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Synthesis of Medium-Sized Bicyclic Compounds by Intramolecular Cyclization of Cyclic β-Keto Radicals Generated from Cyclopropanols Using Manganese(III) Tris(pyridine-2-carboxylate) and Its Application to Total Synthesis of 10-Isothiocyanatoguaia-6-ene

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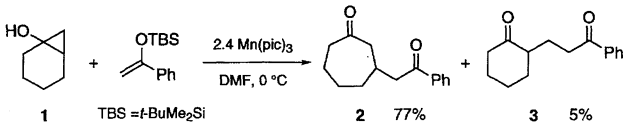
Bicyclic cyclopropanols having an olefinic side chain are oxidized with manganese(III) tris(pyridine-2-carboxylate) to generate cyclic β-keto radicals with ring-expansion. These cyclize intramolecularly, affording bicyclic radical intermediates. The cyclized radicals are trapped with various radical-trapping reagents such as electron-rich or -deficient olefins, tributylstannane and diphenyl diselenide to give the corresponding functionalized products. Stereochemistries of the bicyclic products are well predicted by MM2 force field calculation. A stereoselective total synthesis of an isothiocyano sesquiterpene, 10-isothiocyanatoguaia-6-ene, is achieved using this reaction.

Recently oxidative generation of radical species using metallic oxidant has attracted considerable attention as a useful method for generation of radical species.[1] During our study to develop useful methods for one-electron oxidation of organic molecules,[2] it was found that manganese(III) tris(pyridine-2-carboxylate) ($Mn(pic)_3$) is a very mild and neutral one-electron oxidant. For example, α-keto radicals are generated from β-keto carboxylic acids and react with electron rich olefins to give intermolecular addition products in good yields.[2a] We also reported that treatment of cyclopropanol derivatives with $Mn(pic)_3$ generates β-keto radicals, which, with appropriate choice of reaction conditions, add to either electron-rich or electron-deficient olefins to give the corresponding intermolecular addition products in good yields.[3] In this reaction, oxidation of bicyclo[4.1.0]-heptan-1-ol (**1**) with $Mn(pic)_3$ in the presence of a silyl enol ether gave a ring-expanded cycloheptanone derivative **2** as a major product, as shown in Eq. 1.

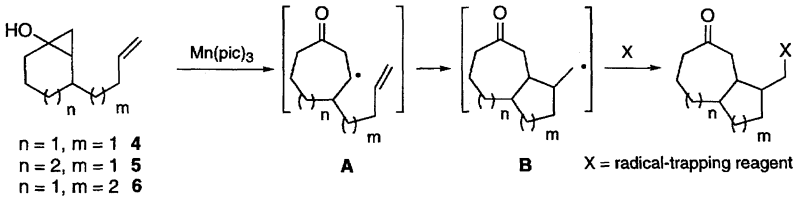


(1)

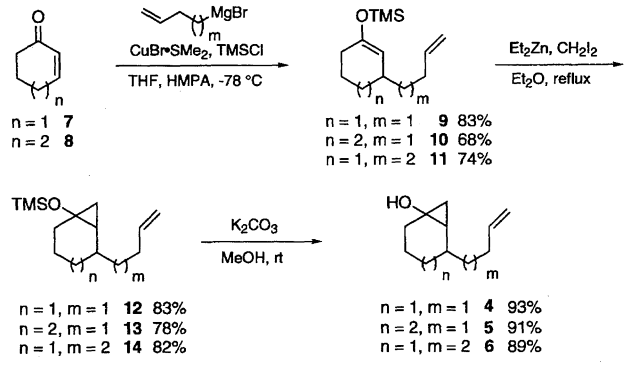
We thought of applying the above reaction to an intramolecular reaction to realize an efficient method for the construction of bicyclic carbon frameworks having medium-sized rings, which are commonly seen in the basic skeletons of various natural products such as guaianolides and pseudoguaianolides.[4] In this paper is reported a full account of this work, including the first total synthesis of 10-isothiocyanatoguaia-6-ene, a novel marine natural product containing an isothiocyanato group.[5]

As substrates we have chosen bicyclo[4.1.0]heptan-1-ol and bicyclo[5.1.0]octan-1-ol derivatives **4**, **5**, and **6** having 3-butenyl or 4-pentenyl group at C_5 or C_6 position (Scheme 1). Oxidation of these compounds with $Mn(pic)_3$ is expected to produce ring-expanded β-keto radicals **A**, which would add to the C–C double bond of the side chain in an *exo* manner intramolecularly[6] to give radical intermediates **B** having bicyclo[5.3.0]decan-3-one or bicyclo[6.3.0]undecan-3-one skeletons. Finally, various functionalities could be introduced by the successive reaction of the radicals **B** with appropriate radical-trapping reagents **X**.

Bicyclo[4.1.0]heptanol and bicyclo[5.1.0]octanol derivatives **4**, **5**, and **6** were prepared in a straightforward manner, as shown in Scheme 2; treatment of cyclic α,β-unsaturated ketones with 3-butenyl- or 4-pentenylmagnesium bromide



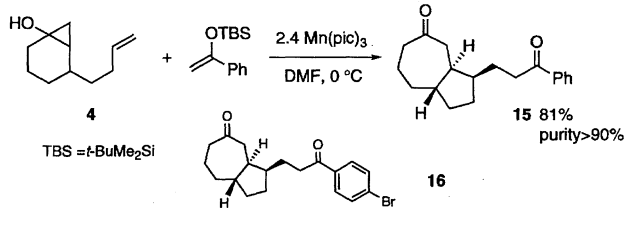
Scheme 1.



Scheme 2.

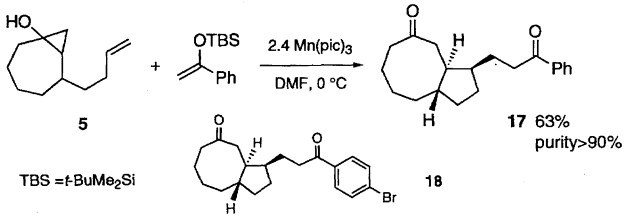
in the presence of a catalytic amount of $CuBr{\cdot}SMe_2$, chlorotrimethylsilane (TMSCl), and HMPA in THF at −78 °C[7] produced the corresponding silyl enol ethers **9**—**11** with an alkenyl side chain. These silyl enol ethers were regioselectively cyclopropanated with diethylzinc and diiodomethane in ether[8] to give diastereomeric mixtures (about 9 : 1, relative stereochemistry undetermined) of the cyclopropanol TMS ethers **12**—**14**. Finally removal of TMS group was carried out by treatment with potassium carbonate in methanol. As these cyclopropanols **4**—**6** were not very stable, they were usually kept at the stage of the TMS ethers and deprotected just before use.

First, the reaction of **4** was examined in the presence of an electron-rich olefin as a radical-trapping reagent. Treatment of **4** with 2.4 molar amounts of $Mn(pic)_3$ in DMF in the presence of 2.5 molar amounts of 1-(*t*-butyldimethylsiloxy)-1-phenylethene at 0 °C produced the desired ring-expanded bicyclo[5.3.0]decan-3-one derivative **15** in 81% yield in more than 90% isomeric purity.[9] Two inseparable minor products were also detected in less than 5% respectively as judged by GC, ^1H NMR, and ^{13}C NMR, but **15** was isolated in a pure form by recrystallization from hexane and ethyl acetate. The stereochemistry of **15** was deduced from the X-ray structural analysis of **16**, synthesized from **4** and 1-(4-bromophenyl)-1-(*t*-butyldimethylsiloxy)ethene, to have the relative stereochemistry shown in Eq. 2.



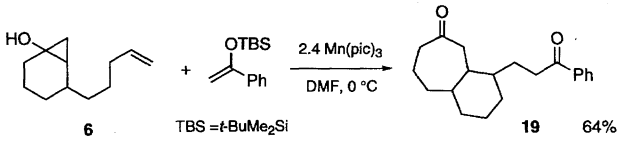
(2)

The same type of intramolecular cyclization with ring expansion proceeded in the case of the bicyclo[5.1.0]octan-1-ol derivative **5**. The reaction of 6-(3-butenyl)bicyclo-[5.1.0]octan-1-ol (**5**) with $Mn(pic)_3$ in the presence of 1-(*t*-butyldimethylsiloxy)-1-phenylethene under the same conditions gave a bicyclo[6.3.0]undecan-3-one derivative **17** in 63% yield. In this case also, **17** was produced in more than 90% isomeric purity, and the stereochemistry of **17** was deduced from the X-ray structural analysis of **18**, which was prepared from **5** and 1-(4-bromophenyl)-1-(*t*-butyldimethylsiloxy)ethene, to have the relative stereochemistry shown in Eq. 3.



(3)

As described above, the reactions proceeded stereoselectively when the ring-expanded radicals added to the olefinic part of the side chain in an exo manner to form a five-membered ring. Then, the reaction of the bicyclo-[4.1.0]heptan-1-ol derivative **6** having 4-pentenyl group at C_5 position was examined. In this case, it was expected that bicyclo[5.4.0]undecan-3-one skeleton would be formed by the attack of the ring-expanded β-keto radical on the olefinic part of the side chain in an *exo* manner. The oxidation of 5-(4-pentenyl)bicyclo[4.1.0]heptan-1-ol (**6**) in the presence of 1-(*t*-butyldimethylsiloxy)-1-phenylethene gave an inseparable mixture of almost equal amounts of two isomeric ring-expanded products **19** in 64% yield (Eq. 4). Although these two products were determined to have the expected bicyclo[5.4.0]undecan-3-one skeletons from NMR spectra, the relative stereochemistry of these products **19** could not be established by spectroscopic methods.

