7.65%.

1,1-Ethylenedioxy-4β-methyl-$\Delta^{6,7}$*-octalin-4aβ-carbaldehyde (**5d**).* To a suspension of pyridinium chlorochromate (117 mg, 0.44 mmol) and AcONa (42 mg, 0.51 mmol) in CH_2Cl_2 (3 ml) was added a solution of **5b** (35 mg, 0.15 mmol) in CH_2Cl_2 (1 ml) at 0 °C. The mixture was stirred for 30 min at 0—5 °C and for 3 h at room temperature, diluted with ether, and passed through short silica gel column eluting with ether. The elute was concentrated and the residue was chromatographed (SiO_2, hexane–AcOEt 3:1) to give 29 mg (84%) of **5d** as an oil: bp 88.5—90.0 °C/0.015 Torr (Kugelrohr); IR (neat) 3015, 2750, 2680, 1712 (C=O), 1662 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.83—1.08 (m, 3, CH_3), 1.27—2.81 (m, 10, CH_2, CH), 3.85—4.01 (m, 4, CH_2O), 9.50, 10.02 (s, 1, CHO). Found: C, 71.31; H, 8.76%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

4β-Methyl-4aβ-methylsulfonyloxymethyl-$\Delta^{6,7}$*-octalin-1-one (**6**).* A solution of **5c** (90 mg, 0.28 mmol) and 70% $HClO_4$ (90 mg) in THF (3 ml) and water (1.5 ml) was stirred for 1 h at 0 °C and for 10 h at room temperature and worked up in the usual manner to give 76 mg (98%) of **6**: IR (neat) 3033, 1710 (C=O), 1656 (C=C), 1177 cm^{-1} (SO_2); ^1H NMR (60 MHz) δ 0.92—1.34 (m, 3, CH_3), 1.57—2.78 (m, 10, CH_2, CH), 2.93, 3.02 (s, 3, SO_2CH_3), 4.18 (s, 2, CH_2O), 5.64 (m, 2, HC=C). Found: C, 57.30; H, 7.66%. Calcd for $C_{13}H_{20}O_4S$: C, 57.34; H, 7.40%.

*5,6-*cis*-5-Methyltricyclo[4.4.1.0*^{1,6}*]undec-8-en-2-one (**7**).* To a solution of **6** (257 mg, 0.95 mmol) in MeOH (2 ml) was added a solution of MeONa (254 mg, 4.7 mmol) in MeOH (2.5 ml). The mixture was stirred for 24 h at room temperature and worked up in the usual manner to give 139 mg (84%) of **7** as an oil: bp 40.5—42.0 °C/0.02 Torr (Kugelrohr); IR (neat) 3079, 3030, 1680 cm^{-1} (C=O); ^1H NMR (60 MHz) δ 0.76—2.83 (m, 11, CH_2, CH), 1.05 (d, 3, J=6 Hz, CH_3), 5.49—5.33 (m, 2, HC=C); ^{13}C NMR δ 14.4 (t, C-11), 18.4 (q, C-12), 25.1 (t, C-10), 26.7 (t, C-4), 29.4 (t, C-7), 31.6 (s, C-6), 32.9 (d, C-5), 34.2 (s, C-1), 36.4 (t, C-3), 122.2, 123.6 (d, C-9, C-8), 210.1 (s, C-2). Found: C, 81.84; H, 9.03%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

