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Skeletal Rearrangement via Alkoxy Radical: Conversion of Epoxydecalin Thiocarbonylimidazolides to Bicyclo[6.3.0]undecanones and Bicyclo[5.3.1]undecanones

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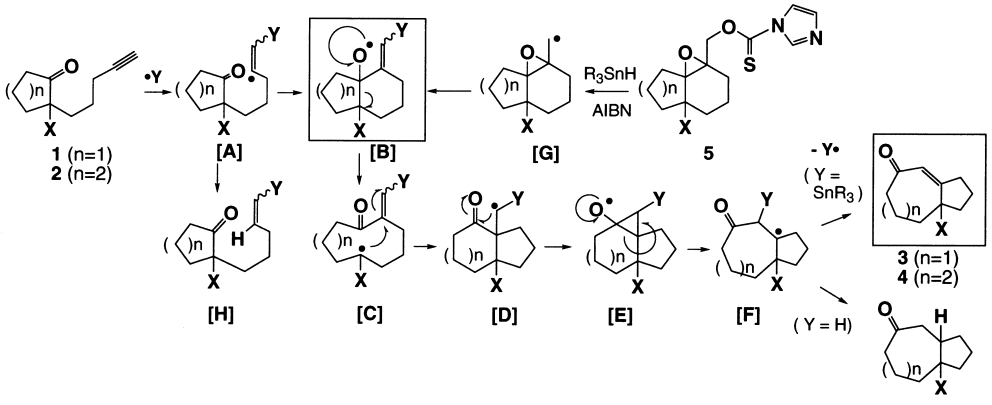
Abstract—The skeletal rearrangement of five types of epoxydecalin thiocarbonylimidazolides was investigated. This reaction proceeded via a 10-membered cyclic carbon radical formed by β-cleavage of alkoxy radicals, and produced two types of skeletal rearranged products; i.e. bicyclo[6.3.0]undecanones and bicyclo[5.3.1]undecanones. The ratio of the products strongly depended on the character and stereochemistry of the substituents. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The formation of C–C bonds by a radical reaction has been recently shown to be a useful method for constructing both carbocycles and heterocycles.[1] We have developed a new radical reaction in which cycloalkanones possessing acetylenic side chains are rearranged to bicyclic ketones by a single step via the β-cleavage of alkoxy radical.[2,3] The proposed mechanism of this reaction is shown in Scheme 1. Vinyl radical [A], generated by the addition of trialkyltin radical to the pentynyl side chain, attacked the carbonyl group to produce allyloxy radical [B]. Radical [C] would be generated by selective β-cleavage of the C–C bond in [B]. Subsequent cyclization should afford [D]. Carbon radical [D] would then attack the carbonyl again, followed by ring-expansion via [E] to give skeleton **3** or **4**. The same type of radical skeletal rearrangement was also reported by Pattenden.[4]



Scheme 1.

Keywords: radical reaction; cyclization.