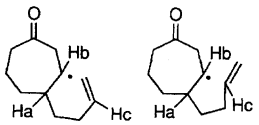


(4)

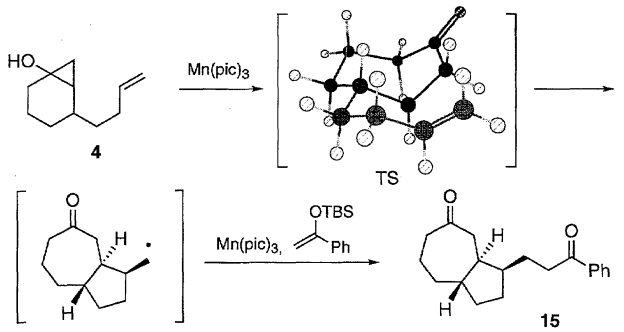
To obtain information on the stereochemistries of these isomeric products **19**, we carried out MM2 force-field calculation of the transition state energies of this radical cyclization.[10] A force-field model has already been successfully applied to several free radical cyclizations to estimate the most favorable transition structures.[11] We used Materia Ver. 3.0 for MM2 calculation and its Conflex module for conformation analysis.[12] MM2 parameters of flexible model developed by Houk[11b] were used for reactive centers and MM2 Prime (1980) parameters which accompanied the progrom were used for the other atoms.[12] To see the validity of such a computational approach, we first compared the theoretical and the experimental results of the cyclization of bicyclo-[4.1.0]heptan-1-ol derivative **4** and bicyclo[5.1.0]octan-1-ol derivative **5**, where the cyclization gave one isomer with high selectivity and its stereochemistry was established by X-ray analysis. Relative transition energies obtained by the MM2 calculation of the representative transition structures derived from **4** are shown in Table 1. *Exo* cyclization was obviously more favorable than *endo* cyclization.[6] And among the *exo* transition structures, the transition state energy with Ha–Hb in the *trans* and Hb–Hc in the *cis* was the lowest (−32.17

Table 1. Transition State Energies (kcal mol^{-1}) for the Cyclization of **4** in Various Conformers

Ha–Hb	Hb–Hc	ΔG (*endo*)	ΔG (*exo*)
cis	*cis*	−27.93	−30.60
cis	*trans*	−29.68	−31.17
trans	*cis*	−31.48	−32.17
trans	*trans*	−28.98	−31.32



kcal mol^{-1}) and the transition state energies of the other structures were larger (> 0.7 kcal mol^{-1}). Consequently, the most favorable transition structure determined by the theoretical calculation coincided with the observed relative stereochemistry of the product **15**, as shown in Eq. 5.

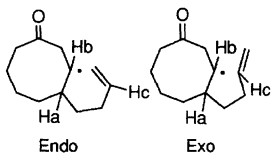


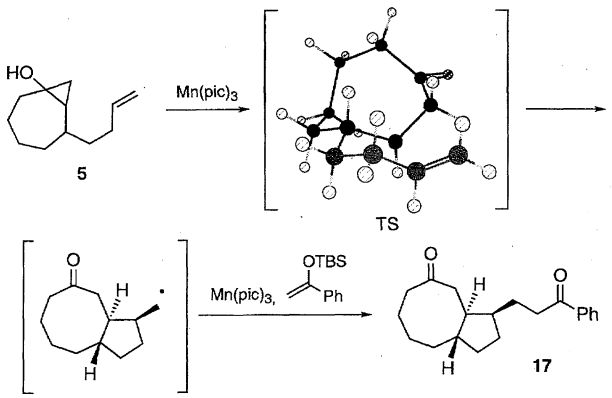
(5)

Table 2 shows the transition state energies for the cyclization of **5**. The energy of the *exo* transition structure with Ha–Hb in the *trans* and Hb–Hc in the *cis* was the lowest (−28.28 kcal mol^{-1}) and the energies of the other structures were sufficiently high (> 1.1 kcal mol^{-1}) to exclude contribution of such structures. In this case also, the calculation coincided with the observed product **17** as shown in Eq. 6. Hence, MM2 calculations could predict the stereochemistry in the oxidatively generated radical cyclizations.

Table 2. Transition State Energies (kcal mol^{-1}) for the Cyclization of **5** in Various Conformers

Ha–Hb	Hb–Hc	ΔG (*endo*)	ΔG (*exo*)
cis	*cis*	−23.83	−26.75
cis	*trans*	−26.50	−27.13
trans	*cis*	−26.10	−28.28
trans	*trans*	−24.45	−27.17

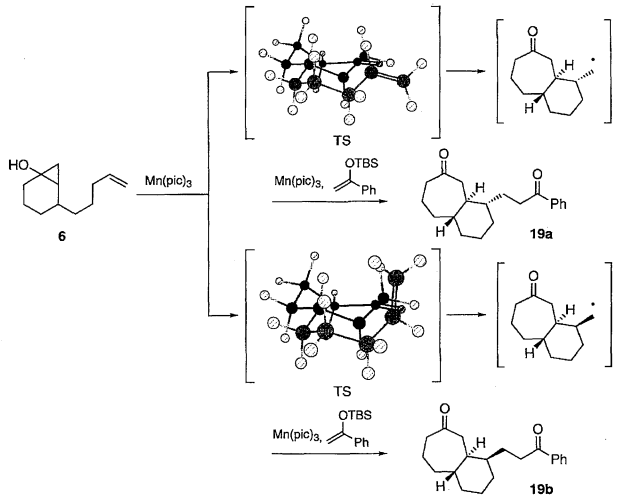




(6)

We then calculated the transition state structures of the radical cyclization of bicyclo[4.1.0]heptan-1-ol **6**, the relative stereochemistry of which we could not have determined by spectroscopic methods. The result is shown in Table 3.

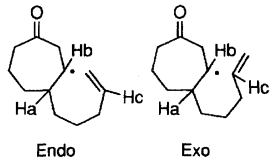
The transition state energies of the *exo* transition structures with both Ha–Hb and Hb–Hc in the *trans* (−34.00 kcal mol^{-1}) and with Ha–Hb in the *trans* and Hb–Hc in the *cis* (−33.63 kcal mol^{-1}) were close and lower than those of all the other structures (< 2.7 kcal mol^{-1}). Based on these results, the two isomeric products obtained should be the isomers of the chiral carbon having the side chain and should be assigned to be **19a** and **19b**, as shown in Eq. 7.[13]



(7)

Table 3. Transition State Energy (kcal mol^{-1}) for the Cyclization of **6** in Various Conformers

Ha–Hb	Hb–Hc	ΔG (*endo*)	ΔG (*exo*)
cis	*cis*	−28.75	−31.92
cis	*trans*	−28.88	−31.23
trans	*cis*	−29.48	−33.63
trans	*trans*	−29.15	−34.00



Next, employing **4** as a substrate, the reactions using some other radical-trapping reagents were examined to introduce various functionalities onto the side chain at C_{10} position of the cyclized bicyclo[5.3.0]decan-3-one system. We have already reported that β-keto radicals oxidatively generated from cyclopropanols using $Mn(pic)_3$ can be directly trapped by PhSeSePh to give β-seleno ketones, or can add to electron-deficient olefins such as acrylonitrile by carrying out the reaction in the presence of n-Bu_3SnH.[3)]

When 5-(3-butenyl)bicyclo[4.1.0]heptan-1-ol (**4**) was treated with $Mn(pic)_3$ in DMF at 0 °C in the presence of 1.5 molar amounts of n-Bu_3SnH as a radical-trapping reagent, a bicyclo[5.3.0]decan-3-one derivative **20**, of which the side chain at C_{10} position is a methyl group, was produced in the yield of 75% with hydrogen atom abstraction of the radical intermediate **B** from n-Bu_3SnH (Scheme 3). The same reaction in the presence of 0.75 molar amount of PhSeSePh instead of n-Bu_3SnH afforded the corresponding cyclized product **21** containing a phenylselenomethyl group at C_{10} position in 68% yield. Furthermore, by carrying out the reaction in the presence of 1.5 molar amounts of n-Bu_3SnH and 3.0 molar amounts of acrylonitrile as an electron-deficient olefin, the addition product **22** was obtained in the yield of 66%. All these reactions proceeded in high stereoselectivity to afford the corresponding products in more than 90% isomeric purity. The stereochemistry of these compounds was not established unambiguously, but it is assumed that these compounds have the same relative stereochemistry as that of **15**.

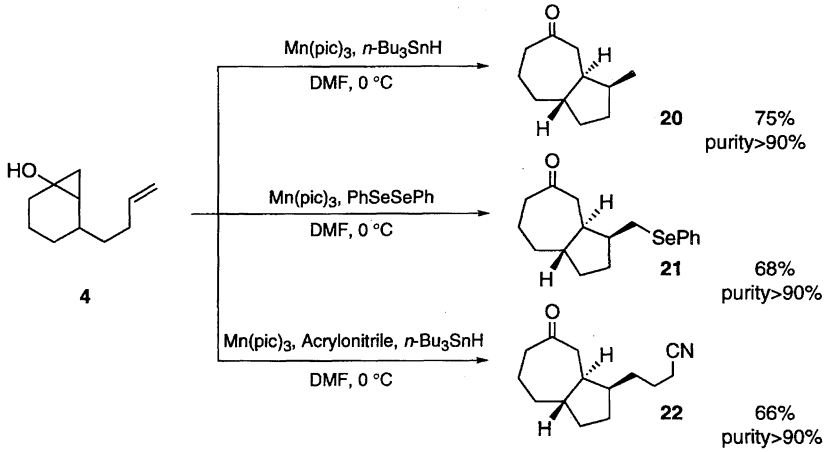
Quite recently, the same type of radical cyclization reaction was reported using $FeCl_3$ as an oxidant,[14)] in which the cyclized radical intermediates were trapped by a chlorine atom and other radical-trapping reagents were not employed.[15)] On the contrary, the present reaction employing $Mn(pic)_3$ as an oxidant enables the use of a variety of radical-trapping reagents and makes it possible to introduce various functionalities onto the side chain of the product.

We next applied this reaction to the total synthesis of 10-isothiocyanatoguaia-6-ene.[16)] Guianolides are one of the largest group of sesquiterpenes and some of them play an important role in organisms.[4)] The ring junction of guaianolides is usually *cis* and most of the synthetic efforts have been focused on the preparation of *cis*-fused guaiane skeleton.[17)]

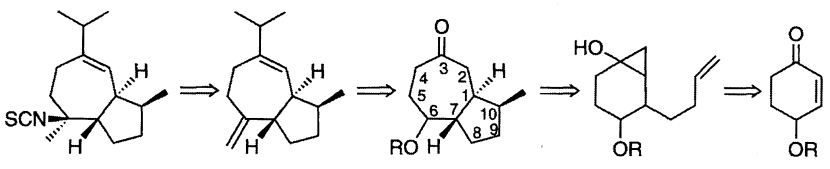
(1R^*, 4R^*, 5S^*, 10R^*)-10-Isothiocyanatoguaia-6-ene is a sesquiterpene isolated from the Palauan sponge *Trachyopsis aplysinoides* and belongs to a rather rare class of bioactive marine natural products which contain an isothiocyano group in the molecule.[16,18)] This compound has a characteristic *trans*-fused bicyclo[5.3.0]decane skeleton with four chiral centers, and the total synthesis of these isothiocyano sesquiterpenoids remains to be explored.[19)]

As already mentioned, the reaction of 5-(3-butenyl)-bicyclo[4.1.0]heptan-1-ol in the presence of n-Bu_3SnH stereoselectively gave trans-fused bicyclo[5.3.0]decan-3-one derivative, which has both the basic skeleton and the correct relative stereochemistry of 10-isothiocyanatoguaia-6-ene. In Scheme 4 is shown a retrosynthetic analysis of 10-isothiocyanatoguaia-6-ene based on this strategy.