trans-*4β,4aβ-Dimethyl-*$\Delta^{6,7}$*-octalin-1-one (**8**) and 5,6-*cis*-5-Methylbicyclo[4.4.1]undec-8-en-2-one (**9**).* To a blue solution of lithium (84 mg, 12.1 mmol) in liquid NH_3 (*ca.* 30 ml) was added a solution of **7** (245 mg, 1.39 mmol) and *t*-BuOH (104 mg, 1.39 mmol) in DME (4 ml). After being stirred for 1.5 h at −78 °C, the blue solution was quenched with NH_4Cl (500 mg), allowed to stand at room temperature until liquid NH_3 had evaporated, and worked up in the usual manner. The crude product was chromatographed (SiO_2, hexane–AcOEt 4:1) to give 202 mg (83%) of **8** (R_f 0.8, hexane–AcOEt 2:1) and 24 mg (10%) of **9** (R_f 0.5). Physical constants together with elemental analyses of **8** and **9** are as follows: **8**, bp 38.0—39.5 °C/0.02 Torr (Kugelrohr); IR (neat) 3025, 1711 (C=O), 1658 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.63 (s, 3, CH_3), 0.91 (d, 3, J=6 Hz, CH_3), 1.53—2.56 (m, 10, CH_2, CH), 5.63 (m, 2, HC=C). Found: C, 80.94; H, 10.27%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. **9**: mp 91.0—95.0 °C; IR (Nujol) 3019, 1698 (C=O), 1656 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.93 (m, 3, CH_3), 1.05—2.56 (m, 13, CH_2, CH), 5.65 (m, 2, HC=C). Found: C, 80.94; H, 9.94%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

trans-*4β,4aβ-Dimethyl-*$\Delta^{6,7}$*-octalin-1-one Ethylene Acetal (**10**).* A mixture of **8** (131 mg, 0.73 mmol), ethylene glycol (700 mg, 11.3 mmol), and *p*-toluenesulfonic acid (40 mg) in benzene (30 ml) was refluxed for 24 h in a Dean-Stark apparatus and worked up in the usual manner to give 158 mg (97%) of **10** as an oil: bp 73.0—75.0 °C/0.03 Torr (Kugelrohr); IR (neat) 3020, 1559 (C=C), 1159, 1092, 1040, 985, 897 cm^{-1}; ^1H NMR (100 MHz) δ 0.81 (s, 3, CH_3), 0.84 (d, 3, J=6 Hz, CH_3), 1.10—2.44 (m, 10, CH_2, CH), 3.72—4.04 (m, 4, CH_2O), 5.61 (br s, 2, HC=C). Found: C, 75.64; H, 10.03%. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%.

trans-*4β,4aβ-Dimethyl-*$\Delta^{6,7}$*-octalin-1β-ol (**12**).* To a suspension of $LiAlH_4$ (64 mg, 1.69 mmol) in THF (2 ml) was added a solution of **8** (100 mg, 0.56 mmol) in THF (2 ml) at 0 °C. The mixture was stirred for 1 h at 0—5 °C and for 9 h at room temperature, and worked up in the usual manner to give 91 mg (90%) of **12** as white crystals: mp 52.5—53.5 °C; IR (Nujol) 3330 (OH), 3012, 1658 cm^{-1} (C=C); ^1H NMR (60 MHz) δ 0.86 (complex d, 3, J=5 Hz, CH_3), 0.88 (s, 3, CH_3), 1.07—2.65 (m, 10, CH_2, CH), 1.64 (s, 1, OH), 3.76 (m, 1, CHO), 5.55 (m, 2, HC=C). Found: C, 79.68; H, 10.99%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

trans-*6α,7α-Epoxy-4β,4aβ-dimethyldecalin-1β-ol (**13a**).* To a solution of *m*-CPBA (208 mg, 1.21 mmol) in CH_2Cl_2 (3 ml) was added a solution of **12** (128 mg, 0.71 mmol) in CH_2Cl_2 (1 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 20 h at 5 °C, washed with aqueous 10% $Na_2S_2O_3$ (3 ml), aqueous 5% NaOH, and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, hexane–AcOEt 2:1) to give 127 mg (91%) of **13a** as an oil: bp 37.0—38.0 °C/0.0075 Torr (Kugelrohr); IR (neat) 3444 (OH), 3020, 1258, 1227, 1150, 1043, 1013 cm^{-1}; ^1H NMR (60 MHz) δ 0.82 (unresolved m, 3, CH_3), 0.88 (s, 3, CH_3), 1.07—2.26 (m, 11, CH_2, CH, OH), 2.98—3.36 (m, 2, CHO), 3.70 (br s, 1, CHO). Found: C, 73.59; H, 10.45%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%.

