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REARRANGEMENT APPROACHES TO CYCLIC SKELETONS. V.[1] FORMAL BRIDGEHEAD SUBSTITUTION OF 1-METHOXYBICYCLO[3.2.2]NON-6-EN-2-ONES AND ITS APPLICATION TO A TOTAL SYNTHESIS OF (±)-WIDDROL

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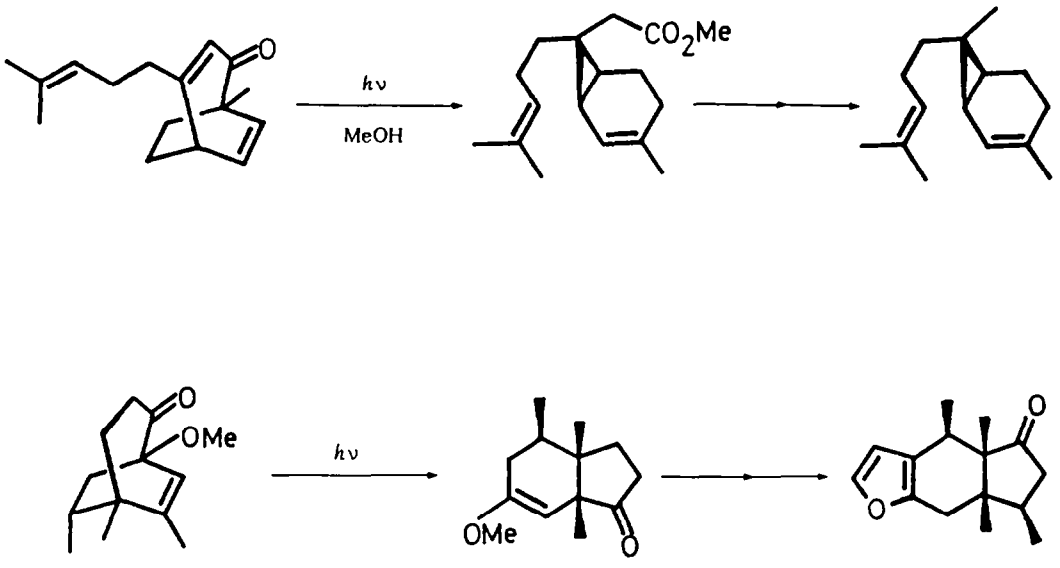
Abstract - The C-1 methoxy group of bicyclo[3.2.2]non-6-en-2-ones is replaced by alkyl, alkenyl, and aryl groups or hydrogen with inversion of the absolute configuration via the two-step sequence consists of Grignard reaction or reduction of the carbonyl followed by pinacol-type rearrangement. This transformation was applied to the total synthesis of the [6-7] fused-ring sesquiterpene widdrol ((±)-**9**). The stereochemistry of the tertiary alcohol of **9** was specifically controlled by employing a bridge-cleaving method.

Sesquiterpenes offer a variety of synthetic targets including [m-n] fused-ring compounds. An important step of a fused-ring sesquitepene synthesis is the skeletal construction which sometimes governs the step economy and the total yield. Many practical methods have already been developed for syntheses of [m-n] fused-ring sesquiterpenes.[3,4] In general, these methods are classified into cyclization, cycloaddition, and rearrangement. The proportion of rearrangement approaches has been increasing in recent years. Among them, more noticeable are rearrangements of bridged polycyclic compounds into fused-ring polycyclic systems.

Bridged polycyclic compounds are easily prepared by cycloaddition or cyclization. Chemical modification of these compounds are highly stereoselective. Most of the rearrangements of bridged compounds to give fused-ring systems are stereospecific processes. These facts are found in rearrangement approaches to fused-ring sesquiterpenes using bicyclo[2.2.1]heptane[5,6] and bicyclo[2.2.2]octane[7-9] derivatives.

Recently, it has been reported that the rearrangement approaches using the bicyclo[3.2.2]nonane derivatives are successful to prepare the [3-6] and [5-6] fused-ring sesquiterpenes, as shown in Scheme 1.[10,11] The [3-6] fused-ring skeleton was constructed by photochemical [3,3]-sigmatropic rearrangement of the bicylo[3.2.2]nona-3,6-dien-2-one (**1**). The primary product of the rearrangement is the ketene derivative which reacts with methanol to give the ester (**2**). (±)-Sesquicarene (**3**) was prepared easily from **2**. The [5-6] fused-ring compound (**5**), the key synthetic intermediate of (±)-pinguisone (**6**), was derived by photochemical [1,3]-acyl migration of the bicyclo[3.2.2]non-6-en-2-one (**4**).

Scheme 1. Rearrangement approaches to the [3-6] and [5-6] fused-ring sesquiterpenes.

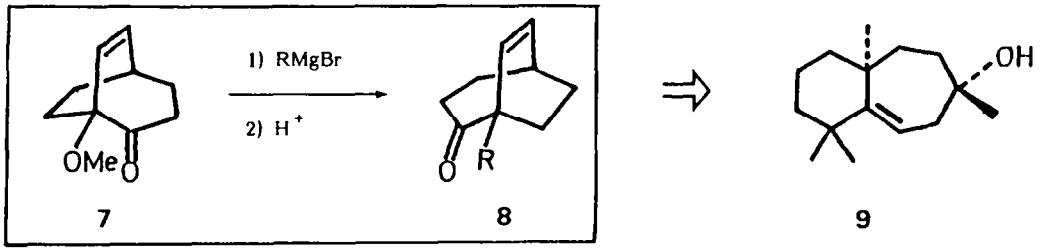


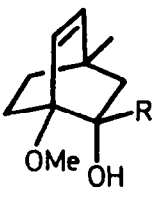
In order to expand this type of synthetic strategy, we have to develop methods for modification of the bridged system as well as those for skeletal transformation. We report herein a method to introduce an alkyl or aryl group at the C-1 bridgehead position of a bicyclo[3.2.2]non-6-en-2-one, namely, conversion of **7** into **8** via Grignard reaction followed by the pinacol-type rearrangement, and its application to the total synthesis of the [6-7] fused-ring sesquiterpene widdrol (**9**) (Scheme 2).

The pinacol-type rearrangement of 1-methoxybicyclo[2.2.2]oct-5-en-2-ols (**10** and **11**), the lower homologs of our system, is known to give bicyclo[3.2.1]octenones (**12** and **13**).[12] Treatment of **10** with an acid gave only **12**, whereas that of **11** afforded **12** and **13** in a ratio of 1 : 1 - 1 : 3. It is interesting whether this kind of selectivity is observed in the rearrangement of bicyclo[3.2.2]-nonenols.

Widdrol was isolated from various species of Widdringtonia[13] and from Thujopsis dolabrata, Sieb. et Zucc,[14] in early 1960's. This compound has attracted widespread attention as a result of its chemical and biochemical relationship to thujopsene[15] and the total synthesis involving the remote stereocontrol of the tertiary alcohol part.[16]

Scheme 2.





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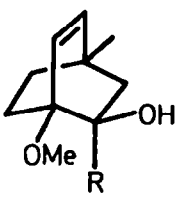

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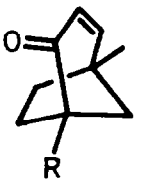


13

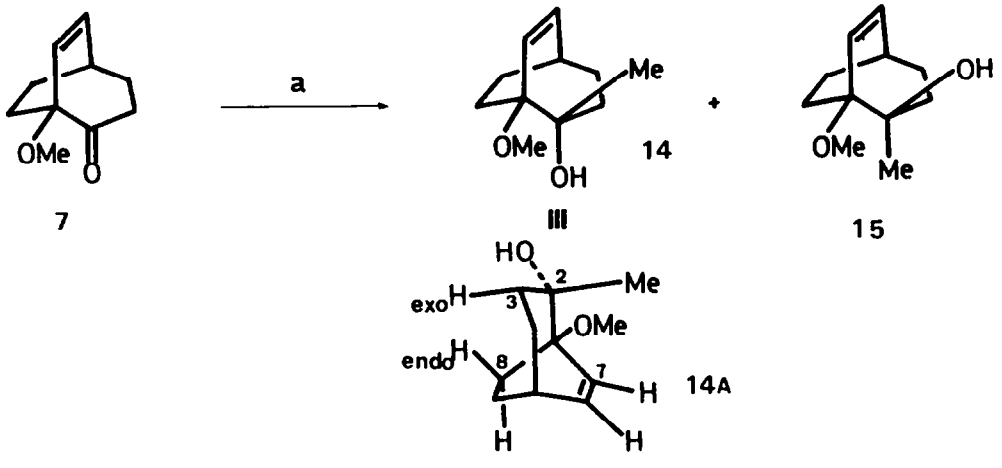
RESULTS

Stereostructures of 1-methoxybicyclo[3.2.2]non-6-en-2-ols.

A reaction of the ketone (**7**) with methylmagnesium bromide gave the alcohols (**14**) and (**15**). The 2-D-NOESY spectrum of **14** shows the presence of the effect between the C-2 methyl protons and the C-7 proton. This reflects that the three-carbon bridge of the stable conformer of **14** should be bent toward the saturated bridge, like the conformer **14A**. The other NMR data for **14** also support this bending; the presence of the long-range coupling between the C-2 methyl protons and the $C\text{-}3_{exo}$ proton ($J<1$ Hz) indicates the dihedral angle between the C-Me bond and the C-H bond is approximately 180°. The signals due to the $C\text{-}8_{endo}$ proton which should be close to the oxygen of the hydroxyl group appear at the relatively lower field, $\delta=2.07$, and show the long-range coupling between the C-7 proton. In contrast, the NMR spectrum of **15** indicates a sharp singlet due to the C-2 methyl protons and no signals due to the methylene protons below $\delta=1.9$.

This unexpected conformational information corresponds with the results of the empirical force-field MM2 method for the bicyclic system.[17] The most stable conformer calculated for bicyclo[3.2.2]-non-6-ene is **16A** whose three-carbon bridge is also bent toward the saturated bridge. The steric energy calculated for **16A** is 1.3 kcal/mol lower than that for **16B**. The basic conformers **17A** and **18A** were calculated 1.3 and 1.7 kcal/mol more stable than **17B** and **18B**, respectively. Unfortunately, we can not calculate accurate steric energies for the conformers of **14** and **15**, because that some torsional parameters are unknown.[18]

Scheme 3.



7 III 14 15 14A

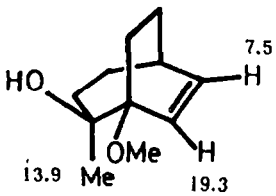
(a) MeMgBr.