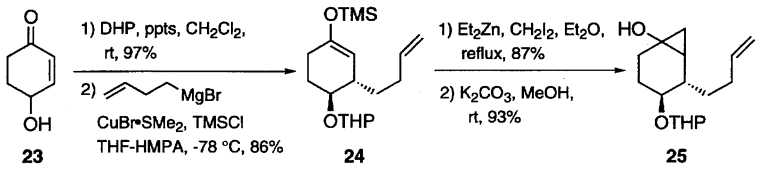
The key intermediate **25** for the oxidative radical cyclization was prepared straightforwardly in good yield from 4-hydroxy-2-cyclohexen-1-one (**23**),[20)] as shown in Scheme 5. Thus, the hydroxy group of 4-hydroxy-2-cyclohexen-1-one was protected as its tetrahydropyranyl (THP) ether by treatment with dihydropyran (DHP) and pyridinium p-toluene-



Scheme 3.



Scheme 4.



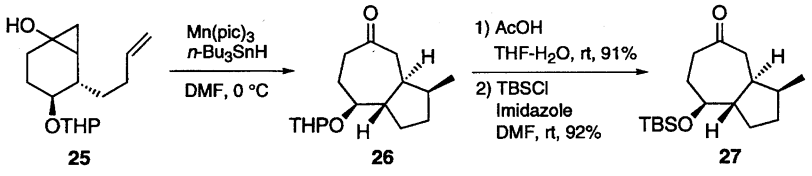
Scheme 5.

sulfonate (ppts) almost quantitatively, and then 3-butenyl group was introduced stereoselectively at C_3 position by 1,4-addition of 3-butenylmagnesium bromide in the same manner as described for the preparation of **4**—**6** to give silyl enol ether **24** as a single detectable isomer in 86% yield.[7] Cyclopropanation of this silyl enol ether **24** was carried out by using diethylzinc and diiodomethane[8] to afford TMS-protected cyclopropanol as about 10 : 1 mixture of stereoisomers (relative stereochemistry undetermined) in 87% yield. Cyclopropanol **25** was obtained by deprotection of TMS group in the presence of a catalytic amount of potassium carbonate in methanol in 93% yield.

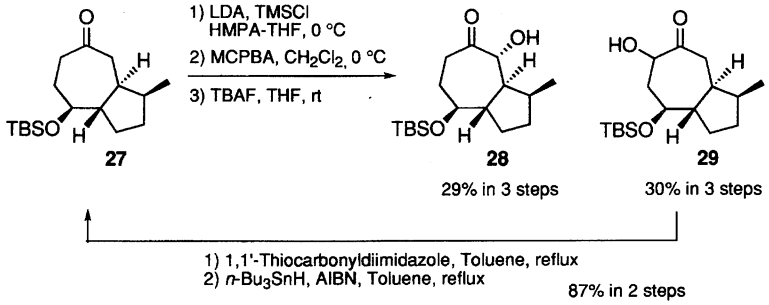
As the substrate with appropriate functionalities for the cyclization was secured, the oxidative intramolecular radical cyclization of the cyclopropanol **25**[9] was examined (Scheme 6). Thus, **25** was treated with 1.5 molar amounts of $Mn(pic)_3$ in the presence of 1.3 molar amounts of n-Bu_3SnH in DMF. The reaction proceeded smoothly at 0 °C and the desired cyclized product **26** with methyl group at C_{10} was obtained in 76% yield in more than 90% isomeric purity. The 500 MHz ^1H NMR spectra indicated that three minor, presumably isomeric, products were present in less than 10%, but these products could not be separated at this stage. For the purpose of simplifying the NMR spectra and attaining higher stability of the hydroxy protective group at C_6, the tetrahydropyranyl group of **26** was removed by acetic acid (AcOH) in THF–water, and then reprotected with t-butyldimethylsilyl chloride (TBSCl) and imidazole in DMF to afford TBS ether **27**.

As the basic skeleton with correct relative stereochemistry for the synthesis of 10-isothiocyanatoguaia-6-ene was obtained, we next examined introduction of isopropyl group at C_3 position along with C_2–C_3 double bond. Model reactions using a substrate having no C_6 hydroxy functionality revealed that regioselective dehydration of the tertiary alcohol, obtained by the reaction with isopropylmagnesium chloride–cerium(III) chloride reagent,[21] proved to be quite difficult. For example, the dehydration under acidic conditions gave an inseparable mixture of olefins in which *exo* olefin was obtained as a major product. Thus, we decided to examine an indirect method for the introduction of C_2–C_3 double bond (Scheme 7). Treatment of the ketone **27** with lithium diisopropylamide (LDA), followed by the addition of TMSCl in THF, gave a regioisomeric mixture of silyl enol ethers, which were, without purification, oxidized with m-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 to give a 1 : 1 mixture of the corresponding α-trimethylsiloxy ketones. Selective deprotection of TMS group with tetrabutylammonium fluoride in THF produced α-hydroxy ketones **28** and **29** in 59% yield from the ketone **27**. The desired isomer **28** was obtained as a single diastereomer by silica gel chromatography.[22] The other isomer **29** could be converted back to the ketone **27** by treatment with 1,1′-thiocarbonyldiimidazole in toluene, followed by reduction with n-Bu_3SnH by a one-pot procedure in 87% yield.[23]

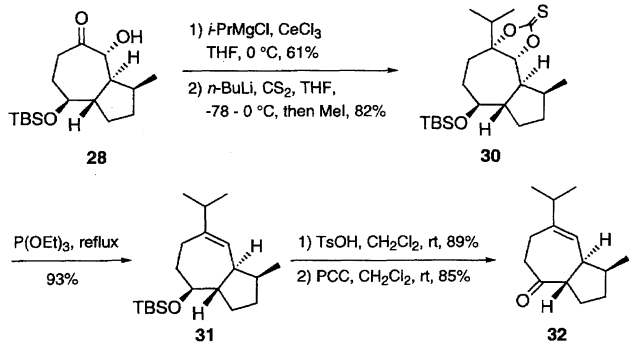
Introduction of isopropyl group to α-hydroxy ketone **28** was carried out with organocerium reagent prepared from isopropylmagnesium chloride and cerium(III) chloride in THF at 0 °C[21] to give the addition product in 61% yield with high stereoselectivity (Scheme 8).[24] The minor isomers



Scheme 6.



Scheme 7.

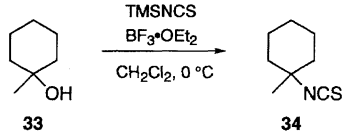


Scheme 8.

derived from the oxidative cyclization step were removed at this stage by recrystallization. Treatment of the diol with *n*-BuLi and carbon disulfide in THF, followed by the addition of methyl iodide, afforded thiocarbonate **30** in the yield of 82%. Reductive olefination of the thiocarbonate **30** was carried out in triethyl phosphite at 140 °C to produce the desired olefin **31** in 93% yield.[25]

As the introduction of isopropyl group with C_2–C_3 double bond was achieved, we undertook the final operation of introducing methyl group and isothiocyano functionality at C_6 position. After the deprotection of TBS group of **31** with TsOH in CH_2Cl_2 in 89% yield, the resulting alcohol was oxidized with pyridinium chlorochromate (PCC) in CH_2Cl_2 to produce ketone **32** in 85% yield.

As no good method for the introduction of isothiocyano group had been reported, we first tried to develop a new method for this purpose. After several experiments, it was found that treatment of tertiary alcohol **33** with trimethylsilyl isothiocyanate in the presence of BF_3·OEt_2 gave the corresponding isothiocyanate **34** in good yield (Eq. 8). However, application of this protocol to the tertiary alcohol **35**, prepared by the addition of methylmagnesium iodide to **32**, brought about only dehydration and a mixture of dienes **36** and **37** was obtained (Eq. 9).



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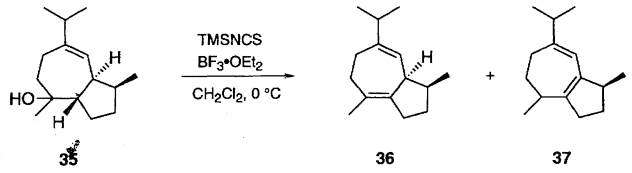


(9)

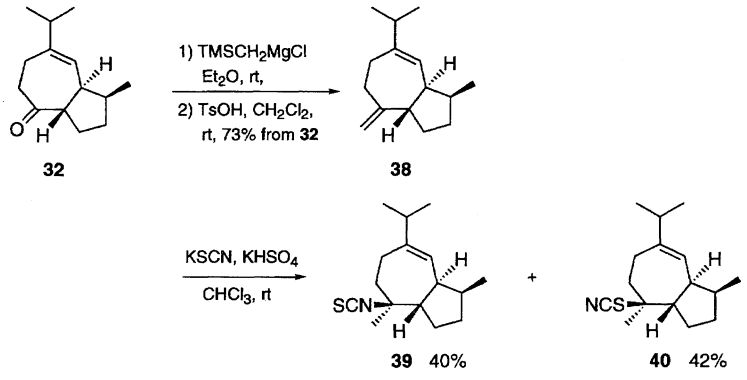
At this point, a paper appeared describing direct addition of isothiocyanic acid to olefins to give isothiocyanates.[26] We decided to employ this method and prepared diene **38** in 73% yield by the reaction of ketone **32** with trimethylsilylmethylmagnesium chloride, followed by treatment of the crude product with TsOH (Scheme 9).[27] Treatment of diene **38** with isothiocyanic acid generated in situ with KSCN and $KHSO_4$ in $CHCl_3$ for 3 d[26] revealed that the reaction was highly site-selective and stereoselective but gave a mixture of two compounds, which were separated easily by silica gel column chromatography to give the desired isothiocyanate **39** in 40% yield accompanied by the isomeric thiocyanate **40** in 42% yield.[28] The ^1H and ^{13}C NMR spectra of **39** completely coincided with those of the literature.[16] Thus the first total synthesis of 10-isothiocyanatoguaia-6-ene was achieved.

Experimental

General. IR spectra were measured with a Horiba FT 300-S spectrometer. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker AM 500 and JEOL α-500 spectrometers with $CHCl_3$ (δ = 7.24 for ^1H NMR) and $CDCl_3$ (δ = 77.0 for ^{13}C NMR) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX 102A mass spectrometer operating at 70 eV. All melting points were uncorrected. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium diphenylketyl. Methanol was distilled from magnesium methoxide and dried over Molecular Sieves 4A. Dichloromethane was distilled from P_2O_5, then CaH_2, and dried over Molecular Sieves 4A. Dimethylformamide (DMF) was dried over P_2O_5, then distilled under reduced pressure and dried over Molecular Sieves 4A. $Mn(pic)_3$ was prepared according to the literature.[29] Flash column chromatography was carried out on Merck Kieselgel 60 Art. 7734. Preparative TLC was performed on silica gel (Wakogel B-5F). All reactions were carried out under an argon atmosphere.