trans-*6α,7α-Epoxy-4β,4aβ-dimethyldecalin-1β-ol Tetrahydropyranyl Ether (**13b**).* A mixture of **13a** (123 mg, 0.63 mmol), 2,3-dihydropyran (1.01 g, 11.9 mmol), and pyridinium *p*-toluenesulfonate[18] (79 mg, 0.31 mmol) in CH_2Cl_2 was stirred for 20 h at room temperature, diluted with ether (5 ml), and worked up in the usual manner. The crude product was chromatographed (SiO_2, hexane–AcOEt 4:1) to give 136 mg (77%) of **13b** as an oil: bp 63.0—66.0 °C/0.004 Torr (Kugelrohr); IR (neat) 1439, 1352, 1202, 1129, 1072, 1031, 1022 cm^{-1}; ^1H NMR (60 MHz) δ 0.70—0.99 (m, 3, CH_3), 0.88 (s, 3, CH_3), 1.06—2.41 (m, 16, CH_2, CH), 2.97—3.33 (m, 2, CHO), 3.33—4.18 (m, 3, CH_2O, CHO),

4.43—5.54 (m, 1, CHO). Found: C, 72.59; H, 10.09%. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06%.

trans-*7α-Hydroxy-4β,4aβ-dimethyldecalin-1β-ol Tetrahydropyranyl Ether (**14a**).* To a blue solution of lithium (84 mg, 12.1 mmol) in liquid NH_3 (*ca.* 25 ml) was added a solution of **13b** (136 mg, 0.48 mmol) in DME (4 ml). The mixture was stirred for 1 h at −78 °C and for 1.5 h at −33 °C, quenched with NH_4Cl (500 mg), and worked up in the usual manner. The crude product was chromatographed (SiO_2, hexane–AcOEt 2:1) to give 116 mg (85%) of **14a** as an oil: bp 123.0—126.0 °C/0.005 Torr (Kugelrohr); IR (neat) 3370 (OH), 1255, 1200, 1132, 1110, 1077, 1056, 1022, 1000 cm^{-1}; ^1H NMR (60 MHz) δ 0.80 (unresolved d, 3, J=6 Hz, CH_3), 0.87 (s, 3, CH_3), 1.08—2.17 (m, 19, CH_2, CH, OH), 3.26—4.00 (m, 3, CH_2O, CHO), 4.12 (m, 1, CHO), 4.45—4.73 (m, 1, CHO). Found: C, 72.16; H, 10.78%. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71%.

trans-*8β-Tetrahydropyranyloxy-4aβ,5β-dimethyldecalin-2-one (**14b**).* To a suspension of pyridinium chlorochromate (299 mg, 1.12 mmol) and AcONa (183 mg, 2.23 mmol) in CH_2Cl_2 (3 ml) was added a solution of **14a** (105 mg, 0.37 mmol) in CH_2Cl_2 (2 ml) at 0 °C. After being stirred for 0.5 h at 0—5 °C and for 3 h at room temperature, the mixture was diluted with ether (3 ml) and passed through a short silica gel column eluting with ether. The elute was concentrated and the residue was chromatographed (SiO_2, hexane–AcOEt 2:1) to give 97 mg (93%) of **14b** as an oil: bp 96.0—99.0 °C/0.01 Torr (Kugelrohr); IR (neat) 1710 cm^{-1} (C=O); ^1H NMR (60 MHz) δ 0.91 (d, 3, J=5 Hz, CH_3), 1.09 (s, 3, CH_3), 1.28—2.99 (m, 18, CH_2, CH), 3.27 (m, 3, CH_2O, CHO), 4.41—4.74 (m, 1, CHO). Found: C, 72.91; H, 10.15%. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06%.