16A X=Y=H
17A X=OH, Y=Me
18A X=Me, Y=OH

16B X=Y=H
17B X=OH, Y=Me
18B X=Me, Y=OH

These stereochemical assignments to **14** and **15** are different from those proposed previously on the basis of lanthanoid-induced shift (LIS) studies on their proton-NMR spectra. Thus, we have re-examined LIS values of these and the related compounds whose structural assignments were unequivocally determined. The results are shown in Fig. 1. The values for the olefinic protons of each exo-alcohol are larger than the corresponding ones of the endo isomer. Although the origin of this observation is uncertain, it should be at least mentioned that the equilibrium constant for the formation of complexed substrates with the shift reagent depend largely upon even stereoisomeric difference between the substrates. Thus, stereochemical assignments of isomeric compounds on the basis of intermolecular LIS studies must be carried out with great care.

Other 1-methoxybicyclo[3.2.2]non-6-en-2-ols (**24** and **25**) for the study of the pinacol-type rearrangement were derived from the ketone (**23**) by treatment with organolithium compounds, Grignard reagents, and reducing agents (Scheme 4, and Table 2 in experimental part). The reactions of **23** with Grignard reagents gave the exo-alcohols **24** mainly, while the reactions with organolithium compounds afforded the endo-alcohols **25** predomonantly. A reaction of **23** with isopropylmagnesium bromide gave the tertiary alcohols (**24d** and **25d**) along with the secondary ones (**24h** and **25h**). Thus, this bicyclic ketone should be regard as a relatively hindered one. The structural assignments of **24** and **25** are based on spectral similarity to **14** and **15**, respectively.



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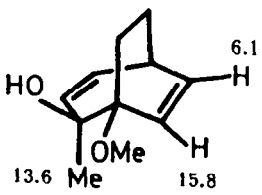

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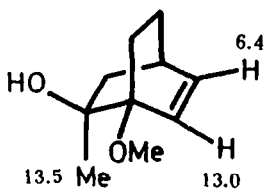

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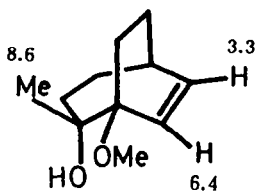

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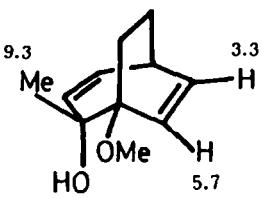

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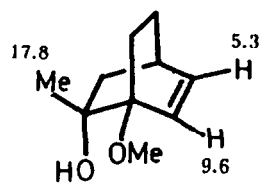

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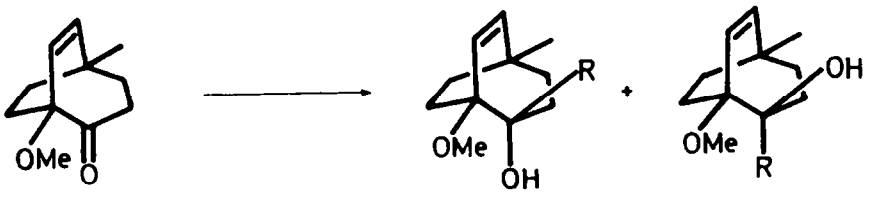
Fig. 1. Representative LIS values for the protons of 1-methoxybicyclo[3.2.2]non-6-en-2-ols and the related compounds using $Eu(fod)_3$.

Scheme 4.



23 24 25

a X=Me, b X=Et, c X=^{n}Bu
d X=^{i}Pr, e X=Ph, f X=vinyl
g X=allyl, h X=H

Pinacol-type rearrangement of 1-methoxybicyclo[3.2.2]non-6-en-2-ols.

This rearrangement proceeds by treating with p-toluensulfonic acid (TsOH). As illustrated in Scheme 5, treatment of the exo-alcohols (**24**) with TsOH gave only the β,γ-unsaturated ketones (**26**). In contrast with these, the endo-alcohols (**25**) were transformed into **26** along with the α,β-unsaturated ketones **27**. Authentic samples of **27a**, **27c**, **27d**, and **27e** were prepared from the respective isomers (**26**) via the four-step sequence: i) catalytic hydrogenation, ii) α-phenylsulfenylation, iii) oxidation to sulfoxides, and iv) desulfenylation. The ketone **27f** was prepared from 5-methyl-1-vinylbicyclo[3.2.2]nonan-2-one which could be derived from **23** by the three-step transformation: i) catalytic hydrogenation, ii) treatment with vinylmagnesium bromide, and iii) pinacol-type rearragement by treating with TsOH.

Each of the exo-alcohols reacted more rapidly than the corresponding endo-isomer. Predominant formation of **26** from **25** was enhanced by appropriate selection of the solvent (runs 4-6, and 9-11). Toluene and benzene are suitable solvents. For the reactions of **25**, the ratio of the products depends the size and nature of the substituent, R. The proportion of **26** increases as the stabilizing effect of the substituent for a carbocation, such as **28**, increases. This and the exclusive formation of **26** from **24** seem to suggest that the stepwise process via the carbenium ion **28** gives only **25** and the

Scheme 5. Pinacol-type rearrangement of 1-methoxybicyclo[3.2.2]non-6-en-2-ols.

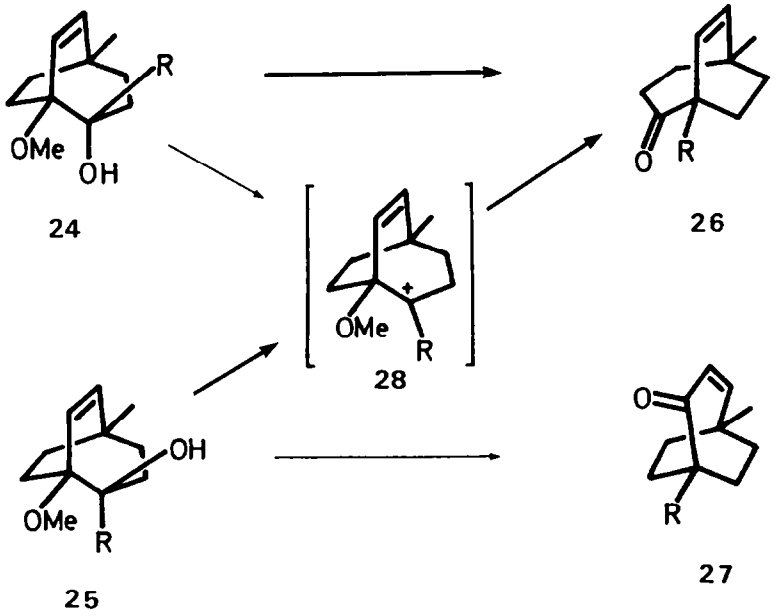


Table 1. Pinacol-type rerrangement of 1-methoxybicyclo[3.2.2]non-6-en-2-ols.

Run	substrate	TsOH/equiv.	solvent	temp/ °C	time/h	products (ratio)[a]	yield/%
1	**24a**	1.0	AcOH-H2O[b]	60	1.5	**26a**	88
2	**24a**	0.1	DCE[c]	reflux	1	**26a**	91
3	**24a**	0.1	PhMe	85	1.1	**26a**	90
4	**25a**	1.0	AcOH-H2O[b]	60	24	**26a**, **27a** (1.1 : 1)	68
5	**25a**	0.1	DCE[c]	reflux	12	**26a**, **27a** (1.4 : 1)	71
6	**25a**	0.1	PhMe	85	12	**26a**, **27a** (3 : 1)	69
7	**24b**	1.0	PhH	reflux	0.5	**26b**	90
8	**24c**	0.1	PhMe	85	0.75	**26c**	91
9	**25c**	0.1	AcOH	85	7	**26c**, **27c** (5.3 : 1)	70
10	**25c**	0.1	DCE[c]	85	7	**26c**, **27c** (4.5 : 1)	89
11	**25c**	0.1	PhMe	85	7	**26c**, **27c** (9.1 : 1)	88
12	**24d**	0.1	PhMe	85	0.5	**26d**	91
13	**25d**	0.1	PhMe	85	1	**26d**, **27d** (24 : 1)	86
14	**24e**	0.1	PhMe	85	0.5	**26e**	99
15	**25e**	0.1	PhMe	85	1.5	**26e**, **27e** (21 : 1)	81
16	**24f**	1.0	PhH	reflux	0.15	**26f**	83
17	**25f**	0.1	PhH	reflux	0.3	**26f**, **27f** (22 : 1)	86
18	**24g**	1.0	PhH	reflux	0.25	**26g**	84
19	**24h**	1.0	PhH	reflux	1	**26h**	81
20	**25h**	1.0	PhH	reflux	8	**27h**	<25

(a) Based on their 90-MHz ^{1}H-NMR spectra. (b) In a ratio of 4 : 1. (c) 1,2-Dichloroethane.

simultaneous migration of the saturated bridge with departure of the hydroxyl group of **25** to give **27** is a minor pathway of the reaction.

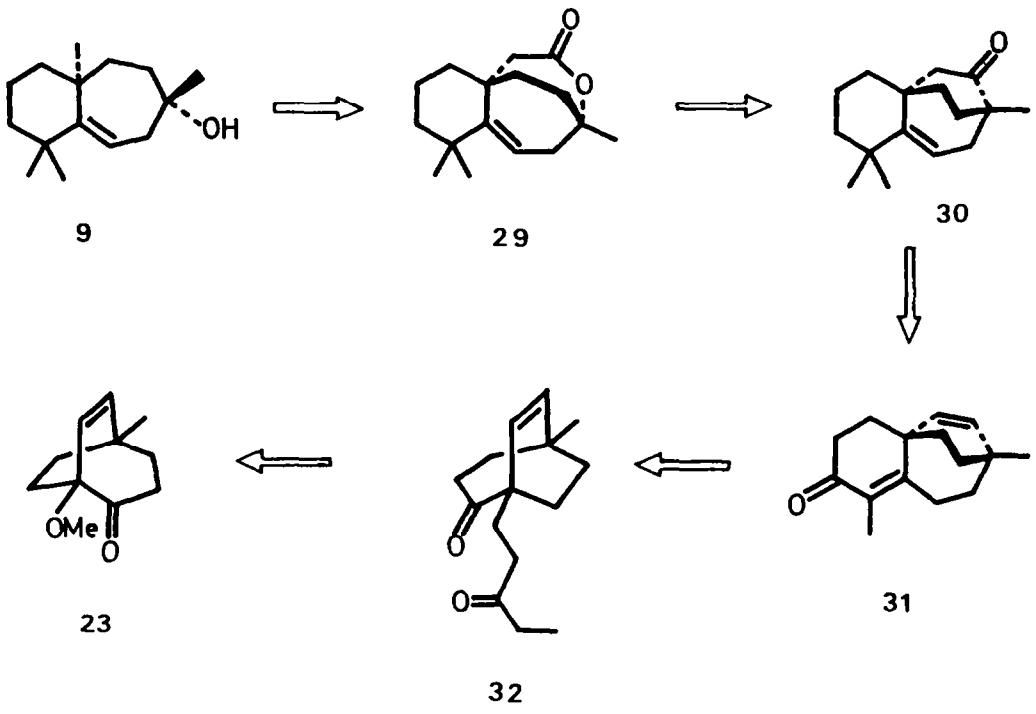
Run 19 shows that the methoxy group of **23** can be replaced by hydrogen. Reactivity of the secondary exo-alcohol **24h** was lower than that of the tertiary exo-alcohols. Acid treatment of the secondary endo-alcohol **25h** did not give good results (run 20). The α, β -unsaturated ketone (**27h**) was derived in 52% yield from the methanesulfonate of **25h** by treating with TsOH (1 equiv.) in boiling benzene for 3 h.