General Procedures for Synthesis of Bicyclic Cyclopropanols Containing An Olefinic Side Chain 4, 5, and 6.

General Procedure for Synthesis of Silyl Enol Ethers 9, 10, and 11. An HMPA (4.0 ml) solution of CuBr·SMe_2 (100 mg,



Scheme 9.

0.49 mmol) was added to a THF (30 ml) solution of 3-butenyl- or 4-pentenyl-magnesium bromide, prepared from the corresponding alkenyl bromide (13 mmol) and magnesium (15 mmol), over 5 minutes at −78 °C. The mixture was stirred for a further 30 min, and a THF solution (20 ml) of the corresponding enone (10 mmol) and chlorotrimethylsilane (2.2 g, 20 mmol) was added dropwise over 30 min at −78 °C. The mixture was stirred for 1 h, and the reaction was quenched with triethylamine (3.0 ml), followed by addition of hexane (50 ml) and pH 7 phosphate buffer. The reaction mixture was filtered, and the filtrate was extracted with hexane. The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography (deactivated with 5% H_2O, hexanes).

3-(3-Butenyl)-1-trimethylsiloxy-1-cyclohexene (9): 83% yield, IR (KBr, neat) 2927, 1664, 1369, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.16 (9H, s), 1.07—1.11 (1H, m), 1.31—1.38 (2H, m), 1.51—1.56 (1H, m), 1.67—1.75 (2H, m), 1.94—1.98 (2H, m), 2.06 (2H, dd, J = 7.5 and 14.7 Hz), 2.10—2.17 (1H, m), 4.78 (1H, s), 4.90 (1H, d, J = 11.4 Hz), 4.98 (1H, d, J = 17.2 Hz), 5.77—5.82 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 0.3, 21.7, 28.7, 30.0, 31.2, 34.0, 36.2, 109.2, 114.2, 139.1, 150.5. Found: C, 69.46; H, 10.47%. Calcd for $C_{13}H_{24}OSi$: C, 69.58; H, 10.77%.

3-(3-Butenyl)-1-trimethylsiloxy-1-cycloheptene (10): 68% yield, IR (KBr, neat) 2922, 1658, 1446, 1253 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.15 (9H, s), 1.25—1.68 (7H, m), 1.82—1.90 (1H, m), 1.98—2.16 (4H, m), 2.30—2.38 (1H, m), 4.77 (1H, d, J = 4.6 Hz), 4.91 (1H, d, J = 17.0 Hz), 4.98 (1H, d, J = 6.7 Hz), 5.75—5.83 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 0.3, 25.2, 29.7, 31.6, 34.0, 35.2, 35.7, 36.6, 114.2, 114.4, 139.0, 154.6. Found: *m/z* 238.1761. Calcd for $C_{14}H_{26}OSi$: M, 238.1754.

3-(4-Pentenyl)-1-trimethylsiloxy-1-cyclohexene (11): 74% yield, IR (KBr, neat) 2927, 1664, 1448, 1367, 1189 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.16 (9H, s), 1.03—1.11 (1H, m), 1.20—1.32 (2H, m), 1.35—1.43 (2H, m), 1.48—1.57 (1H, m), 1.64—1.70 (1H, m), 1.71—1.77 (1H, m), 1.89—1.98 (2H, m), 2.01 (2H, q, J = 6.7 Hz), 2.07—2.13 (1H, m), 4.77 (1H, d, J = 1.2 Hz), 4.91 (1H, d, J = 10.2 Hz), 4.97 (1H, d, J = 17.0 Hz), 5.75—5.83 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 0.3, 21.8, 26.3, 28.8, 30.0, 34.0, 34.5, 36.5, 109.5, 114.2, 139.0, 150.3. Found: C, 70.32; H, 10.81%. Calcd for $C_{14}H_{26}OSi$: C, 70.53; H, 10.99%.

General Procedure for Synthesis of Cyclopropanol Trimethylsilyl Ethers 12, 13, and 14. To a diethyl ether solution (10 ml) of a silyl enol ether (10 mmol) was added a hexane solution (1.0 mol dm^{-3}, 12 ml, 12 mmol) of diethylzinc, and then diiodomethane (1.0 ml, 12 mmol) was slowly added to the mixture. The mixture was stirred for 8 h at room temperature and then refluxed for 2 h. Saturated aqueous ammonium chloride was added to the mixture, and the products were extracted with diethyl ether. The organic layer was washed with brine, and dried over $MgSO_4$. After the evaporation of the solvent, the crude product was purified by column chromatography (deactivated with 5% H_2O, hexanes). Products were obtained as an inseparable mixture of diastereomers (ca. 90 : 10), and ^1H and ^{13}C NMR data were described for the major isomers. Relative stereochemistry was not determined.

5-(3-Butenyl)-1-trimethylsiloxybicyclo[4.1.0]heptane (12): 83% yield, IR (KBr, neat) 2927, 1460, 1357, 1253 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.11 (9H, s), 0.27 (1H, t, J = 5.0 Hz), 0.82 (1H, dd, J = 5.0 and 12.3 Hz), 0.79—0.93 (3H, m), 1.22—1.36 (1H, m), 1.42—1.61 (4H, m), 1.75—1.82 (1H, m), 2.08—2.17 (3H, m), 4.91 (1H, d, J = 10.4 Hz), 4.98 (1H, d, J = 17.1 Hz), 5.75—5.83 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 1.4, 18.9, 21.3, 24.7, 29.9, 31.5, 32.0, 37.5, 37.6, 57.2, 114.3, 138.9. Found: C, 70.56; H, 10.74%. Calcd for $C_{14}H_{26}OSi$: C, 70.53; H, 10.99%.

6-(3-Butenyl)-1-trimethylsiloxybicyclo[5.1.0]octane (13): 78% yield, IR (KBr, neat) 2924, 1643, 1448, 1251 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.10 (9H, s), 0.32 (1H, t, J = 5.5 Hz), 0.67 (1H, dt, J = 6.2 and 9.5 Hz), 0.75—0.83 (1H, m), 1.00 (1H, dd, J = 5.3 and 9.7 Hz), 1.08—1.22 (2H, m), 1.36—1.51 (3H, m), 1.53—1.62 (2H, m), 1.70—1.77 (1H, m), 1.81—1.88 (1H, m), 2.00—2.18 (2H, m), 2.26 (1H, dd, J = 6.4 and 14.5 Hz), 4.89 (1H, d, J = 10.2 Hz), 4.97 (1H, d, J = 17.1 Hz), 5.73—5.81 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 1.4, 24.0, 25.0, 30.3, 31.2, 31.8, 36.0, 37.3, 38.0, 43.1, 59.6, 114.0, 139.3. Found: C, 71.42; H, 10.90%. Calcd for $C_{15}H_{28}OSi$: C, 71.37; H, 11.17%.

5-(4-Pentenyl)-1-trimethylsiloxybicyclo[4.1.0]heptane (14): 82% yield, IR (KBr, neat) 2927, 1454, 1356, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.11 (9H, s), 0.27 (1H, t, J = 4.8 Hz), 0.78—0.94 (4H, m), 1.24—1.32 (1H, m), 1.34—1.48 (5H, m), 1.54—1.62 (1H, m), 1.74—1.82 (1H, m), 2.00—2.07 (2H, m), 2.12—2.17 (1H, m), 4.91 (1H, d, J = 10.2 Hz), 4.98 (1H, d, J = 17.2 Hz), 5.76—5.84 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 1.4, 18.9, 21.3, 24.8, 26.7, 30.1, 32.0, 33.9, 37.8, 38.1, 57.2, 114.2, 139.1. Found: C, 71.34; H, 10.95%. Calcd for $C_{15}H_{28}OSi$: C, 71.37; H, 11.17%.

General Procedure for Preparation of Cyclopropanols 4, 5, and 6. Potassium carbonate (50 mg, 0.36 mmol) was added to a methanol solution (30 ml) of a cyclopropyl trimethylsilyl ether (10 mmol), and the solution was stirred for 1 h at room temperature. The reaction was quenched with pH 7 phosphate buffer, and most of the methanol was removed under vacuum. The residual solution was extracted with ethyl acetate, and the organic layer was dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 10 : 1). Products were obtained as an inseparable mixture of diastereomers (ca. 90 : 10), and ^1H and ^{13}C NMR data were presented for the major isomers. Relative stereochemistry was not determined. These cyclopropanols were immediately used for the oxidation reactions, since they are not very stable at room temperature.

5-(3-Butenyl)bicyclo[4.1.0]heptan-1-ol (4): 93% yield, IR (KBr, neat) 3342, 2917, 1452, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.30 (1H, t, J = 4.7 Hz), 0.78—0.95 (4H, m), 1.23—1.36 (1H, m), 1.42—1.54 (3H, m), 1.57—1.64 (1H, m), 1.75 (1H, dt, J = 5.4 and 12.6 Hz), 2.08—2.17 (2H, m), 2.17—2.26 (2H, m), 4.91 (1H, d, J = 11.6 Hz), 4.98 (1H, d, J = 17.1 Hz), 5.75—5.84 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 19.1, 21.1, 25.4, 30.1, 31.3, 31.6, 37.2, 37.4, 56.0, 114.3, 138.9. Found: *m/z* 166.1350. Calcd for $C_{11}H_{18}O$: M, 166.1357.

6-(3-Butenyl)bicyclo[5.1.0]octan-1-ol (5): 91% yield, IR (KBr, neat) 3340, 2920, 1446, 1232 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.34 (1H, t, J = 5.5 Hz), 0.69—0.83 (2H, m), 1.00 (1H, dd, J = 5.0 and 9.5 Hz), 1.15—1.27 (2H, m), 1.30—1.51 (3H, m), 1.55—1.62 (1H, m), 1.64—1.70 (2H, m), 1.80—1.90 (2H, m), 2.03—2.18 (2H, m), 2.24—2.29 (1H, m), 4.89 (1H, d, J = 10.0 Hz), 4.96 (1H, d, J = 17.2 Hz), 5.73—5.82 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 24.2, 25.5, 31.2, 31.3, 31.8, 36.3, 37.2, 38.0, 43.1, 58.4, 114.1, 139.3. Found: *m/z* 180.1520. Calcd for $C_{12}H_{20}O$: M, 180.1514.