trans-*8β-Hydroxy-4aβ,5β-dimethyldecalin-2-one (**15a**).* A solution of **14b** (96 mg, 0.34 mmol) and pyridinium *p*-toluenesulfonate (20 mg, 0.08 mmol) in EtOH (3 ml) was stirred for 20 h at 60—63 °C. The mixture was concentrated and the residue was chromatographed (SiO_2, hexane–AcOEt 2:1) to give 64 mg (95%) of **15a** as a white solid: mp 87.0—88.5 °C; IR (Nujol) 3405 (OH), 1695 cm^{-1} (C=O); ^1H NMR (100 MHz) δ 0.91 (d, 3, J=6 Hz, CH_3), 1.13 (s, 3, CH_3), 1.25—2.09 (m, 8, CH_2, CH), 2.00 (s, 1, OH), 2.13—2.99 (m, 4, CH_2CO), 3.76 (br s, 1, CHO); ^{13}C NMR δ 13.2 (q, C-9), 15.6 (q, C-10), 25.3 (t, C-6), 34.2 (t, C-7), 35.9 (s, C-4a), 38.2 (t, C-3), 39.6 (t, C-4), 42.1 (d, C-8a), 42.1 (t, C-1), 42.7 (d, C-5), 70.7 (d, C-8), 213.3 (s, C-2). Found: C, 73.26; H, 9.99%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%.

trans-*4aβ,5β-Dimethyl-8β-methylsulfonyloxydecalin-2-one (**15b**).* A mixture of **15a** (60 mg, 0.31 mmol), $MeSO_2Cl$ (178 mg, 1.55 mmol), and pyridine (1.5 ml) was stirred for 1 h at 0 °C and for 2 h at room temperature, quenched with cold water and worked up in the usual manner to give 73 mg (88%) of **15b**; IR (neat) 1710 (C=O), 1378, 1178 cm^{-1} (SO_2); ^1H NMR (100 MHz) δ 0.94 (d, 3, J=6 Hz, CH_3), 1.08 (s, 3, CH_3), 1.17—2.87 (m, 12, CH_2, CH), 3.00 (s, 3, SO_2CH_3), 4.72 (m, 1, CHO). Found: C, 57.06; H, 8.28%. Calcd for $C_{13}H_{22}O_4S$: C, 56.92; H, 8.08%.

*4aβ,5β-Dimethyl-$\Delta^{1,8a}$-octalin-2-one (**16a**).* A mixture of **15b** (73 mg, 0.266 mmol) and DMSO (2 ml) was heated at 130—140 °C for 2 h, and worked up in the usual manner. The crude product was chromatographed (SiO_2, hexane–AcOEt 3 : 1) to give 33 mg (64%) of **16a** as an oil: bp 72.5—75.0 °C/0.02 Torr (Kugelrohr) (lit,[17] 96.0—99.0 °C/0.2 Torr); IR (neat) 1675 (C=O), 1615 (C=C), 1235, 1188, 1030, 955, 877 cm^{-1}; ^1H NMR (60 MHz) δ 0.93 (unresolved d, 3, J=6 Hz, CH_3), 1.10 (s, 3, CH_3), 1.10—2.53 (m, 11, CH_2, CH), 5.69 (br s, 1, HC=C); ^{13}C NMR δ 15.3 (q, C-10), 16.0 (q, C-9), 26.5 (t, C-7), 30.5 (t, C-8), 33.3 (t, C-6), 34.0 (t, C-3), 35.5 (t, C-4), 39.0 (s, C-4a), 43.2 (d, C-5), 124.0 (d, C-1), 171.4 (s, C-8a), 199.7 (s, C-2).