The main mode of this pinacol-type rearrangement is very similar to that of the lower homologs **10** and **11**.[12]

A total synthesis of (±)-widdrol (**9**).

Our approach to widdrol was based on stereospecific elaboration of the tertiary alcohol part by a ring-cleavage method. As shown in Scheme 6, it was anticipated that widdrol (**9**) would be accessible from the lactone (**29**), which in turn would be produced upon Baeyer-Villiger oxidation of the ketone (**30**). The synthetic precursor of ketone **30** can be seen to be the conjugated ketone (**31**) which in turn might be prepared from the diketone (**32**). This diketone would be derived from **23** via the pinacol-type rearrangement.

Scheme 6.

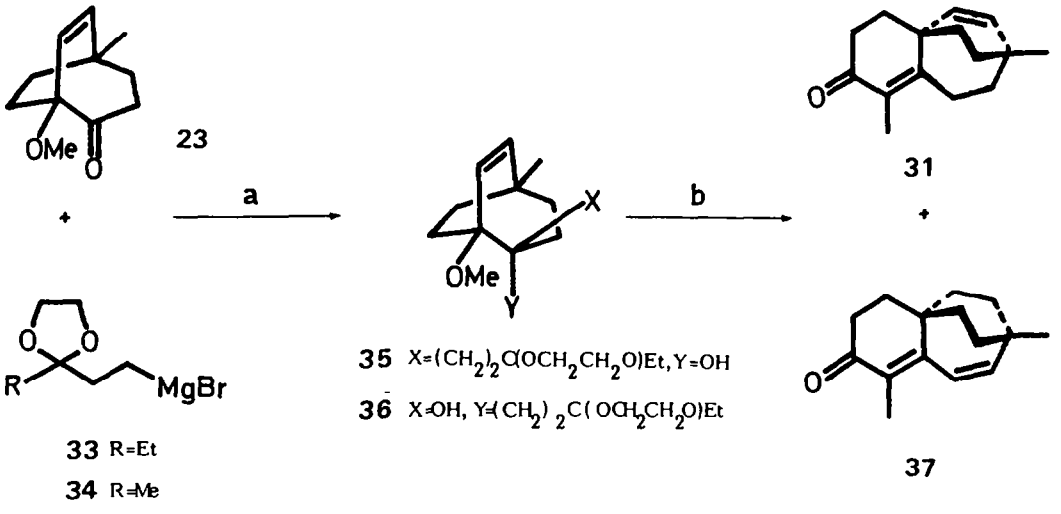


The Grignard reagent (**33**)[19] was derived from 2-(2-bromoethyl)-2-ethyl-1,3-dioxolane by the slightly modified method developed for 3,3-ethylenedioxybutylmagnesiumbromide (**34**).[20] A reaction of the Grignard reagent (**33**) with **23** in THF to give the alcohols (**35** and **36**) was very slow at room temperature; complete consumption of **23** was observed only after 18 hours. In the case of **34** which shows similar reactivity, the rate of addition to a carbonyl compound was increased by selection of the solvent.[20] Our procedure developed to accelerate the reaction is irradiation with ultrasound. The ketone **23** was consumed within 1.5 h, when a mixture of **23** and **33** (3 equiv.) was sonicated in THF at 25 °C. The total yield of the alcohols is high enough (>90%) in each case.

Treatment of the alchohols with 0.1-1.0 equiv. of TsOH in boiling benzene gave a complex mixture of the products. When 2 equivalents of TsOH was employed, each of the alcohols was transformed into the 5 : 1 mixture of the tricyclic dienones (**31** and **37**) in good yield. This transformation is due to the tandem [pinacol-type rearrangement]-[aldol-type condensation]. Formation of **37** from the exo-alcohol **35** had not been expected on the basis of the data described previously. This fact may suggest that **35** and **36** are interconvertible under the reaction conditions. The oxygen atom of the side chain may participate in the early stage of the tandem transformation. The desired dienone **31** was purified by recrystallization from hexane.

Selective methylation of **31** to give **38** was carried out in 88% yield by treating with potassium pentoxide and methyl iodide in THF. Contamination with **37** did not hinder this methylation. The product **38** was separated easily from unreacted **37** by silica-gel column chromatography. Wolff-Kishner reduction of **38** was performed under rigorously oxygen-free conditions to give the hydrocarbon **39** in 81% yield. When the reaction mixture was allowed to contact with atomosphere, the etheno bridge of **39** was redused. Hydroboration of **39** using thexylborane followed by hydrogen peroxide oxidation gave a mixture of two alcohols in 60% and 26% yields, respectively. Collins oxidation of the major alcohol gave the desired ketone **30** in 90% yield. The regioisomer **40** was obtained from the minor alcohol in 89% yield. The UV spectrum of **40** indicates the presence of a chromophore due to the β,γ-unsaturated ketone.

Scheme 8.

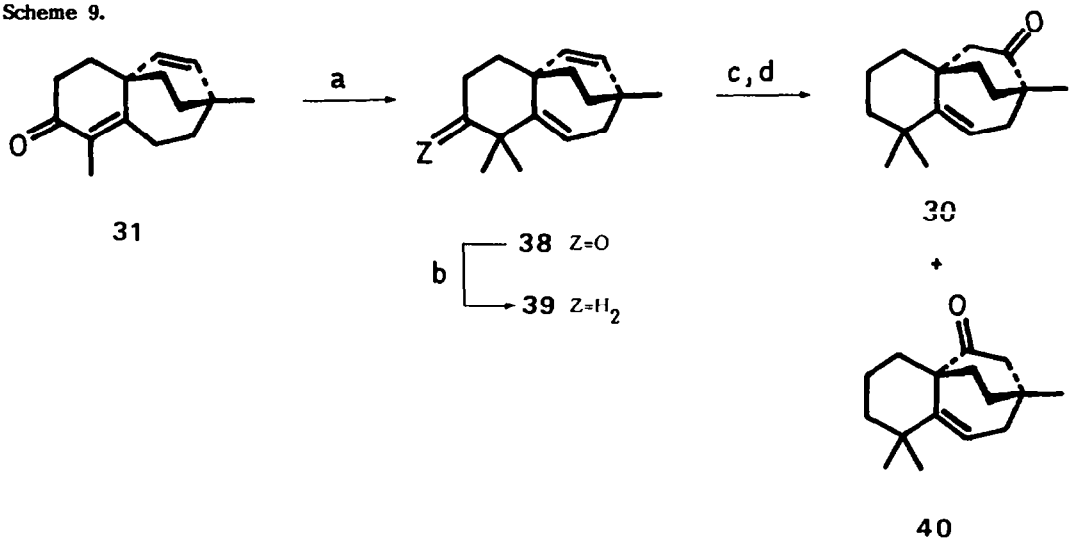


(a) Sonication, THF. (b) TsOH (2 equiv.), PhH, reflux.

Baeyer-Villiger oxidation of **30** was examined under various conditions. The trisubstituted olefin was oxidized rapidly by peracids and **30** was inert to hydrogen peroxide. A conbination of bis-(trimethylsilyl)peroxide and BF_3 etherate[21] was only adaptable to this end. The lactone **29** was derived in 43% yield.

Reduction of **29** with $LiAlH_4$ gave the diol **41**, whose primary and tertiary hydroxyl groups were protected as a t-butyldimethylsilyl ether and an acetate, respectively. The silyl ether was cleaved by acetic acid in aqueous THF.[22] Collins oxidation of the resulting alcohol gave the aldehyde **42** (in 60% yield from **29**). Decarbonylation of **42** was carried out using chlorotris(triphenylphosphine)-rhodium.[23] With just one equivalent of Wilkinson's complex, heating of a benzonitrile solution of

Scheme 9.

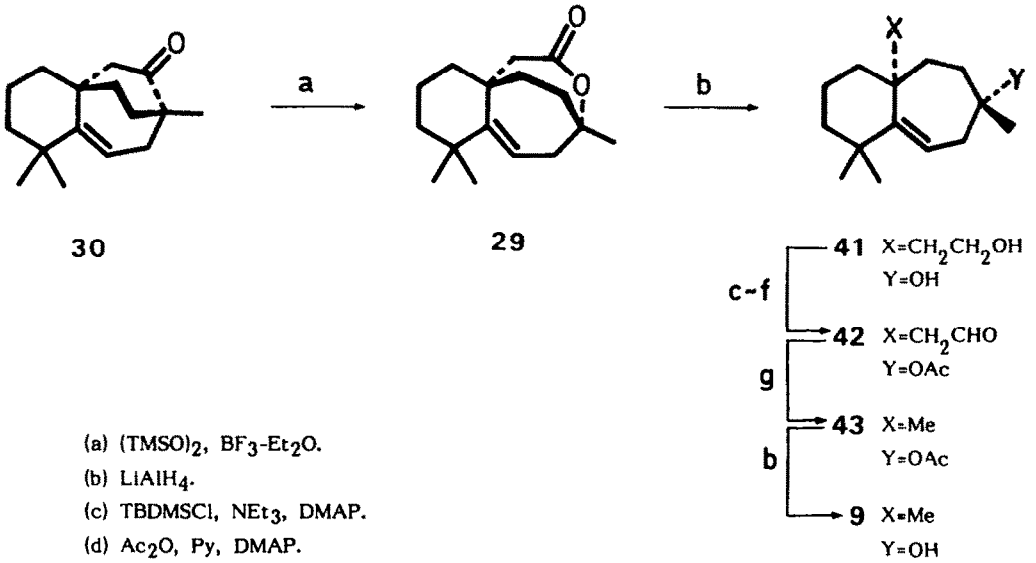


(a) $KOC(Me)_2Et$, MeI, THF. (b) NH_2NH_2-H_2O, KOH, $HO(CH_2)_3OH$.
(c) i $(Me)_2CHC(Me)_2BH_2$; ii H_2O_2, NaOH. (d) CrO_3-2Py, CH_2Cl_2.