5-(4-Pentenyl)bicyclo[4.1.0]heptan-1-ol (6): 89% yield, IR (KBr, neat) 3303, 2925, 1454, 1348 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.29 (1H, t, J = 4.7 Hz), 0.75—0.94 (4H, m), 1.24—1.32 (1H, m), 1.33—1.49 (5H, m), 1.56—1.62 (1H, m), 1.72—1.78 (1H, m), 1.97—2.04 (2H, br), 2.13—2.19 (2H, m), 4.89 (1H, d, J = 10.4 Hz), 4.96 (1H, d, J = 17.2 Hz), 5.74—5.83 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 19.1, 21.1, 25.4, 26.5, 30.2, 31.7, 33.9, 37.7, 37.8, 55.9, 114.2, 139.0. Found: *m/z* 180.1490. Calcd for $C_{12}H_{20}O$: M, 180.1513.

General Procedure for Synthesis of Bicyclic Compounds by Trapping the Radical Intermediates with Silyl Enol Ethers. To a DMF suspension (3.0 ml) of $Mn(pic)_3$ (0.51 g, 1.2 mmol) was added a DMF solution (5.0 ml) of a cyclopropanol (1.0 mmol) and a silyl enol ether (3.0 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at this temperature. The reaction was quenched with pH 7 phosphate buffer, and the mixture was filtered through Celite. The filtrate was extracted with diethyl ether, and the extract was dried over $MgSO_4$. The crude mixture was purified by thin layer chromatography (hexanes : ethyl acetate = 4 : 1).

(1*R, 7*S**, 10*R**)-(±)-10-(3-Oxo-3-phenylpropyl)bicyclo[5.3.0]decan-3-one (15):** 81% yield, IR (KBr, disk) 2908, 1685, 1448, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.15—1.27 (2H, m), 1.33—1.46 (2H, m), 1.52—1.67 (3H, m), 1.76—1.85 (2H, m), 1.86—1.93 (3H, m), 2.01—2.07 (2H, m), 2.44—2.50 (2H, m), 2.54 (1H, dt, J = 3.6 and 15.9 Hz), 2.87 (1H, ddd, J = 6.2, 9.2, and 16.4 Hz), 2.97 (1H, ddd, J = 5.2, 9.6, and 16.4 Hz), 7.44 (2H, t, J = 7.6 Hz), 7.53 (1H, t, J = 7.6 Hz), 7.92 (2H, d, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.6, 24.8, 29.8, 32.4, 35.8, 37.3, 42.8, 43.8, 44.3, 45.2, 47.0, 128.0, 128.6, 133.0, 136.7, 200.4, 214.8. Found: C, 80.54; H, 8.43%. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51%.

(1*R, 7*S**, 10*R**)-(±)-10-[3-(4-Bromophenyl)-3-oxopropyl]-bicyclo[5.3.0]decan-3-one (16):** 51% yield, IR (KBr, disk) 2912, 1689, 1579, 1351 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.18—1.27 (2H, m), 1.30—1.46 (2H, m), 1.51—1.66 (3H, m), 1.75—1.84 (2H, m), 1.86—1.93 (3H, m), 2.00—2.10 (2H, m), 2.43—2.57 (3H, m), 2.83 (1H, ddd, J = 6.1, 9.3, and 16.8 Hz), 2.93 (1H, ddd, J = 5.1, 9.5, and 16.8 Hz), 7.58 (2H, d, J = 8.6 Hz), 7.78 (2H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.5, 24.8, 29.7, 32.4, 35.7, 37.3, 42.7, 43.6, 44.2, 45.1, 46.9, 128.1, 129.5, 131.7, 135.7, 199.1, 214.6. Found: C, 62.60; H, 6.42; Br, 22.01%. Calcd for $C_{19}H_{23}O_2Br$: C, 62.82; H, 6.32; Br, 22.00%.

(1*R, 8*S**, 11*R**)-(±)-11-(3-Oxo-3-phenylpropyl)bicyclo[6.3.0]undecan-3-one (17):** 63% yield, IR (KBr, disk) 2941, 1693, 1597, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.14—1.28 (3H, m), 1.38—1.46 (1H, m), 1.48—1.64 (4H, m), 1.74—1.85 (4H, m), 1.86—1.99 (2H, m), 2.00—2.10 (1H, m), 2.30 (1H, dd, J = 3.2 and 11.5 Hz), 2.34—2.39 (2H, m), 2.62 (1H, t, J = 12.1 Hz), 2.85 (1H, ddd, J = 5.9, 9.7, and 16.2 Hz), 2.96 (1H, ddd, J = 4.9, 10.0, and 16.2 Hz), 7.53 (2H, t, J = 7.7 Hz), 7.43 (1H, t, J = 7.7 Hz), 7.92 (2H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.7, 25.9, 26.8, 29.2, 30.3, 33.7, 37.0, 41.9, 42.5, 43.1, 44.7, 48.1, 128.0, 128.5, 132.9, 136.9, 200.3, 216.9. Found: C, 80.41; H, 8.59%. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78%.

(1*R, 8*S**, 11*R**)-(±)-11-[3-(4-Bromophenyl)-3-oxopropyl]-bicyclo[6.3.0]undecan-3-one (18):** 68% yield, IR (KBr, disk) 2941, 1680, 1452, 1402, 1203 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.14—1.27 (3H, m), 1.37—1.45 (1H, m), 1.48—1.64 (4H, m), 1.73—1.86 (4H, m), 1.87—1.97 (2H, m), 2.00—2.08 (1H, m), 2.29 (1H, dd, J = 3.2 and 11.6 Hz), 2.35—2.40 (2H, m), 2.61 (1H, t, J = 12.2 Hz), 2.81 (1H, ddd, J = 5.9, 9.7, and 16.0 Hz), 2.92 (1H, ddd, J = 5.0, 10.0, and 16.0 Hz), 7.57 (2H, d, J = 8.6 Hz), 7.78 (2H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.8, 25.7, 26.8, 29.2, 30.3, 33.9, 37.0, 41.9, 42.4, 43.2, 48.2, 128.1, 129.5, 131.9, 135.8, 199.3, 216.7. Found: C, 63.49; H, 6.64; Br, 21.28%. Calcd for $C_{20}H_{25}BrO_2$: C, 63.67; H, 6.68; Br, 21.18%.

11-(3-Oxo-3-phenylpropyl)bicyclo[5.4.0]undecan-3-one (19): Obtained as an inseparable mixture of two stereoisomers. 64% yield, IR (KBr, neat) 2941, 1701, 1684, 1450, 1281 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.82—1.10 (3H, m), 1.15—1.29 (2H, m), 1.33—1.47 (3H, m), 1.55—1.63 (2H, m), 1.67—1.90 (5H, m), 1.99—2.06 (0.5H, m), 2.07 (0.5H, d, J = 11.3 Hz), 2.25—2.36 (1H, m), 2.44—2.53 (1H, m), 2.61 (0.5H, dd, J = 1.3 and 12.0 Hz), 2.79—2.87 (1H, m), 2.92 (0.5H, t, J = 11.3 Hz), 2.97—3.08 (1H, m), 7.41—7.45 (2H, m), 7.50—7.54 (1H, m), 7.93—7.96 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 19.7, 19.9, 22.1, 22.6, 25.9, 28.1, 28.9, 32.0, 34.8, 34.9, 35.1, 35.3, 36.8, 37.2, 40.0, 40.8, 41.2, 43.5, 43.7, 45.6, 45.7, 45.8, 47.2, 48.8, 127.9, 128.0, 128.5, 128.6, 132.9, 133.0, 136.9, 137.0, 200.3, 200.5, 214.6, 215.2. Found: C, 80.21; H, 8.92%. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78%.

General Procedure for Synthesis of Bicyclic Compounds with Other Radical Trapping Reagent. To a DMF suspension (3.0 ml) of $Mn(pic)_3$ (0.63 g, 1.5 mmol) and a radical trapping reagent (1.5 mmol of n-Bu_3SnH or 0.75 mmol of PhSeSePh) was added a DMF solution (5.0 ml) of cyclopropanol **4** (166 mg, 1.0 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched by pH 7 phosphate buffer, and the mixture was filtered through Celite. The filtrate was extracted with diethyl ether and the extract was dried over $MgSO_4$. After evaporation of the solvent, the crude mixture was purified by thin layer chromatography (hexanes : ethyl acetate = 4 : 1).

(1*R, 7*R**, 10*R**)-(±)-10-Methylbicyclo[5.3.0]decan-3-one (20):** 75% yield, IR (KBr, neat) 2925, 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.81 (3H, d, J = 7.4 Hz), 1.15—1.29 (3H, m), 1.48—1.66 (2H, m), 1.76—1.93 (4H, m), 2.02—2.08 (1H, m), 2.11—2.16 (1H, m), 2.37 (1H, dd, J = 12.0, 16.2 Hz), 2.44—2.55 (3H, m); ^{13}C NMR ($CDCl_3$) δ = 16.0, 24.6, 32.1, 32.5, 36.1, 37.6, 44.0, 44.2, 45.2, 45.6, 215.0. Found: *m/z* 166.1364. Calcd for $C_{11}H_{18}O$: M, 166.1357.

(1*R, 7*S**, 10*S**)-(±)-10-Phenylselenomethylbicyclo[5.3.0]-decan-3-one (21):** 68% yield, IR (KBr, neat) 2929, 1697, 1441 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.17—1.27 (2H, m), 1.50—1.67 (3H, m), 1.83—1.96 (4H, m), 2.03—2.09 (1H, m), 2.28—2.35 (1H, m), 2.40—2.60 (4H, m), 2.64 (1H, t, J = 11.4 Hz), 2.97 (1H, dd, J = 4.4 and 11.4 Hz), 7.18—7.24 (3H, m), 7.41—7.47 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 24.9, 30.2, 30.7, 32.2, 35.6, 43.4, 43.8, 44.3, 44.9, 47.1, 126.7, 129.1, 130.5, 132.5, 214.1. Found: C, 63.27; H, 6.82%. Calcd for $C_{17}H_{22}OSe$: C, 63.55; H, 6.90%.