*3α-(1-Hydroxy-1-methylethyl)-4aβ,5β-dimethyl-$\Delta^{1,8a}$-octalin-2-one (**16b**).* To a stirred solution of *i*-Pr_2NLi (103 mg, 0.96 mmol) in THF (1.5 ml) was added a solution of **16a** (19 mg, 0.11 mmol) in THF (0.5 ml). After being stirred for 40 min at −78 °C, a solution of $ZnCl_2$ (14 mg, 0.11 mmol) in ether (0.5 ml) was added and to this mixture acetone (62 mg, 1.1 mmol) was added. The mixture was stirred for 10 min, quenched with cold aqueous 5% tartaric acid, and extracted with ether–benzene. The extract was washed with brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, hexane–AcOEt 4:1) to give 20 mg (79%) of **16b**; IR (neat) 3440 (OH), 3027, 1650 (C=O), 1626 cm^{-1} (C=C); ^1H NMR (100 MHz) δ 0.93 (unresolved d, 3, J=6 Hz, CH_3), 1.14 (s, 3, CH_3), 1.23 (s, 6, CH_3), 1.29—2.62 (m, 10, CH_2, CH), 4.72 (br s, 1, OH), 5.70 (s, 1, HC=C); ^{13}C NMR δ 15.1 (q, C-10), 15.9 (q, C-9), 24.6 (q, C-12), 26.2 (t, C-7), 28.3 (q, C-13), 30.4 (t, C-8), 32.9 (t, C-6), 38.6 (t, C-4), 39.6 (s, C-4a), 43.6 (d, C-5), 51.2 (d, C-3), 72.4(s, C-11), 124.6 (d, C-1), 172.0 (s, C-8a), 203.3 (s, C-2), Found: C, 76.33; H. 10.37%. Calcd for $C_{15}H_{24}O_2$: C, 76.32; H, 10.24%.

dl-*Dehydrofukinone (**1**).* To a solution of **16b** (18 mg, 0.076 mmol) in pyridine (0.5 ml) was added $MeSO_2Cl$ (74 mg, 0.65 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature and for 2 h at 40—45 °C, quenched with cold water, and worked up in the usual manner. The crude product was chromatographed (SiO_2, hexane–AcOEt 4:1) to give 12 mg (72%) of a mixture of double bond isomers **17** (3-isopropenyl:3-isopropylidene *ca.* 5:1 based on ^1H NMR): bp 47.0—52.0 °C/0.01 Torr (Kugelrohr); IR (neat) 1674 (C=O), 1624 (C=C), 883 cm^{-1}; ^1H NMR (60 MHz) δ 4.83, 4.98 (br s, HC=C). Without further separation of the double bond isomers, **17** was passed through an activated alumina 300 (Nakarai Chemicals) column (10 g) with hexane–AcOEt (10:1) to give **1** in a quantitative yield: bp 48.0—53.0 °C/0.01 Torr (Kugelrohr); IR (neat) 1663 (C=O), 1629 (C=C), 1459, 1439, 1373, 1294, 1221, 1196, 1101, 1035, 884, 846 cm^{-1}; ^1H NMR (100 MHz) δ 0.92 (unresolved m, 3, CH_3), 0.97 (s, 3, CH_3), 1.16—1.66 (m, 5, CH_2, CH), 1.85, 2.09 (s, 3, $C=C(CH_3)_2$), 2.16—2.40 (m, 5, CH_2), 2.88 (d, 1, J= 14 Hz, COCH), 5.76 (s, 1, HC=C); ^{13}C NMR δ 15.4 (q, C-10), 16.0 (q, C-9), 22.0 (q, C-12), 22.5 (q, C-13), 26.5 (t, C-7), 30.5 (t, C-8), 32.5 (t, C-6), 41.0 (t, C-4), 41.9 (s, C-4a), 42.5 (d, C-5), 126.1 (d, C-1), 128.1 (s, C-3), 142.1(s, C-11), 168.6 (s, C-8a), 192.2 (s, C-2).

*Conversion of **17** into **1** with $RhCl_3 \cdot 2H_2O$.* A solution of **17** (26 mg, 0.12 mmol) and $RhCl_3 \cdot 2H_2O$ (2 mg, 0.008 mmol) in EtOH (2.5 ml) was heated at 95—100 °C for 6 h in a sealed tube. The mixture was concentrated and the residue was chromatographed (SiO_2, hexane–AcOEt 4:1) to give 18 mg (86%) of **1**.

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