42 at 143 °C gave the decarbonylation product **43** in 93% yield. Finally, reduction of **43** with $LiAlH_4$ gave the tertiary alcohol, in 96% yield, whose spectroscopic properties are identical with those of natural widdrol **9**.

The present studies disclose that introduction of a side chain at the C-1 bridgehead of a bicyclo-[3.2.2]non-6-en-2-one has been accomplished via Grignard reaction to the 1-methoxy derivative followed by pinacol-type rearrangement of the resulting alcohols and this transformation is applicable to the total synthesis of the [6-7] fused-ring sesquiterpene widdrol.

Scheme 10.



(a) $(TMSO)_2$, BF_3-Et_2O.
(b) $LiAlH_4$.
(c) TBDMSCl, NEt_3, DMAP.
(d) Ac_2O, Py, DMAP.
(e) AcOH, H_2O, THF (1 : 3 : 10)
(f) CrO_3-2Py, CH_2Cl_2.
(g) $Rh(PPh_3)Cl$, PhCN.

Experimental

General. Melting points were determined with a Yamato MP-21 capillary melting point apparatus and are uncorrected. UV (in cyclohexane) and IR spectra (in CCl_4) were recorded on Hitachi Model 323 and 215 spectrometers, respectively. ^1H NMR spectra (in CCl_4, unless otherwise noted) were obtained on JEOL JEOL JNM-PMX60, Varian EM-390 90 MHz, and JEOL XL-400 NMR specrometers, using tetramethylsilane as an internal standared. The mass spectral studies were conducted using a Hitachi M-52 spectrometer. Tetrahydrofuran (THF) and ether were distilled from benzophenone-sodium under argon, immediately prior to use. Dichloromethane and 1,2-dichloroethane were distilled from P_2O_5 and stored on 4A molecular sieves. Benzene and toluene were distilled from P_2O_5 and stored over sodium wire. Bis(trimethylsilyl)-peroxide,[24] S-phenyl benzenethiosulfonate,[25] and PCC[26] were prepared by using literature procedures. All reactions were monitored by analytical TLC using E. Merck precoated silica gel $60F_{254}$ plates. Column chromatography was carried out with E. Merck silica gel 60 (70-230 mesh ASTM). Sonication was csrried out using a Shimmyoudai 150 W ultrasonic cleaner.

1-Methoxy-endo-2-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**14**) and its C-2 stereoisomer (**15**). (As general procedure).

To a solution of the ketone (**7**, 359 mg, 2.39 mmol) in THF (5 ml) was added 1 M methylmagnesium bromide solution in THF (3.6 ml) at -78 °C under argon, and the mixture was stirred for 30 min. Saturated aqueous ammonium chloride solution was added, and the products were extracted with three portions of ether. The combined extracts were washed with water and saturated brine, and dried over $MgSO_4$. After removal of the solvent, the remaining oil was chromatographed on silica gel (10g; 20 : 1 then 10 : 1 hexane, ethyl acetate). There were obtained **14** (107.2 mg, 27%) and **15** (168.8 mg, 43%).

14: Colorless oil; IR 3580 (m), 3050 (w), 1130 (s), 1110 (s), 1095 (s), 1080 (s), and 715 (s); NMR ($CDCl_3$) δ=6.24 (H_6, dd, J=9.8 and 7.6 Hz), 5.91 (H_7, d, J=9.8 Hz), 3.27 (OMe, s), 2.36 (H_5, m), 2.07 ($H_{8\text{-endo}}$, m), 1.93 ($H_{3\text{-exo}}$, broad ddd, J=14.2, 14.2, and 5.9 Hz), 1.78-1.55 (5H, m), 1.47 (1H, m), and

1.15 (Me, d, J=0.97 Hz); MS (13.5 eV) m/z (rel intensity) 182 (M^+, 98.1), 167 (3.8), 164 (34.6), 150 (10.2), 124 (100), and 84 (65.6).

15: Colorless oil; IR 3560 (broad s), 3040 (w), 1135 (m), 1100 (sh), and 1090 (s); NMR ($CDCl_3$) δ=6.33 (H_6, dd, J=9.8 and 7.4 Hz), 6.08 (H_7, d, J=9.8 Hz), 3.32 (OMe, s), 2.46 (H_5, broad), 1.86-1.53 (7H, m), 1.43 (1H, m), and 1.21 (Me, s); MS (13.5 eV) m/z (rel intensity) 182 (M^+, 50.8), 164 (15.9), 124 (100), 111 (11.8), and 84 (20.3).

Table 2. Preparation of 1-methoxybicyclo[3.2.2]non-6-en-2-ols **24** and **25**.[a]

Reagent	solvent	temp./°C	products (yield/%)
MeMgI	ether	0	**24a** (59) **25a** (30)
MeLi	ether	-78	**24a** (18) **25a** (72)
EtMgBr	ether	-78	**24b** (64) **25b** (18)
^{n}BuMgBr	ether	0	**24c** (38), **25c** (30)
^{n}BuLi	THF	-78	**24c** (18), **25c** (52)
^{i}PrMgBr	ether	0	**24d** (18), **24h** (32), **25d** (12), **25h** (7)
^{i}PrBr,Li[b]	THF	0	**24d** (15), **25d** (30)
PhMgBr	ether	0	**24e** (18), **25d** (42)
PhBr,Li[b]	THF	0	**24e** (14), **25e** (51)
CH_2=CHMgBr	THF	-78	**24f** (66), **25f** (13)
CH_2=$CHCH_2$MgBr	ether	-25	**24g** (64), **25g** (23)
LiB(CHMeEt)$_3$H	THF	-78	**24h** (55), **25h** (23)
LiALH(OBut)$_3$	ether	-20	**24h** (52), **25h** (32)

(a) For general procedure; see preparation of **14** and **15**. (b) Irradiation of ultrasounds for 1 h.

1-Methoxy-endo-2,5-dimethylbicyclo[3.2.2]non-6-en-exo-2-ol (**24a**): Colorless oil; IR 3580 (m), 3060 (w), 1140 (s), 1095 (s), and 720 (s) cm^{-1}; NMR δ=5.77 (2H, s), 3.23 (3H, s), 2.59 (1H, broad s), 2.2-1.1 (8H, m), 1.06 (3H, d, J<1H), and 1.00 (3H, s). Found: C, 73.00; H, 10.42%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%.

1-Methoxy-exo-2,5-dimethylbicyclo[3.2.2]non-6-en-endo-2-ol (**25a**): Colorless oil; IR 3575 (w), 3550 (w), 3040 (w), 1100 (sh), 1080 (s), and 710 (w) cm^{-1}; NMR δ=5.91 (1H, d, J=8.9 Hz), 5.81 (1H, d, J=8.9 Hz), 3.26 (3H, s), 1.93 (1H, broad s), 1.8-1.1 (8H,m), 1.10 (3H, s), and 1.04 (3H, s); MS (13.5 eV) m/z (rel intensity) 196 (M^+, 7), 179 (7), 178 (11), 163 (31), and 124 (100).

1-Methoxy-endo-2-ethyl-5-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**24b**). Colorless oil; IR 3575 (m), 3040 (w), 1140 (s), 1095 (s), 980 (s), and 720 (s) cm^{-1}; NMR δ=5.78 (1H, d, J=10.2 Hz), 5.76 (1H, d, J=10.2 Hz), 3.21 (3H, s), 2.31 (1H, broad s), 2.3-1.1 (10H, m), 1.00 (3H, d, J<1H), and 0.78 (3H, t, J=7.2 Hz).

1-Methoxy-exo-2-ethyl-5-methylbicyclo[3.2.2]non-6-en-endo-2-ol (**25b**). Colorless oil; IR 3600 (sh), 3560 (w), 3040 (w), 1095 (s), and 970 (m) cm^{-1}; NMR δ=5.89 (1H, d, J=9.7 Hz), 5.80 (1H, d, J=9.7 Hz), 3.23 (3H, s), 1.96 (1H, broad s), 1.85-1.1 (10H, m), 1.04 (3H, s), and 0.86 (3H, t, J=7.2 Hz).

1-Methoxy-endo-2-butyl-5-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**24c**). Colorless oil; IR 3570 (m), 3040 (w), 1145 (m), 1138 (m), 1095 (s), 980 (s), and 720 (s) cm^{-1}; NMR δ=5.85 (1H, d, J=9.9 Hz), 5.83 (1H, d, J=9.9 Hz), 3.20 (3H, s), 2.37 (1H, broad s), 2.2-0.75 (17H, m), and 1.00 (3H, s). Found: C, 75.31; H, 11.21%. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99%.

1-Methoxy-exo-2-butyl-5-methylbicyclo[3.2.2]non-6-en-endo-2-ol (**25c**). Colorless oil; IR 3600 (sh), 3560 (w), 3040 (w), 1095 (s), and 980 (m) cm^{-1}; NMR δ=5.89 (1H, d, J=9.0 Hz), 5.81 (1H, d, J=9.0 Hz), 3.22 (3H, s), 1.95 (1H, broad s), 1.85-0.8 (17H, m), 1.04 (3H, s). Found: C, 75.85; H, 10.92%. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99%.

1-Methoxy-endo-2-isopropyl-5-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**24d**). Colorless oil; IR 3570 (m), 3040 (w), 1130 (s), 1090 (s), 985 (s), and 715 (s) cm^{-1}; NMR δ=5.94 (1H, dd, J=9.0 and 0.75 Hz), 5.78 (1H, dd, J=9.0 and 1.0 Hz), 3.20 (3H, s), 2.50 (1H, broad s), 2.1-1.1 (9H, m), 1.00 (3H, s), 0.83 (3H, d, J=7.2 Hz), and 0.79 (3H, d, J=7.2 Hz). Found: C, 74.87; H, 10.76%. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%.

1-Methoxy-exo-2-isopropyl-5-methylbicyclo[3.2.2]non-6-en-endo-2-ol (**25d**). Colorless oil; IR 3600 (sh), 3560 (w), 3045 (w), 1095 (s), and 980 (m) cm^{-1}; NMR δ=5.94 (1H, d, J=9.8 Hz), 5.78 (1H, d, J=9.8 Hz), 3.26 (3H, s), 2.2-1.25 (10H, m), 1.06 (3H, s), 0.94 (3H, d, J=7.2 Hz), and 0.89 (3H, d, J=7.2 Hz). Found: C, 74.96; H, 10.73%. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%.