(1*R, 7*R**, 10*R**)-(±)-10-(3-Cyanopropyl)bicyclo[5.3.0]-heptan-3-one (22).** To a DMF suspension (0.75 ml) of $Mn(pic)_3$ (108 mg, 0.26 mmol), acrylonitrile (66 mg, 1.25 mmol), and n-Bu_3SnH (73 mg, 0.25 mmol) was added a DMF solution (0.25 ml) of cyclopropanol **4** (27 mg, 0.16 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched by pH 7 phosphate buffer, and the mixture was filtered through Celite. The filtrate was extracted with ether and the extract was dried over $MgSO_4$. After evaporation of the solvent, the crude mixture was purified by thin layer chromatography (hexanes : ethyl acetate = 6 : 1). 66% yield, IR (KBr, neat) 2933, 2245, 1697, 1452 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.13—1.33 (5H, m), 1.40—1.61 (4H, m), 1.67—1.82 (2H, m), 1.84—1.95 (3H, m), 1.95—2.03 (1H, m), 2.03—2.08 (1H, m), 2.28—2.53 (5H, m); ^{13}C NMR ($CDCl_3$) δ = 17.3, 24.2, 24.9, 29.2, 29.7, 32.5, 35.8, 42.3, 43.8, 43.9, 45.1, 47.0, 119.6, 214.3. Found: *m/z* 219.1631. Calcd for $C_{14}H_{21}NO$: M, 219.1622.

Total Synthesis of 10-Isothiocyanatoguaia-6-ene 4-(2-Tetrahydropyranyloxy)-2-cyclohexen-1-one. To a dichloromethane solution (25 ml) of pyridinium p-toluenesulfonate (255 mg, 1.0 mmol) and 4-hydroxy-2-cyclohexen-1-one (5.11 g, 46 mmol), prepared from 1,3-cyclohexadiene according to the literature,[20] was added a dichloromethane solution (25 ml) of dihydropyran (6.0 g, 71 mmol) and the mixture was stirred for 10 h at room temperature. After addition of diethyl ether, the mixture was washed with aqueous sodium hydrogencarbonate and the organic layer was dried over $MgSO_4$. After evaporation of the solvent, the crude product was

purified by column chromatography (hexanes) to give the product (8.67 g, 44 mmol) in 97% yield. IR (KBr, neat) 2943, 1685, 1448, 1379 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.49—1.61 (4H, m), 1.69—1.74 (1H, m), 1.77—1.83 (1H, m), 1.90—1.99 (0.5H, m), 2.03—2.11 (0.5H, m), 2.25—2.38 (2H, m), 2.53—2.58 (1H, m), 3.48—3.51 (1H, m), 3.84—3.89 (1H, m), 4.45—4.50 (1H, m), 4.74—4.78 (1H, m), 5.94 (1H, d, J = 10.3 Hz), 6.89 (0.5H, dt, J = 2.0 and 10.3 Hz), 6.97 (0.5H, ddd, J = 1.5, 2.5, and 10.3 Hz). Found: C, 67.06; H, 8.27%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.21%.

(3R^*, 4R^*)-(±)-3-(3-Butenyl)-4-(2-tetrahydropyranyloxy)-1-trimethylsiloxy-1-cyclohexene (24). An HMPA solution (20 ml) of CuBr·SMe_2 (543 mg, 2.6 mmol) was added to a THF solution (75 ml) of 3-butenylmagnesium bromide, prepared from 3-butenyl bromide (9.06 g, 67 mmol) and magnesium (1.68 g, 67 mmol), over 5 min at −78 °C. The mixture was stirred for a further 30 min, and a THF solution (50 ml) of 4-(2-tetrahydropyranyloxy)-2-cyclohexen-1-one (9.05 g, 47 mmol) and chlorotrimethylsilane (10.1 g, 94 mmol) was added to the mixture dropwise over 30 min at −78 °C. The mixture was stirred for 1 h, and the reaction was quenched with triethylamine (5.0 ml), followed by addition of hexane (100 ml) and pH 7 phosphate buffer. The mixture was filtered through Celite and the filtrate was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography (deactivated with 5% H_2O, hexanes) to give the product (12.8 g, 40 mmol) in 86% yield. IR (KBr, neat) 2942, 1666, 1373, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.15 (9H, s), 1.22—1.43 (1H, m), 1.47—1.60 (4H, m), 1.60—1.74 (2H, m), 1.75—1.90 (2H, m), 1.95—2.28 (5H, m), 3.41—3.50 (1.5H, m), 3.55—3.60 (0.5H, m), 3.85—3.95 (1H, m), 4.60—4.63 (0.5H, m), 4.69—4.72 (0.5H, m), 4.73 (1H, s), 4.90—4.95 (1H, m), 5.00 (1H, d, J = 17.1 Hz), 5.73—5.86 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 0.25, 19.8, 20.0, 25.0, 25.5, 25.6, 27.6, 27.9, 28.1, 30.7, 30.9, 31.1, 31.2, 32.9, 33.0, 39.6, 40.0, 62.4, 62.8, 73.1, 77.4, 95.2, 99.8, 105.8, 106.2, 114.2, 114.4, 138.7, 138.9, 149.7, 150.1. Found: C, 66.19; H, 9.81%. Calcd for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.93%.

(4R^*, 5R^*)-(±)-5-(3-Butenyl)-4-(2-tetrahydropyranyloxy)-1-trimethylsiloxybicyclo[4.1.0]heptane. To a diethyl ether solution (50 ml) of silyl enol ether **24** (5.45 g, 17 mmol) was added a hexane solution (1.0 mol dm^{-3}, 18 ml) of diethylzinc, and then diiodomethane (1.9 ml, 24 mmol) was slowly added to the mixture. The reaction mixture was stirred for 8 h at room temperature and then refluxed for 2 h. A saturated aqueous ammonium chloride was added carefully and organic materials were extracted with diethyl ether. The organic layer was washed with brine, and dried over $MgSO_4$. After the evaporation of the solvent, the crude product was purified by column chromatography (deactivated with 5% H_2O, hexanes) to give the product (4.96 g, 15 mmol) in 87% yield. The product was obtained as an inseparable mixture of diastereomers (ca. 90 : 10 for cyclopropanation), and ^1H and ^{13}C NMR data were described for the major isomers. Relative stereochemistry of cyclopropane ring was not determined. IR (KBr, neat) 2943, 1443, 1359, 1254 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.09 (9H, s), 0.40—0.44 (1H, m), 0.78—0.92 (2H, m), 1.31—1.42 (2H, m), 1.43—1.59 (4H, m), 1.62—1.70 (1H, m), 1.73—1.85 (3H, m), 1.90—2.03 (2H, m), 2.03—2.15 (1H, m), 2.17—2.30 (2H, m), 3.08—3.15 (0.5H, m), 3.30—3.37 (0.5H, m), 3.41—3.50 (1H, m), 3.82—3.91 (1H, m), 4.52—4.57 (0.5H, m), 4.66—4.69 (0.5H, m), 4.91 (1H, d, J = 11.2 Hz), 4.97—5.05 (1H, m), 5.76—5.87 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 1.3, 19.0, 19.1, 19.7, 20.2, 22.9, 23.0, 25.4, 25.46, 25.50, 28.7, 30.5, 30.7, 31.1, 31.16, 31.24, 33.2, 33.3, 43.3, 43.8, 56.6, 56.8, 62.5, 63.1, 75.1, 81.4, 94.7, 101.6, 114.2, 114.3, 138.8, 139.0. Found: m/z 254.1735. Calcd for $C_{14}H_{26}O_2Si$: M($C_{19}H_{34}O_3Si$)-THP, 254.1702.

(4R^*, 5R^*)-(±)-5-(3-Butenyl)-4-(2-tetrahydropyranyloxy)bicyclo[4.1.0]heptan-1-ol (25). Potassium carbonate (50 mg, 0.36 mmol) was added to a methanol solution (50 ml) of the cyclopropyl trimethylsilyl ether (4.52 g, 13.4 mmol), and the mixture was stirred for 1 h. The reaction was quenched with pH 7 phosphate buffer, and most of the methanol was removed in vacuo. The residual solution was extracted with ethyl acetate, and the extract was dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 9 : 1) to give the product (3.32 g, 12.5 mmol) in 93% yield. The cyclopropanol was immediately used for the oxidation reaction, since it is not very stable at room temperature. IR (KBr, neat) 3427, 2941, 1446, 1356 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.46 (1H, t, J = 4.6 Hz), 0.82—0.94 (3H, m), 1.32—1.55 (6H, m), 1.63—2.04 (6H, m), 2.06—2.12 (1H, m), 2.20—2.30 (2H, m), 3.10—3.15 (0.5H, m), 3.31—3.35 (0.5H, m), 3.42—3.50 (1H, m), 3.83—3.92 (1H, m), 4.52—4.56 (0.5H, m), 4.67—4.70 (0.5H, m), 4.92 (1H, d, J = 11.2 Hz), 5.00—5.07 (1H, m), 5.76—5.87 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 19.27, 19.32, 19.6, 20.1, 23.6, 23.8, 25.26, 25.34, 25.5, 28.4, 30.4, 30.5, 30.7, 31.0, 31.1, 31.2, 33.1, 33.3, 43.0, 43.7, 55.3, 55.5, 62.5, 63.0, 75.0, 81.3, 94.7, 101.5, 114.0, 114.3, 138.8, 139.0. Found: m/z 266.1873. Calcd for $C_{16}H_{26}O_3$: M, 266.1882.

(1R^*, 6R^*, 7R^*, 10R^*)-(±)-10-Methyl-6-(2-tetrahydropyranyloxy)bicyclo[5.3.0]decan-3-one (26). To a DMF suspension (30 ml) of $Mn(pic)_3$ (5.46 g, 13 m mol) and n-Bu_3SnH (3.73 g, 13 mol) was added a DMF solution (20 ml) of cyclopropanol **25** (3.32 g, 12 mmol) at 0 °C, and the mixture was stirred for 1 h at 0 °C. The reaction was quenched by pH 7 phosphate buffer, and the mixture was filtered through Celite. The filtrate was extracted with diethyl ether and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 4 : 1) to give the product (2.84 g, 11 mmol) in 76% yield. IR (KBr, neat) 2949, 1703, 1452, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.79 (1.5H, d, J = 7.4 Hz), 0.80 (1.5H, d, J = 7.4 Hz), 1.20—1.33 (1H, m), 1.46—1.60 (5H, m), 1.65—1.87 (6H, m), 2.02—2.18 (3H, m), 2.22—2.54 (4H, m), 3.34 (0.5H, dt, J = 5.0 and 10.0 Hz), 3.43—3.52 (1.5H, m), 3.86—3.93 (1H, m), 4.62—4.65 (0.5H, m), 4.68—4.71 (0.5H, m); ^{13}C NMR ($CDCl_3$) δ = 15.6, 15.7, 19.6, 20.1, 25.3, 25.4, 28.3, 29.5, 29.6, 31.1, 31.2, 31.7, 31.8, 31.9, 37.7, 37.9, 38.6, 39.2, 40.4, 40.7, 44.6, 44.7, 50.6, 51.6, 62.7, 63.2, 80.7, 86.1, 95.0, 101.6, 213.6, 213.8. Found: C, 71.97; H, 9.93%. Calcd for $C_{16}H_{26}O_3$: C, 72.15; H, 9.83%.