1-Methoxy-5-methyl-endo-2-phenylbicyclo[3.2.2]non-6-en-exo-2-ol (**24e**). Colorless oil; IR 3570 (m), 3105 (w), 3070 (w), 3040 (w), 1115 (sh), 1105 (sH), 1085 (s), 720 (s), and 700 (s) cm^{-1}; NMR δ=8.45- 8.3 (2H, m), 8.15-8 (3H, m), 5.71 (1H, dd, J=9.5 and 1 Hz), 5.40 (1H, dd, J=9.5 and 1.0 Hz), 3.39 (1H, broad), 3.17 (3H, s), 2.5-1.3 (8H, m), and 1.07 (3H, s).

1-Methoxy-5-methyl-exo-2-phenylbicyclo[3.2.2]non-6-en-endo-2-ol (**25e**). Colorless oil; IR 3580 (broad w), 3105 (w), 3070 (w), 3040 (w), 1090 (s), and 703 (s) cm^{-1}; NMR δ=8.55-8.4 (2H, m), 8.25-8.05 (3H, m), 6.01 (1H, d, J=9.0 Hz), 5.92 (1H, d, J=9.0 Hz), 3.05 (3H, s), 2.4-1.2 (8H, m), and 1.10 (3H, s), MS (13.5 eV) m/z (rel intensity) 258 (M^+ 27), 243 (6), 240 (90), and 125 (100).

1-Methoxy-5-methyl-endo-2-vinylbicyclo[3.2.2]non-6-en-exo-2-ol (**24f**). Colorless oil; IR 3570 (m), 3105 (w), 3070 (w), 3040 (w), 1115 (sh), 1105 (sH), 1085 (s), 720 (s), and 718 (s) cm^{-1}; NMR δ=6.08 (1H, dd, J=16.5 and 10.2 Hz), 5.83 (1H, d, J=9.0 Hz), 5.77 (1H, dd, J=9.0 Hz), 5.16 (1H, dd, J=16.5 and 2.2 Hz), 4.89 (1H, dd, J=10.5 and 2.2 Hz), 3.19 (3H, s), 2.70 (1H, broad s), 2.2-1.1 (8H, m), and 1.01 (3H, s); MS (13.5 eV) m/z (rel intensity) 208 (M^+ 6), 190 (20.5), and 94 (100). Found: C, 74.61; H, 9.73%. Calcd for $C_{13}H_{20}O_2$: C, 74.96 H, 9.68%.

1-Methoxy-5-methyl-exo-2-vinylbicyclo[3.2.2]non-6-en-endo-2-ol (**25f**). Colorless oil; IR 3600 (broad w), w), 3550 (s), 3095 (w), 3040 (w), 1110 (s), 1095 (s), 1085 (sh), and 715 (m) cm^{-1}; NMR δ=5.98 (1H, dd, J=16.5 and 10.5 Hz), 5.90 (1H, d, J=9.8 Hz), 5.84 (1H, d, J=9.8 Hz), 5.20 (1H, dd, J=16.5 and 1.8 Hz), 4.96 (1H, dd, J=10.5 and 1.8 Hz), 3.21 (3H, s), 2.10 (1H, broad s), 1.95-1.05 (8H, m), and 1.06 (3H, s). MS (13.5 eV) m/z (rel intensity) 208 (M^+ 8), 190 (34), 175 (30.5), and 94 (100). Found: C, 75.22; H, 9.73%. Calcd for $C_{13}H_{20}O_2$: C, 74.96 H, 9.68%.

1-Methoxy-endo-2-allyl-5-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**24g**). Colorless oil; IR 3580 (m), 3090 (w), 3040 (w), 1095 (s), and 720 cm^{-1}; NMR δ=5.83 (2H, s), 5.82 (1H, dddd, J=16.0, 10.6, 8.3, and 5.7 Hz), 4.97 (1H, broad s), 4.81 (1H , broad d, J=10.6 Hz), 3.21 (3H, s), 2.48 (1H, broad s), 2.3-1.1 (10H, m), and 1.00 (3H, s).

1-Methoxy-exo-2-allyl-5-methylbicyclo[3.2.2]non-6-en-endo-2-ol (**25g**). Colorless oil; IR 3600 (sh), 3575 (w), 3090 (w), 3045 (w), 1095 (s), and 915 (m) cm^{-1}; NMR δ=5.92 (1H, d, J=9.3 Hz), 5.85 (1H, m), 5.83 (1H, d, J=9.3 Hz), 5.03 (1H, broad s), 3.21 (1H, m), 3.25 (3H, s), 2.45 (1H, ddt J= 14.3, 6.0, and 1.5 Hz)), 2.03 (1H, dd, J=14.3 and 8.7 Hz), 1.85-1.1 (8H, m), and 1.04 (3H, s).

1-Methoxy-5-methylbicyclo[3.2.2]non-6-en-exo-2-ol (**24h**). Colorless oil; IR 3580 (m), 3040 (w), 1095 (s), and 720 (s) cm^{-1}; NMR δ=5.84 (2H, s), 3.38 (1H, m), 3.24 (3H, s), 2.85 (1H, broad), 2.1-1.1 (8H, m), and 1.02 (3H, s).

1-Methoxy-5-methylbicyclo[3.2.2]non-6-en-endo-2-ol (**25h**). Colorless oil; IR 3580 (broad w), 3045 (w), 1095 (s), 1075 (s), 1055 (s), and 715 (s) cm^{-1}; NMR δ=5.75 (2H, s), 3.41 (1H, t, J=5.3 Hz), 3.21 (3H, s), 2.17 (1H, broad), 2.0-1.1 (8H, m), and 1.04 (3H, s). Hz), 4.89 (1H, dd, J=10.5 and 2.2 Hz), 3.19 (3H, s), 2.70 (1H, broad s), 2.2-1.1 (8H, m), and 1.01 (3H, s).

General Procedure for Pinacol-type Rearrangement. 1,5-Dimethylbicyclo[3.2.2]non-6-en-2-one (**26a**).

(a) A solution of **24a** (104.9 mg, 0.534 mmol) and TsOH (105.7 mg, 1 equiv.) in 80% acetic acid (5.5 ml) was heated at 60 °C for 90 min. The solution was diluted with ether, washed with several portions of water, saturated aqueous $NaHCO_3$ solution, and brine, dried over $MgSO_4$, and then concentrated in vacuo. Column chromatography (3 g of silica gel; 15 : 1 hexane-ethyl acetate) of the residue (106.7 mg) gave **26a** in 88% yield (76.8 mg, 0.47 mmol).

(b) A solution of **24a** (111.3 mg, 0.567 mmol) and TsOH (10 mg, 0.053 mmol) in toluene (3.8 ml) was heated at 85 °C for 70 min. Evaporation of the solvent followed by chromatography (4 g of silica gel; 20 : 1 hexane-ethyl acetate) gave **26a** in 90% yield (83.8 mg, 0.51 mmol).

26a: Colorless oil; IR 3035 (w), 1705 (s), and 710 (m) cm^{-1}; NMR δ=5.82 (1H, d, J=9.0 Hz), 5.59 (1H, d, J=9.0 Hz), 2.47 (2H, m), 2.05-1.3 (6H, m), 1.13 (3H, s), and 1.11 (3H, s); MS (25 eV), m/e (rel intensity) 164 (M^+, 42), 149 (8), 108 (100), and 103 (98). Found: C, 80.74; H, 9.97%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82%. The 2,4-DNP derivative of **26a**: Mp 170.5-171.5 °C. Found: C, 59.27; H, 5.95; N, 16.24%. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27%.

1-Ethyl-5-methylbicyclo[3.2.2]non-6-en-2-one (**26b**). Colorless oil; IR 3035 (w), 1705 (s), and 715 (m) cm^{-1}; NMR δ=5.89 (1H, d, J=9.0 Hz), 5.64 (1H, d, J=9.0 Hz), 2.6-2.35 (2H, m), 2.0-1.4 (8H, m), 1.11 (3H, s), and 0.79 (3H, t, J=7.2 Hz). Found: C, 80.99; H, 10.33%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

1-Butyl-5-methylbicyclo[3.2.2]non-6-en-2-one (**26c**). Colorless oil; IR 3035 (w), 1705 (s), and 715 (m) cm^{-1}; NMR δ=5.87 (1H, d, J=9.0 Hz), 5.65 (1H, d, J=9.0 Hz), 2.55-2.35 (2H, m), 2.0-1.1 (12H, m), 1.11 (3H, s), and 0.91 (3H, dd, J=7.5 and 5.7 Hz). Found: C, 80.71; H, 11.61%. Calcd for $C_{14}H_{24}O$: C, 80.94; H, 11.71%.

1-Isopropyl-5-methylbicyclo[3.2.2]non-6-en-2-one (**26d**). Colorless oil; IR 3045 (w), 1700 (s), and 710 (s) cm^{-1}; NMR δ=5.90 (1H, d, J=9.0 Hz), 5.66 (1H, d, J=9.0 Hz), 2.6-2.2 (2H, m), 2.0-1.4 (8H, m), 1.10 (3H, s), 0.82 (3H, d, J=6.5 Hz), and 0.76 (3H, t, J=6.5 Hz). Found: C, 80.93; H, 10.75%. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%.

5-Methyl-1-phenylbicyclo[3.2.2]non-6-en-2-one (**26e**). Colorless needles; mp 76.5-78.0 °C; IR 3110 (w), 3075 (w), 3045 (w), 1710 (s), and 700 (s) cm^{-1}; NMR δ=7.3-6.9 (5H, m), 5.21 (1H, d, J=9.0 Hz), 5.03

(1H, d, J=9.0 Hz), 2.9-1.4 (8H, m), and 1.16 (3H, s); MS (25 eV) m/z (rel intensity) 226 (M^+, 45.3), 211 (8), 170 (100), and 155 (65). Found: C, 84.95 H, 7.93%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%.

5-Methyl-1-vinylbicyclo[3.2.2]non-6-en-2-one (**26f**). Colorless oil; IR 3090 (w), 3030 (w), 1705 (s), and 708 (m) cm^{-1}; NMR δ=6.27 (1H, dd, J=17.0 and 11.0 Hz), 5.95 (1H, d, J=9.0 Hz), 5.89 (1H, d, J=9.0 Hz), 5.07 (1H, dd, J=11.0 and 1.0 Hz), 4.97 (1H, dd, J=17.0 and 1.0 Hz), 2.48 (2H, t, J=7.2 Hz), 2.2-1.4 (6H, m), and 1.16. The 2,4-DNP derivative: Mp 162.0-163.0 °C (decomp). Found: C, 60.63; H, 5.71; N, 15.46%. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.72%.

1-Allyl-5-methylbicyclo[3.2.2]non-6-en-2-one (**26g**). Colorless oil; IR 3080 (w), 3040 (w), 1705 (s), and 712 (s) cm^{-1}; NMR δ=6.05-5.35 (3H, m), 5.1-4.8 (2H, m), 2.55-2.2 (4H, m), 2.0-1.4 (6H, m), and 1.11 (3H, s). The 2,4-DNP derivative: Mp 135.5-136.5 °C (decomp). Found: C, 61.85; H, 6.28; N, 14.92%. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.99; N, 15.13%.

5-Methylbicyclo[3.2.2]non-6-en-2-one (**26h**). Colorless oil; IR 3045 (w), 1710 (s), and 715 (s) cm^{-1}; NMR δ=6.05-5.85 (2H, m), 2.92 (1H, broad), 2.5-2.3 (2H, m), 2.0-1.4 (8H, m), and 1.14 (3H, s). The 2,4-DNP derivative: Mp 173.0-174.0 °C. Found: C, 58.15 H, 5.58; N, 16.82%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.18; H, 5.49; N, 16.96%.

General Procedure for Preparation of bicyclo[3.2.2]non-3-en-2-ones (**27**). 1,5-Dimethylbicyclo[3.2.2]-non-3-en-2-one (**27a**).

Catalytic hydrogenation of **24a** in ethanol was carried out using 5% Pd-C to give 1,5-dimethylbicyclo[3.2.2]nonan-2-one. A solution this ketone (176.6 mg, 1.06 mmol) in THF (2 ml) was added to a solution of lithium diisopropylamide (1.22 mmol) in THF (2 ml) at -78 °C. After stirring for 30 min, the solution was allowed to warm to room temperature and stand for 15 min. To this enolate solution, cooled to -78 °C, was added a solution of S-henyl benzenethiosulfonate (292.9 mg, 1.17 mmol) in THF (3 ml). The mixture was allowed to warm slowly to room temperature, treated with saturated aqueous NH_4Cl solution, and extracted with two portions of ether. The combined extracts were washed with saturated brine and dried over Na_2SO_4. Evaporation of the solvent gave a mixture of the sulfides (301 mg), which was treated with sodium periodate (249.9 mg, 1.21 mmol) in 90% methanol at 30 °C for 20 h. The reaction mixture was extracted with three portions of dichloromethane. The combined extracts were dried over $MgSO_4$ and concentrated. The remaining oil was chromatographed on silica gel (12 g; 10 : 1 benzene-ethyl acetate) to give a mixture of the sulfoxides (237.9 mg, 0.82 mmol, 77%). The mixture (187.5 mg, 0.645 mmol) was heated under reflux in toluene (6.5 ml) with calcium carbonate (130 mg, 1.29 mmol) for 3 h. The reaction mixture was diluted with ether, washed with water and saturated brine, dried over $MgSO_4$, and concentrated. Chromatography of the remaining oil (134.7 mg) on silica gel (5 g; 25 : 1 hexane-ethyl acetate) gave **27a** as colorless oil (85.4 mg, 0.549 mmol, 80.5%).

27a: Colorless oil; IR 3035 (w), 1670 (s), and 1385 (m) cm^{-1}; NMR δ=6.52 (1H, d, J=11.0 Hz), 5.92 (1H, d, J=11.0 Hz), 1.57 (8H, s), 1.19 (3H, s), and 1.15 (3H, s); MS (25 eV) m/e (rel intensity) 154 (M^+, 56), 149 (18.2), 136 (12.5), 108 (77.8), and 107 (100). The 2,4-DNP derivative: Mp 133.5-135.0 °C; C, 59.53; H, 6.12; N, 16.02%. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27%.

1-Butyl-5-methylbicyclo[3.2.2]non-3-en-2-one (**27c**). Colorless oil; IR 3030 (w), 1670 (s), and 1380 (m) cm^{-1}; NMR δ=6.47 (1H, d, J=11.0 Hz), 5.90 (1H, d, J=11.0 Hz), 1.55 (8H, s), 1.6-1.0 (6H, m), 1.18 (3H, s), and 0.90 (3H, m); MS (25 eV) m/z (rel intensity) 206 (M^+, 100), 191 (39), 178 (43.5), 177 (33), 163 (9.3), 150 (70) and 149 (84.8). Found: C, 81.75; H, 10.86%. Calcd for $C_{14}H_{22}O$: C, 81.50; H,10.75%.

1-Isopropyl-5-methylbicyclo[3.2.2]non-3-en-2-one (**27d**). Colorless oil; IR 3030 (w) and 1670 (s) cm^{-1}; NMR δ=6.43 (1H, d, J=11.0 Hz), 5.92 (1H, d, J=11.0 Hz), 2.27 (1H, septet, J=7.1 Hz), 1.8-1.2 (8H, m), 1.18 (3H, s), and 0.78 (6H, d, J=7.1 Hz). MS (25 eV) m/z (rel intensity) 192 (M^+, 100), 177 (51.5), 164 (22.3), 163 (7.8), 150 (10.3), and 149 (55). Found: C, 80.99; H, 10.54%. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%.

5-Methyl-1-phenylbicyclo[3.2.2]non-3-en-2-one (**27e**). Colorless needles; mp 58.0-59.5 °C; IR 3110 (w), 3080 (w), 3045 (w), 1785 (s), 1455 (m), and 700 (s) cm^{-1}; NMR δ=7.6-6.85 (5H, m), 6.56 (1H, d, J=11.0 Hz), 6.00 (1H, d, J=11.0 Hz), 2.45-1.55 (8H, m), and 1.24 (3H, s); MS (25 eV) m/z (rel intensity) 226 (M^+, 97.8), 211 (21.5), 198 (25.5), 170 (100), and 130 (21). The 2,4-DNP derivative of **27e**: Mp 157.0-158.0 °C. Found: C, 64.97; H, 5.52; N, 13.49%. Calcd for $C_{22}H_{22}N_4O_4$: C, 65.01; H, 5.46%; N, 13.78%.

5-Methyl-1-vinylbicyclo[3.2.2]non-3-en-2-one (**27f**).

Catalytic hydrogenation of **23** (1.014 g, 5.62 mmol) in ethanol (17 ml) using 5% Pd-C (100 mg) gave 1-methoxy-5-methylbicyclo[3.2.2]nonan-2-one (962 mg, 5.27 mmol, 94%): colorless oil; IR 1725 (s) cm^{-1}; NMR δ=3.09 (3H, s), 2.42 (2H, t, J=7.5 Hz), 2.11-1.31 (10H, m), and 0.98 (3H, s); MS (25 eV) m/z (rel intensity) 182 (M^+, 9.5), 154 (12.2), 135 (34), and 84 (100).

A solution of vinylmagnesium bromide in THF (0.8 M, 12.5 ml) was added to a solution of the ketone (901.6 mg, 4.95 mmol) in THF at 0 °C and stirred for 30 min. The mixture was allwed to warm to room temperature and stand for 1 h. After treating with aqueous NH_4Cl solurtion at 0 °C, the mixture was extracted with two portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$ and concentrated. The remaining oil (1.019 g) was chromatographed on silica gel (25 g; 10 : 1 hexane-ethyl acetate) to give 1-methoxy-5-methyl-2-vinylbicyclo[3.2.2]nonan-2-ol (862.4 mg, 4.11 mmol, 83%).

Pinacol-type rearragement of this alcohol (795.2 mg, 3.78 mmol) was carried out in benzene (38 ml) by treating with TsOH (720 mg, 3.78 mmol). The solution was heated under reflux for 30 min, diluted with ether, washed with saturated aqueous $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concen-

trated. Chromatography of the remaining oil (717.3 mg) on silica gel (35 g; 30 : 1 hexane-ethyl acetate) gave 5-methyl-1-vinylbicyclo[3.2.2]nona-2-one (119.9 mg, 0.67 mmol, 16 %): Colorless oil; IR 3090 (w), 3020 (w), 1705 (s), and 920 (m) cm^{-1}; NMR δ=6.05 (1H, dd, J=17.0 and 11.0 Hz), 4.94 (1H, dd, J=11.0 and 1.0 Hz), 4.83 (1H, dd, J=17.0 and 1.0 Hz), 2.51 (2H, t, J=7.2 Hz), 2.0-1.4 (10H, m), and 1.16 (3H, s). The 2,4-DNP derivative: Mp 161.0-162.0 °C (decomp). Found: C, 60.67; H, 5.71; N, 15.61%. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63%.

This ketone (90.7 mg, 0.51 mmol) was transformed into **27f** (45.6 mg, 0.26 mmol, 51%) by a similar method to that employed for the synthesis of **27a**.

27f: Colorless oil; IR 3100 (w), 3035 (w), 1670 (s), and 920 (m) cm^{-1}; NMR δ=6.65 (1H, d, J=9.0 Hz), 6.05 (1H, dd, J=17.0 and 11.0 Hz), 5.93 (1H, d, J=9.0 Hz), 4.97 (1H, dd, J=11.0 and 1.0 Hz), 4.88 (1H, dd, J=17.0 and 1.0 Hz), 1.9-1.4 (8H, m), and 1.21 (3H, s).

5-methylbicyclo[3.2.2]non-3-en-2-one (**27h**). Methanesulfonyl chloride (0.03 ml, 0.36 mmol) was added to a solution of the secondary alcohol **25h** (42.0 mg, 0.23 mmol), triethylamine (0.05 ml, 0.39 mmol), and 4-dimethylaminopyridine (DMAP, 5 mg) in dichloromethane (1.2 ml) at room temperature. After standing overnight, the reaction mixture was diluted with ether, washed with aqueous NH_4Cl solution and brine, and dried over Na_2SO_4. Evaporation of the solvent gave the mesylate (53.3 mg). A solution of the mesylate and TsOH (44.5 mg, 0.23 mmol) in benzene (2.3 ml) was heated under reflux for 3 h. The solution was diluted with ether, washed with saturated aqueous $NaHCO_3$ solution and saturated brine, dried over $MgSO_4$, and concentrated. Chromatography of the remaining oil (27.0 mg) on silica gel (4 g; 20 : 1 hexane-ethyl acetate) gave **27h** as colorless oil (18.2 mg, 0.12 mmol, 52%).