(1R^*, 6R^*, 7R^*, 10R^*)-(±)-6-Hydroxy-10-methylbicyclo[5.3.0]decan-3-one. Acetic acid (40 ml) was added to a THF–H_2O solution (60 ml, 2 : 1) of tetrahydropyranyloxy ketone **26** (4.50 g, 16.9 mmol), and the mixture was stirred for 24 h at room temperature. The solvent was evaporated and the resulting mixture was neutralized with saturated $NaHCO_3$ solution. The organic materials were extracted with ethyl acetate, and the extract was dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 2 : 1) to give the hydroxy ketone (2.80 g, 15.4 mmol) in 91% yield. IR (KBr, neat) 3434, 2954, 1697, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.79 (3H, d, J = 7.1 Hz), 1.32—1.38 (1H, m), 1.46—1.54 (1H, m), 1.66—1.78 (3H, m), 1.80—1.92 (2H, m), 2.04—2.12 (2H, m), 2.12—2.18 (1H, m), 2.36—2.49 (3H, m), 2.50—2.57 (1H, m), 3.47 (1H, dt, J = 3.2 and 10.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 15.5, 29.1, 31.9, 33.1, 37.8, 38.9, 40.4, 44.8, 52.2, 77.7, 213.7. Found: C, 72.21; H, 9.82%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

(1R^*, 6R^*, 7R^*, 10R^*)-(±)-6-*t*-Butyldimethylsiloxy-10-meth-

ylbicyclo[5.3.0]decan-3-one (27). To a DMF solution (10 ml) of the hydroxy ketone (2.00 g, 11.0 mmol) and TBSCl (1.75 g, 11.6 mmol) was added a DMF solution (10 ml) of imidazole (0.79 g, 12.0 mmol) and the mixture was stirred for 3 h at room temperature. The reaction was quenched by pH 7 phosphate buffer, and organic materials were extracted with diethyl ether. The organic layer was washed with brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 20 : 1) to give the product (2.99 g, 10.1 mmol) in 92% yield. IR (KBr, neat) 2954, 1704, 1254, 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.03 (3H, s), 0.04 (3H, s), 0.79 (3H, d, J = 7.1 Hz), 0.85 (9H, s), 1.22—1.28 (1H, m), 1.31—1.39 (1H, m), 1.67—1.85 (5H, m), 1.90—1.96 (1H, m), 2.00—2.07 (1H, m), 2.10—2.16 (1H, m), 2.34—2.42 (2H, m), 2.44—2.51 (1H, m), 3.42 (1H, dt, J = 3.4 and 9.8 Hz); ^{13}C NMR($CDCl_3$) δ = −4.6, −4.0, 16.0, 17.9, 25.8, 30.4, 31.9, 33.8, 37.9, 39.0, 40.2, 44.9, 52.9, 78.8, 213.8. Found: C, 68.81; H, 10.64%. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.87%.

Synthesis of Hydroxy Ketone 28 and 29. To a THF–hexane solution of LDA, prepared from diisopropylamine (1.45 g, 14.4 mmol) and a hexane solution of *n*-BuLi (1.6 mol dm^{-3}, 10 ml, 16.0 mmol) in THF (20 ml), was added a THF solution (20 ml) of the ketone **27** (2.81 g, 9.5 mmol) at 0 °C, and the mixture was stirred for 30 min. An HMPA solution (9 ml) of TMSCl (2.73 g, 25.2 mmol) was added, and the mixture was stirred for 3 h. The reaction was quenched with pH 7 phosphate buffer, and the organic layer was separated. The aqueous layer was extracted with diethyl ether, and the combined organic phase was dried over $MgSO_4$. After evaporation of the solvent, the crude product was used for the next step without further purification.

To a dichloromethane solution (10 ml) of the above crude product was added $NaHCO_3$ (1.38 g, 16.4 mmol) and a dichloromethane solution (25 ml) of *m*-chloroperbenzoic acid (2.25 g, 13.1 mmol) at 0 °C, and the resulting mixture was stirred for 3 h at this temperature. Saturated Na_2SO_3 solution and diethyl ether were added to the mixture, and organic materials were extracted with diethyl ether. The extract was dried over $MgSO_4$, and then the solvent was evaporated. To the residue was added a THF solution of tetrabutylammonium fluoride (1.0 mol dm^{-3}, 4 ml, 4.0 mmol), and the mixture was stirred for 1 h at room temperature. The reaction was quenched with pH 7 phosphate buffer, and the product was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, and then evaporated. The crude product was purified with column chromatography (hexanes : ethyl acetate = 4 : 1) to give two isomeric products (0.85 g, 2.7 mmol and 0.90 g, 2.9 mmol) in 29 and 30% yield.

(1*R, 2*S**, 6*R**, 7*R**, 10*R**)-(±)-6-*t*-Butyldimethylsiloxy-2-hydroxy-10-methylbicyclo[5.3.0]decan-3-one (28):** IR (KBr, neat) 3467, 2954, 1701, 1254 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.03 (3H, s), 0.04 (3H, s), 0.86 (9H, s), 1.00 (3H, d, J = 7.0 Hz), 1.33—1.45 (2H, m), 1.50 (1H, dt, J = 6.0 and 11.3 Hz), 1.67—1.76 (1H, m), 1.82—1.93 (2H, m), 2.08—2.20 (2H, m), 2.38—2.50 (2H, m), 2.70 (1H, ddd, J = 3.2, 6.9, and 17.5 Hz), 3.38—3.43 (1H, m), 3.77 (1H, d, J = 3.7 Hz), 4.13 (1H, dd, J = 3.7 and 11.6 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.6, −4.1, 15.3, 18.0, 25.8, 29.9, 30.5, 32.2, 35.3, 36.8, 47.9, 48.5, 77.36, 77.44, 212.9. Found: *m/z* 312.2108. Calcd for $C_{17}H_{32}O_3Si$: M, 312.2120.

(1*R, 6*R**, 7*R**, 10*R**)-(±)-6-*t*-Butyldimethylsiloxy-4-hydroxy-10-methylbicyclo[5.3.0]decan-3-one (29):** IR (KBr, neat) 3471, 2954, 1705, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.078 (3H, s), 0.082 (3H, s), 0.82 (3H, d, J = 7.2 Hz), 0.86 (9H, s), 1.28—1.34 (1H, m), 1.40—1.47 (1H, m), 1.63—1.71 (2H, m), 1.78—1.84 (1H, m), 1.88—1.96 (1H, m), 2.02—2.10 (1H, m), 2.14—2.22 (2H, m), 2.43 (1H, dd, J = 12.7 and 19.4 Hz), 2.62 (1H, dd, J = 2.6 and 19.4 Hz), 3.64 (1H, dt, J = 3.9 and 10.4 Hz), 3.81 (1H, d, J = 4.2 Hz), 4.31 (1H, ddd, J = 2.6, 4.2, and 12.3 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.6, −4.0, 15.4, 18.0, 25.8, 30.4, 32.3, 37.7, 37.9, 41.6, 43.6, 52.6, 72.2, 76.0, 212.7. Found: *m/z* 312.2110. Calcd for $C_{17}H_{32}O_3Si$: M, 312.2120.

Transformation of 29 to 27. To a toluene solution (1.0 ml) of 1,1′-thiocarbonyldiimidazole (100 mg, 0.56 mmol) was added a toluene solution (1.0 ml) of hydroxy ketone **29** (72 mg, 0.23 mmol), and the mixture was refluxed for 1 h. A toluene solution (1.0 ml) of *n*-Bu_3SnH (80 mg, 0.28 mmol) and AIBN (5.0 mg) were added to the resulting mixture, and the mixture was further refluxed for 1 h. The solvent was evaporated, and the crude product was purified by thin layer chromatography (hexanes : ethyl acetate = 20 : 1) to give **27** (59 mg, 0.29 mmol) in 87% yield.

(1*R, 2*S**, 3*S**, 6*R**, 7*R**, 10*R**)-(±)-6-*t*-Butyldimethylsiloxy-3-isopropyl-10-methylbicyclo[5.3.0]decane-3,4-diol.** To a THF suspension (10 ml) of organocerium reagent, prepared from $CeCl_3 \cdot 7H_2O$ (2.50 g, 6.70 mmol) and isopropylmagnesium chloride (2.0 mol dm^{-3}, 3.0 ml) according to the literature,[22] was added a THF solution (10 ml) of hydroxy ketone **28** (673 mg, 2.20 mmol) at 0 °C, and the mixture was stirred for 1 h at this temperature. The reaction was quenched with acetic acid, and the product was extracted with diethyl ether and the extract was dried over $MgSO_4$. After the evaporation of solvent, the crude product was purified by column chromatography (hexanes : ethyl acetate = 4 : 1) to give the product (466 mg, 1.31 mmol) in 61% yield. Hydroxy ketone **28** was recovered in 20% yield. IR (KBr, disk) 3436, 2952, 1255, 1072 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.08 (3H, s), 0.09 (3H, s), 0.75 (3H, d, J = 7.0 Hz), 0.84 (3H, d, J = 7.0 Hz), 0.91 (3H, d, J = 6.9 Hz), 1.00 (9H, s), 1.30 (1H, dd, J = 7.8 and 11.0 Hz), 1.41—1.56 (5H, m), 1.61—1.72 (2H, m), 1.78 (1H, s), 1.80—1.85 (1H, m), 2.02 (1H, sept, J = 6.9 Hz), 2.03—2.09 (1H, m), 2.15 (1H, q, J = 7.0 Hz), 2.20—2.28 (1H, m), 3.46—3.50 (1H, m), 3.49 (1H, ddd, J = 2.4, 5.8, and 8.2 Hz); ^{13}C NMR (C_6D_6) δ = −4.4, −3.6, 14.0, 16.6, 17.9, 18.2, 22.2, 26.1, 29.0, 30.2, 32.3, 34.6, 37.2, 44.2, 46.8, 74.7, 76.0, 77.7. Found: C, 67.29; H, 11.08%. Calcd for $C_{20}H_{40}O_3Si$: C, 67.36; H, 11.30%.