27h: IR 3030 (w) and 1675 (s) cm^{-1}; NMR δ=6.58 (1H, d, J=11.0 Hz), 5.92 (1H, dd, J=11.0 and 2.0 Hz), 2.67 (1H, m), 2.0-1.4 (8H, m), and 1.20 (3H, s); MS (25 eV), m/e (rel intensity) 150 (M^+, 51.5), 135 (7.3), 132 (10.6), 107 (33.6), 104 (58.3), and 28 (100). The 2,4-DMP derivative: Mp 89-90 °C. (100). Found: C, 58.37; H, 5.57; N, 16.80%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.18; H, 5.49; N, 16.96%.

Preparation of 2-Ethyl-2-[2-[2-hydroxy-1-methoxy-5-methylbicyclo[3.2.2]non-6-en-2-yl]ethyl]-1,3-dioxolanes (**35** and **36**).

1) Magnesium (880 mg, 36.25 mmol), placed in a two-necked flask, was heated with a heat-gan under stream of argon. Into the flask were added a solution of 2-(bromoethyl)-2-ethyl-1,3-dioxolane (3.8 g, 18.13 mmol) and 1,2-dibromoethane (0.06 ml) in THF (20 ml). After sonication for 30 min at 20-25 °C, to the solution of the Grignard reagent (**33**) was added a solution of **23** (1.31 g, 7.27 mmol) in THF (20 ml). The mixture was sonicated for 1.5 h at 20-25 °C, the treated with saturated aqueous NH_4Cl solution, and extracted with several portions of ether. The combined extracts were washed with saturated brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue (3.13 g) was purified by chromatography (90 g of SiO_2; 8:1 hexane-ethyl acetate) to give **35** (1.11 g, 49%) and **36** (1.00 g, 44%).

2) To a solution of **33**, derived from the bromide (3.50 g, 16.7 mmol), magnesium (1.20 g, 49.5 mmol), and 1,2-dibromoethane (0.05 ml) in THF (30 ml), was added a solution of **23** (1.03 g, 5.71 mmol) in THF (10 ml). The mixture was stirred at 20-25 °C for 18 h, treated with saturated aqueous NH_4Cl solution, and extracted with two portions of ether. A workup similar to that described above followed by chromatography (50 g of SiO_2, 10 : 1 then 4 : 1 hexane-ethyl acetate) gave **35** (932 mg, 53%) and **36** (720 mg, 41%).

35: Colorless needles; mp 57-58 °C; IR 3570 (w), 1090 (s), and 1075 (s) cm^{-1}; NMR δ=5.81 (2H, s), 3.82 (4H, s), 3.23 (3H, s), 2.45 (1H, bs), 2.1-1.1 (15H, m), 1.01 (3H, s), and 0.85 (3H, t, J=7.5 Hz); MS (25 eV) m/z (rel intensity) 310 (M^+, 0.4), 292 (3.4), and 248 (100). Found: C, 69.90; H, 9.83%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

36: Colorless oil; IR 3550 (w), 1090 (s), and 1075 (s) cm^{-1}; NMR δ=5.89 (1H, d, J=9.3 Hz), 5.78 (1H, d, J=9.3 Hz), 3.84 (4H, s), 3.25 (3H, s), 2.1-1.1 (15H, m), 1.05 (3H, s), and 0.87 (3H, t, J=7.5 Hz); MS (25 eV) m/z (rel intensity) 310 (M^+, 0.6), 292 (19.7), and 248 (100). Found: C, 69.45; H, 10.00%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

Tandem Pinacol-type Rearrangement-Aldol Condensation to give 5,9-Dimethyltricyclo[7.2.2.0^{1,6}]-trideca-5,10-dien-4-one (**31**).

1) A solution of **35** (358.6 mg, 1.15 mmol) and TsOH (440 mg, 2.31 mmol) in benzene (11.6 ml) was heated under reflux for 45 min. The benzene solution was diluted with ether, washed with saturated aqueous $NaHCO_3$ solution and brine, dried over $MgSO_4$, and then concentrated in vacuo. Column chromatography (9 g of silica gel; 30 : 1 hexane-ethyl acetate) of the residue (243 mg) gave a 5 : 1 mixture of **31** and 5,9-dimethyltricyclo[7.2.2.0^{1,6}]trideca-5,7-dien-4-one (**37**), (206.0 mg, 82%). Careful recrystallization from hexane gave **31** as colorless needles.

2) Under similar conditions to those of run-1, **36** (534.9 mg, 1.72 mmol) was converted into a 5 : 1 mixture of **31** and **37** (304.9 mg, 82%).

3) A crude mixture of **35** and **36** (1.1994g, derived from 518.4 mg (2.88 mmol) of **23**) was heated under reflux in benzene (19 ml) with TsOH (1.09 g, 5.75 mmol) for 1 h. A similar workup to that was used in run-1 gave a 5 : 1 mixture of **31** and **37** (433.7 mg, 70% from **23**).

31: Mp 35.5-36.5 °C; IR 1666 (s) cm^{-1}; ^1H NMR δ=5.94 (1H, d, J=8.9 Hz), 5.83 (1H, d, J=8.9 Hz), 2.75-1.80 (8H, m), 1.67 (3H, s), 1.65-1.4 (4H, m), and 1.08 (3H, s); ^{13}C NMR δ=198.05 (s), 160.25 (s), 140.87 (d), 131.34 (d), 127.29 (s), 40.27 (s), 38.97 (t), 35.45 (t), 34.92 (t), 34.53 (s), 33.81 (t), 33.62 (t), 30.03 (t), 29.70 (q), and 10.84 (q); MS (25 eV), m/e (rel intensity) 217 (100) and 188 (71.3). Found: C, 83.06; H, 9.38%. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.

Preparation of 5,5,9-Trimethyltricyclo[7,2,2,0^{1,6}]trideca-6,10-dien-4-one (**38**) and isolation of **37**.

A solution of potassium t-pentoxide in THF (10 ml) was prepared from potassium hydride (35 % dispersion in mineral oil, 180 mg, 1.57 mmol) and t-pentyl alcohol (0.420 ml, 4.05 mmol) under argon at room temperature. To the mixture was added a solution of a 5 : 1 mixture of **31** and **37** (338.7 mg,

1.57 mmol) in THF (5.7 ml), and the mixture was heated at 55 °C for 1 h. After addition of iodomethane (0.39 ml, 6.26 mmol), the mixture was heated under reflux for 2 h. The reaction mixture was treated with saturated NH_4Cl solution, and extracted with three portions of ether. The ethereal extracts were combined, washed with saturated brine, and dried over $MgSO_4$. Evaporation of the solvent, followed by chromatography (5g of SiO_2; 30 : 1 benzene-ethyl acetate) of the residue (377.5 mg) gave **38** (265.7 mg, 1.15 mmol, 74%) and unreacted **37** (53.3 mg, 0.246 mmol, 16%).

37: Colorless oil; IR 1665 (s) cm^{-1}; ^1H NMR δ=6.34 (1H, d, J=11.0 Hz), 5.95 (1H, d, J=11,0 Hz), 2.37 (2H, m), 2.05-1.20 (10H, m), and 1.10 (3H, s); ^{13}C NMR δ=199.07 (s), 161.07 (s), 149.36 (d), 129.16 (d), 127.52 (d), 38.48 (s), 37.65 (t), 35.50 (s), 34.37 (2C, t), 33.84 (t), 32.14 (2C, t), 30.33 (q), and 10.98 (q); MS (25 eV) m/z (rel intensity) 216 (M^+, 100), 201 (16.1), and 188 (21.2).

38: Colorless needles; mp 48.5-49.5 °C; IR 1716 (s) cm^{-1}; ^1H NMR δ=5.92 (1H, d, J=9.3 Hz), 5.68 (1H, d, J=9.3 Hz), 5.23 (1H, t, J=4.1 Hz), 2.45-1.40 (10H, m), 1.21 (3H, s), 1.16 (3H, s), and 1.04 (3H, s); MS (25 eV) m/z (rel intensity) 230 (M^+, 52.8), 215 (21.7), and 188 (100). Found: C, 83.39; H, 9.82%. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63%.

Preparation of 5,5,9-Trimethyltricyclo[7,2,2,$0^{1,6}$]trideca-6,10-diene (**39**) by Wolff-Kishner Reduction of **38**.

To a solution of **38** (228.2 mg, 0.991 mmol) in 1,3-propanediol (11 ml) was added 80% hydrazine-hydrate (0.12 ml, 1.98 mmol) under argon atmosphere. Water was removed carefully by distillation under argon with monitoring consumption of **38** by silica-gel TLC. To the solution of the hydrazones was added potassium hydroxide (85.5%, 0.65 g, 9.91 mmol), and the mixture was heated under reflux for 40 h under nitrogen. The reaction mixture was cooled to 0 °C, acidified with 6 M HCl, and extracted with two portions of hexane. The extracts were combined, washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. Evaporation of the solvent, followed by chromatography (6g of 10% $AgNO_3$-SiO_2; 25 : 1 benzene-ethyl ether) of the residue (188.9 mg) gave **39** (173.7 mg, 0.803 mmol, 81%).

16: Colorless oil; IR 3030 (w), 2960 (sh), 2950 (s), and 2880 (s) cm^{-1}; NMR δ=5.79 (1H, d, J=8.7 Hz), 5.55 (1H, d, J=8.7 Hz), 5.11 (1H, t, J=4.2 Hz), 2.3-1.25 (12H, m), 1.08 (3H, s), 1.04 (3H, s), and 0.99 (3H, s); MS (25 eV) m/z (rel intensity) 216 (M^+, 92.7) and 201 (100).

Preparation of 5,5,9-Trimethyltricyclo[7,2,2,$0^{1,6}$]tridec-6-en-10-one (**30**) and its regioisomer (**40**).

To a solution of borane-THF complex (0.436M, 2.67 ml) was added dropwise 2,3-dimethyl-2-butene (0.155 ml, 1.31 mmol) at 0 °C. After standing 2 h at 0 °C, to the resulting thexylborane solution was added a solution of **39** (94.3 mg, 0.436 mmol) in THF (2 ml). The mixture was stirred at 0 °C for 1.5 h. After successive addition of ethanol (4.5 ml), 3 M aqueous NaOH (2 ml), and 30% hydrogen-peroxide (2 ml) at 0 °C, the reaction mixture was heated under reflux for 1.5 h. The mixture was extracted with two portions of ether. The ethereal extracts were combined, washed with saturated brine, and dried over $MgSO_4$. Evaporation of the solvent followed by chromatography (5g of silica gel; 25 : 1 benzene-ethyl acetate) of the residue (113.2 mg) gave alcohol-A (61.6 mg, 0.263 mmol, 60%) and alcohol-B (26.3 mg, 0.112 mmol, 26%).