Thiocarbamate 30. A hexane solution of *n*-BuLi (1.6 mol dm^{-3}, 1.44 ml, 2.30 mmol) was added to a THF solution (15 ml) of the above diol (411 mg, 1.15 mmol), and the mixture was stirred for 1 h at −78 °C. A THF solution (10 ml) of carbon disulfide (1.0 g, 17.8 mmol) was added and the mixture was stirred for 2 h at 0 °C. Methyl iodide (1.5 ml, 16.2 mmol) was added to the mixture and the reaction was quenched with pH 7 phosphate buffer. The resulting mixture was extracted with diethyl ether, and the extract was dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (hexanes : ethyl acetate = 20 : 1) to give the product (376 mg, 0.95 mmol) in 82% yield. IR (KBr, disk) 2956, 1298, 1271, 1076 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.03 (3H, s), 0.05 (3H, s), 0.84 (9H, s), 0.93 (3H, d, J = 7.1 Hz), 1.03 (3H, d, J = 6.7 Hz), 1.06 (3H, d, J = 6.7 Hz), 1.22—1.30 (1H, m), 1.34—1.39 (1H, m), 1.53—1.60 (1H, m), 1.62—1.72 (2H, m), 1.78 (1H, dd, J = 12.5 and 14.8 Hz), 1.91 (1H, ddd, J = 4.6, 8.8, and 13.8 Hz), 1.98—2.07 (3H, m), 2.12 (1H, dd, J = 8.8 and 14.8 Hz), 2.40—2.47 (1H, m), 3.33 (1H, dt, J = 4.6 and 9.8 Hz), 4.52 (1H, d, J = 11.3 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.7, −3.7, 14.7, 15.6, 16.5, 17.9, 25.8, 26.2, 29.0, 31.7, 31.8, 35.0, 36.7, 45.1, 46.3, 77.0, 88.0, 95.0, 190.9. Found: C, 63.27; H, 9.31; S, 8.12%. Calcd for $C_{21}H_{38}O_3SSi$: C, 63.27; H, 9.60; S, 8.04%.

(1*R, 6*S**, 7*S**, 10*S**)-(±)-6-*t*-Butyldimethylsiloxy-3-isopro-**

pyl-10-methylbicyclo[5.3.0]dec-2-ene (31). Thiocarbamate **30** (200 mg, 0.50 mmol) was dissolved in triethyl phosphite (10 ml), and the mixture was heated at 140 °C for 24 h. Triethyl phosphite was evaporated, and the crude mixture was purified by thin layer chromatography (hexanes : ethyl acetate = 20 : 1) to give the product (151 mg, 0.47 mmol) in 93% yield. IR (KBr, neat) 2954, 1464, 1257, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.04 (3H, s), 0.05 (3H, s), 0.86 (9H, s), 0.88 (3H, d, J = 6.8 Hz), 0.94 (3H, d, J = 6.7 Hz), 0.95 (3H, d, J = 6.5 Hz), 1.17—1.37 (3H, m), 1.58 (1H, quint, J = 9.2 Hz), 1.68—1.75 (1H, m), 1.83—1.88 (1H, m), 1.90—2.06 (3H, m), 2.12—2.16 (2H, m), 2.20 (1H, sept, J = 6.8 Hz), 3.42 (1H, dt, J = 4.1 and 9.4 Hz), 5.47 (1H, brs); ^{13}C NMR ($CDCl_3$) δ = −4.5, −3.8, 16.4, 18.1, 21.1, 21.4, 25.1, 26.0, 29.5, 32.3, 36.2, 37.0, 37.1, 43.7, 49.1, 80.9, 123.3, 148.5. Found: C, 74.45; H, 11.69%. Calcd for $C_{20}H_{38}OSi$: C, 74.47; H, 11.87%.

(1*R, 6*S**, 7*S**, 10*S**)-(±)-3-Isopropyl-10-methylbicyclo-[5.3.0]dec-2-en-6-ol.** $TsOH \cdot H_2O$ (20 mg, 0.11 mmol) was added to a dichloromethane solution (10 ml) of bicyclodecene **31** (110 mg, 0.34 mmol), and the mixture was stirred for 10 h at room temperature. Saturated aqueous sodium hydrogencarbonate was added and the mixture was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified by thin layer chromatography (hexanes : ethyl acetate = 8 : 1) to give the product (63 mg, 0.30 mmol) in 89% yield. IR (KBr, neat) 3354, 2956, 1460, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (3H, d, J = 6.8 Hz), 0.95 (3H, d, J = 6.7 Hz), 0.96 (3H, d, J = 6.5 Hz), 1.17—1.24 (1H, m), 1.32—1.37 (1H, m), 1.41—1.59 (3H, m), 1.73—1.80 (1H, m), 1.94—2.10 (4H, m), 2.14—2.25 (3H, m), 3.43 (1H, dt, J = 4.1 and 9.6 Hz), 5.49 (1H, brs); ^{13}C NMR ($CDCl_3$) δ = 16.4, 21.0, 21.3, 25.2, 28.2, 32.3, 35.4, 36.9, 37.0, 44.0, 48.6, 80.1, 123.1, 148.7. Found: *m/z* 208.1853. Calcd for $C_{14}H_{24}O$: M, 208.1827.

(1*R, 7*S**, 10*S**)-(±)-3-Isopropyl-10-methylbicyclo[5.3.0]-dec-2-en-6-one (32).** To a dichloromethane suspension (1 ml) of PCC (205 mg, 0.95 mmol) was added a dichloromethane solution (4 ml) of the above alcohol (46 mg, 0.22 mmol) and the mixture was stirred for 3 h at room temperature. The mixture was diluted with diethyl ether and filtered through Celite. The solvent was evaporated, and the crude product was purified by column chromatography (hexanes : ethyl acetate = 8 : 1) to give the product (39 mg, 0.19 mmol) in 85% yield. IR (KBr, neat) 2958, 1705, 1462 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.86 (3H, d, J = 7.0 Hz), 1.00 (3H, d, J = 6.8 Hz), 1.01 (3H, d, J = 6.8 Hz), 1.34—1.39 (1H, m), 1.61—1.76 (2H, m), 2.06 (1H, dd, J = 8.9 and 15.9 Hz), 2.17—2.47 (6H, m), 2.54—2.60 (1H, m), 2.91—2.98 (1H, m), 5.58 (1H, d, J = 3.1 Hz); ^{13}C NMR ($CDCl_3$) δ = 15.2, 21.2, 21.5, 21.9, 25.8, 31.8, 37.4, 37.9, 42.7, 46.8 53.9, 123.4, 147.5, 213.4. Found: *m/z* 206.1676. Calcd for $C_{14}H_{22}O$: M, 206.1671.

(1*R, 7*R**, 10*R**)-(±)-3-Isopropyl-10-methyl-6-methylenebicyclo[5.3.0]dec-2-ene (38).** To a diethyl ether solution (3 ml) of ketone **32** (24.2 mg, 0.117 mmol) was added a diethyl ether solution (1 mol dm^{-3}, 0.50 ml, 0.50 mmol) of trimethylsilylmethylmagnesium chloride, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated aqueous ammonium chloride solution, and the mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. Then the residue was treated with $TsOH \cdot H_2O$ (24 mg, 0.13 mmol) in dichloromethane (2 ml) for 5 min at r.t. The reaction was quenched with aqueous $NaHCO_3$ and the mixture was extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and the crude mixture was purified by thin layer chromatography (hexanes) to give the product (17.5 mg, 0.086 mmol) in 73% yield.

IR (KBr, neat) 2954, 1637, 1460, 1377 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.90 (3H, d, J = 7.5 Hz), 0.96 (3H, d, J = 7.5 Hz), 0.98 (3H, d, J = 7.5 Hz), 1.25—1.32 (1H, m), 1.67—1.74 (1H, m), 1.77—1.90 (2H, m), 1.98—2.02 (2H, m), 2.16—2.25 (3H, m), 2.25—2.29 (2H, br), 2.47 (1H, t, J = 10.5 Hz), 4.67 (1H, s), 4.70 (1H, s), 5.56 (1H, brs); ^{13}C NMR ($CDCl_3$) δ = 17.1, 21.3, 21.5, 27.6, 30.0, 32.9, 36.8, 37.36, 37.41, 47.66, 47.72, 106.0, 123.9, 148.5, 155.0.

10-Isothiocyanatoguaia-6-ene (39). To a chloroform solution (2 ml) of diene **38** (11.5 mg, 0.056 mmol) was added a chloroform solution (5 ml) of isothiocyanic acid, prepared from potassium hydrogensulfate (1.40 g) and potassium thiocyanate (0.90 g). The mixture was stirred for 3 d at room temperature. The solvent was evaporated and the crude mixture was purified by thin layer chromatography (hexanes : ethyl acetate = 20 : 1) to give 10-isothiocyanatoguaia-6-ene (**39**) (6.0 mg, 0.023 mmol, 40%) and 10-thiocyanatoguaia-6-ene (**40**)[28] (6.3 mg, 0.024 mmol, 42%). Spectroscopic data (^1H and ^{13}C NMR) of **39** were identical with the literature.[16]

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13) Other MM2 parameters were also examined. When MM2 UEC parameters contained in Materia Ver. 3.0 were used instead of the MM2 Prime (1980) parameters, the same diastereomers, **19a** and **19b**, were obtained by the transition state analysis of the cyclization of **6** (Transition state energies of **19a** (-33.73 kcal mol^{-1}) and **19b** (-33.19 kcal mol^{-1}) are close and lower than those of all the other structures by 2.3 kcal mol^{-1}). But in the cyclization of **4**, MM2 UEC parameters gave less reliable results compared to MM2 Prime (1980) parameters. In this case, energies of the *exo* transition structures with Ha–Hb in the *trans* and Hb–Hc in the *cis* (-32.33 kcal mol^{-1}) and with both Ha–Hb and Hb–Hc in the trans (-31.95 kcal mol^{-1}) were close and the energy difference between the two isomers was smaller than that between **19a** and **19b**.

Montecarlo approach with MM2* parameters by the use of Macromodel Ver. 5.0 gave similar results to those obtained with MM2 UEC parameters. It also predicted transition structures of **19a** (-150.96 kJ mol^{-1}) and **19b** (-148.87 kJ mol^{-1}) as the most stable in the cyclization of **6**, which are lower than all the other structures by 8.4 kJ mol^{-1}. But in the cyclization of **4**, energies of *exo* transition strucures with Ha–Hb in the *trans* and Hb–Hc in the *cis* (-144.23 kJ mol^{-1}) and with Ha-Hb in the *cis* and Hb–Hc in the *trans* (-143.26 kJ mol^{-1}) were qutie close.

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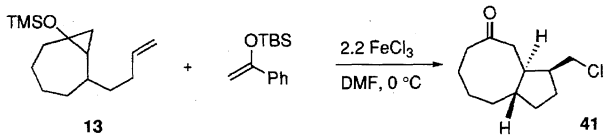

13 41

Chart 1. Scheme for Ref. 15.

15) The reaction of a trimethylsilyl ether of cyclopropanol **13** with $FeCl_3$ in the presence of 1-(*t*-butyldimethylsiloxy)-1-phenylethene was attempted according to Ref. 14. However, the addition product **17** was not obtained at all, and a chlorinated product **41** was obtained in 33% yield (Chart 1).

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