Alcohol-A: Colorless needles; mp 54.0-55.0 °C; IR 3645 (w) and 1052 (s) cm^{-1}; NMR δ=5.31 (1H, dd, J=5.7 and 4.1 Hz), 3.51 (1H, dd, J=6.9 and 2.3 Hz), 2.4-1.2 (15H, m), 1.08 (6H, s), and 0.89 (3H, s); MS (25 eV) m/z (rel intensity) 234 (M^+, 9.8), 232 (5.8), 216 (48.5), and 201 (100).

Alcohol-B: Colorless needles; mp 37.0-38.0 °C; IR 3630 (w) and 1038 (m) cm^{-1}; NMR δ=5.41 (1H, dd, J=5.7 and 3.3 Hz), 3.92 (1H, dd, J=6.9 and 2.3 Hz), 2.3-1.2 (15H, m), 1.10 (3H, s), 1.05 (3H, s), and 0.87 (3H, s); MS (25 eV) m/z (rel intensity) 234 (M^+, 43.3), 219 (37.8), 216 (46.4), and 201 (100).

To a solution of Collins reagent (170 mg, 0.631 mmol) in CH_2Cl_2 (2 ml) was added a solution of alcohol-A (14.8 mg, 0.063 mmol) in CH_2Cl_2 (2 ml). After 6 min stirring at room temperature, the mivture was decanted, and the black residue was washed with several portions of ether. The organic layer was combined, washed successively with 5% NaOH solution, 5% HCl, saturated $NaHCO_3$ solution, and saturated brine, dried over $MgSO_4$,and concentrated. Chromatography (3g of silica gel; 25 : 1 hexane-ethyl acetate) of the residue (15.0 mg) gave **30** (13.2 mg, 0.057 mmol, 90%).

30: Colorless oil; UV 280 nm (ε 69); IR 1720 (s) cm^{-1}; NMR δ=5.42 (1H, t, J=4.5 Hz), 2.56 (1H, dd, J=16.8 and 2.0 Hz), 2.2-1.3 (14H, m), 1.10 (6H, bs), and 0.96 (3H, s); MS (25 eV) m/z (rel intensity) 232 (M^+, 64.5) and 117 (100).

A similar treatment of alcohol-B (16.9 mg, 0.0727 mmol) to that employed for the synthesis of **30** followed by chromatography on silica gel (3g g of silica gel; 30 : 1 hexane-ethyl acetate) gave **40** (15.0 mg, 0.065 mmol, 89%).

40: Colorless oil; UV 230 (sh, ε 1700), 300 (170), 310 nm (150); IR 1715 (s) cm^{-1}; NMR δ=5.56 (1H, dd, J=5.3 and 4.1 Hz), 2.6-1.2 (14H, m), 1.11 (3H, s), and 0.97 (6H, s); MS (25eV) m/z (rel intensity) 232 (M^+, 63.7) and 217 (100). Found: C, 82.55; H, 10.50%. Calcd for $C_{15}H_{24}O$: C, 82.70; H, 10.41%.

Preparation of 5,5,9-Trimethyl-10-oxatricyclo[7.3.2.$0^{1,6}$]tetradec-6-en-11-one (**29**) by Baeyer-Villiger Oxidation of **30** Using $(TMSO)_2$ and BF_3-Etherate and the Related Attempts.

1) To a solution of the ketone **30** (120.2 mg, 0.517 mmol) and bistrimethylsilylperoxide (440 mg, 2.59 mmol) in CH_2Cl_2 (5 ml) was added BF_3-etherate (0.320 ml, 2.59 mmol) at -20 °C. After 1 h stirring at -20--10 °C, the reaction was quenched with 5% aqueous $Na_2S_2O_3$. The mixture was allowed to warm to room temperature, and extracted with two portions of ether. The extracts were combined, washed with saturated $NaHCO_3$ solution and saturated brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography (6 g of silica gel; 10 : 1 hexane-ethyl acetate) of the remaining oil (142.8 mg) gave **29** (54.9 mg, 0.221 mmol, 43%).

29: Colorless needles; mp 106-107 °C; IR 1720 (broad s) cm^{-1}; NMR δ=5.50 (1H, dd, J=5.7 and 4.1 Hz), 2.98 (1H, broad d, J=16.2 Hz, $W_{1/2}$=3 Hz), 2.49 (1H, d, J=16.2 Hz), 2.5-1.2 (12H, m), 1.32 (3H, s), 1.11 (3H, s), and 1.09 (3H, s); MS (13.5 eV) m/z (rel intensity) 248 (M^+, 100), 233 (3.9), 206 (83.2), 189 (43.9), 188 (58.5), 179 (26.7), 177 (80.2) 166 (46.2) and 82 (10.2).

2) To a solution of **30** (61.3 mg, 0.264 mmol) and bistrimethylsilylperoxide (55.5 mg, 3.17 mmol)

in CH_2Cl_2 (2 ml) was added a solution of trimethylsilyl trifluoromethanesulfonate[27] (0.010 ml) in CH_2Cl_2 (5 ml) at -78 °C. After 5 h stirring at -78 °C, the mixture was allowed to warm to -20 °C and to stand for 1 h. The reaction mixture was treated with 5% $Na_2S_2O_3$ solution and extracted with two portions of ether. The extracts were combined, washed with saturated $NaHCO_3$ solution and saturated brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography (5 g of silica gel; 10 : 1 hexane-ethyl acetate) of the remaining oil (61.3 mg) gave unreacted **30** (31.2 mg, 51%).

Preparation of (±)-Widdrol (**9**). To a suspension of $LiAlH_4$ (20 mg, 0.530 mmol) in ether (2.5 ml) was added a solution **29** (27.0 mg, 0.11 mmol) in ether (2.5 ml) at 0 °C. After 30 min stirring, the resulting suspension was treated by successive dropwise addition of two drops of water, two drops of 15% NaOH solution, and six drops of water, and then allowed to warm to room temperature with stirring. Filtration followed by concentration gave the diol **41** as a white solid (37.3 mg); NMR δ=5.35 (1H, m), 3.50 (2H, m), 2.5-0.8 (16H, m), 1.07 (6H, s), and 0.88 (3H, s); MS (13.5 eV) m/z (rel intensity) 234 (M^+-18, 70.3), 208 (64.1), 190 (100), and 189 (56).

In order to protect the primary hydroxyl group selectively, the solid was treated with t-butyldimethylchlorosilane (20 mg, 0.13 mmol), triethylamine (two drops), and a small amount of DMAP in CH_2Cl_2 (3 ml) under argon at room temperature. After standing overnight, the reaction mixture was diluted with ether, washed with water and saturated NH_4Cl solution, dried over $MgSO_4$, and concentrated in vacuo. Chromatography (15 : 1 hexane-ethyl acetate) of the residue (56.2 mg) gave the monosilyl ether as colorless oil (30.5 mg, 0.084 mmol, 77%).

To protect the tertiary hydroxyl group, acetic anhydride (0.1 ml) was added to a solution of the monosilyl ether (29.5 mg, 0.81 mmol) in triethylamine (2 ml) containing a small amount of 4-dimethylaminopyridine, and the mixture was allowed to stand overnight at room temperature. The mixture was diluted with ether, washed with saturated aqueous NH_4Cl solution, dried over $MgSO_4$, and concentrated. Chromatography (3 g of silica gel; 30 : 1 hexane-ethyl acetate) of the residue (42.5 mg) gave the acetate as a colorless oil (29.5 mg, 0.073 mmol, 90 %).

In order to remove the silyl group, the acetate (29.5 mg) was treated with a mixture of THF (0.16 ml), water (0.16 ml), and acetic acid (0.48 ml) at room temperature. After standing overnight, the reaction mixture was diluted with ether, washed successively with water, saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography (4 g of silica gel; 10 : 1 hexane-ethyl acetate) of the residue (16.6 mg) gave the hydroxyl acetate as a colorless oil: NMR δ=5.87 (1H, dd, J=9.2 and 6.8 Hz), 3.9-3.4 (2H, m), 2.7-0.8 (15H, m), 1.91 (3H, s), 1.44 (3H, bs), 1.11 (3H, s), and 1.08 (3H, bs)).

Collins oxidation of the hydroxyl acetate was carried out by treating with the reagent (140 mg) in dry CH_2Cl_2 (3 ml). A workup similar to that used for preparation of **30** gave the aldehyde **42** as a colorless oil (18.4 mg, 0.063 mmol, 87%; NMR δ=9.76 (1H, t, J=2.8 Hz), 5.62 (1H, t, J=8.0 Hz), 3.1-1.0 (14H, m), 1.92 (3H, s), 1.47 (3H, bs), and 1.14 (6H, s)).

A mixture of the aldehyde (18.4 mg, 0.063 mmol), Wilkinson's complex (58.2 mg, 0.063 mmol), and benzonitrile (0.5 ml) was heated at at 145 °C for 6 min with stirring. The bulk of benzonitrile was removed by Kugelrohr distillation (100 °C/3 Torr), and the residue was rinsed with ethanol, filtered, and washed with ethanol. After evaporation of the solvent, chromatography (5 g of silica gel; 20 : 1 hexane-ethyl acetate) of the residue (23.8 mg) gave the acetate **43** as colorless oil (15.5 mg, 0.059 mmol, 93%); NMR δ=5.39 (1H, dd, J=8.0 and 6.4 Hz), 2.7-1.0 (12H, m), 1.89 (3H, s), 1.43 (3H, s), 1.21 (3H, s), and 1.09 (6H, s).

To a suspension of $LiAlH_4$ (20 mg, 0.53 mmol) in ether (2 ml) was added a solution of the acetate (10.2 mg, 0.039 mmol) at 0 °C. After 30 min stirring, a similar workup to that described previously followed by chromatography on silica gel (3 g; 5 : 1 hexane-ethyl acetate) gave (±)-widdrol (8.2 mg, 0.037 mmol, 96%): Mp 82-83 °C (hexane); ^1H NMR ($CDCl_3$) δ=5.54 (1H, dd, J=9.1 and 6.0 Hz), 2.52 (1H, ddd, J=14.0, 6.0, and 1 Hz), 2.01 (1H, dd, J=14.0 and 9.1 Hz), 1.8-1.2 (10H, m), 1.23 (3H, d, J<1 Hz), 1.21 (3H, d, J<1 Hz), 1.10 (3H, s), and 1.09 (3H, s); MS (25 eV) m/z (rel intensity) 222 (M^+, 20.1), 204 (29.4), 189 (26.5), and 152 (100).

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