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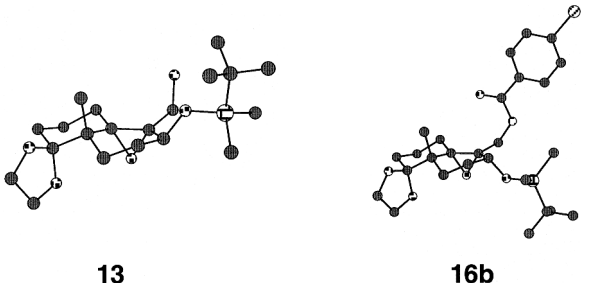
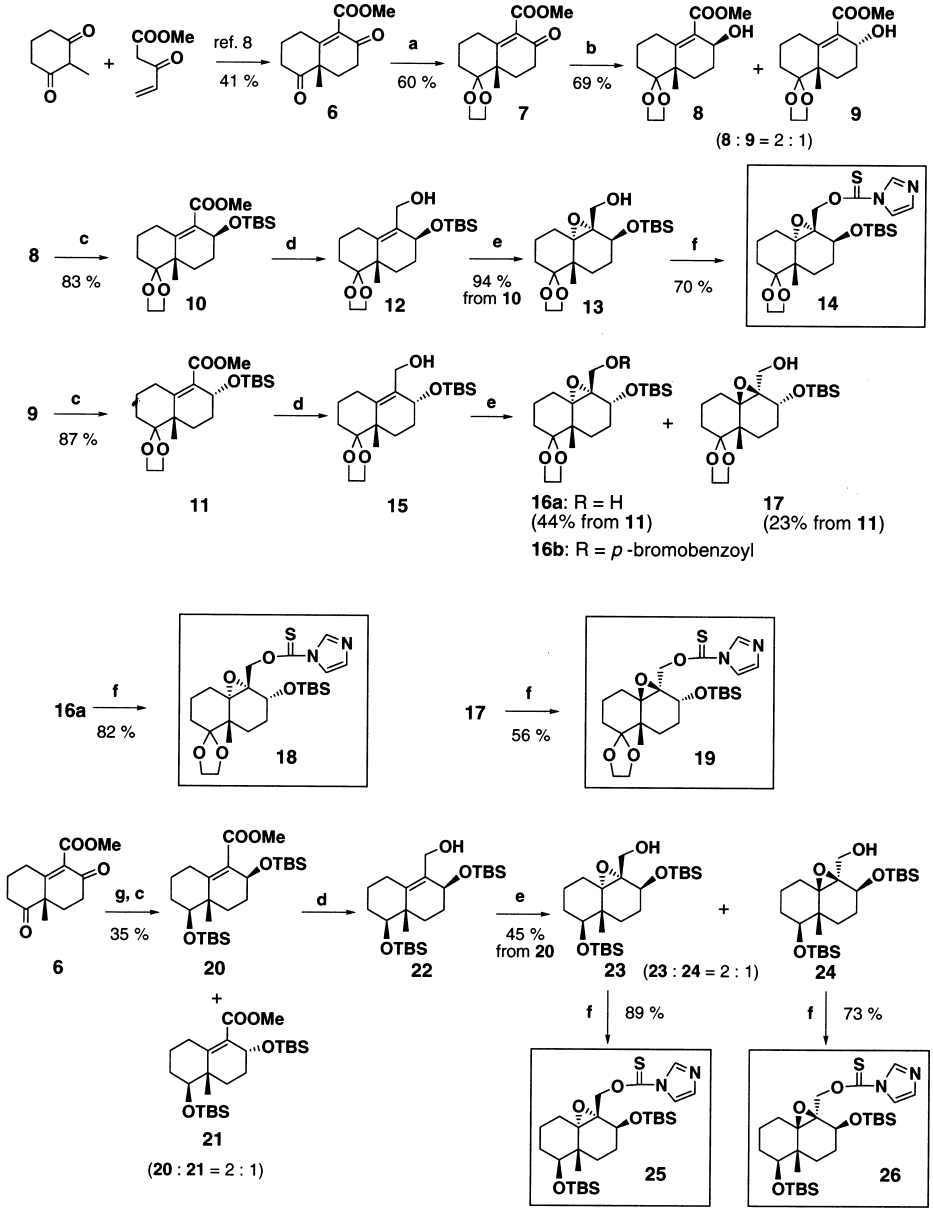


Figure 1. X-Ray structures of mono-acetalepoxides **13** and **16b**.

It was apparent that the step, in which alkoxy radical intermediate [B] was generated, strongly influenced the efficiency of this rearrangement. When X was the silyloxy group, this reaction proceeded smoothly. However, when X was a carbon functional group, such as an alkyl or alkoxycarbonyl group, the reduction product [H] was the major product and the rearranged products were obtained in less than 20% yield. Among the several methods used to generate alkoxy radical from alcohol,[5,6] homolytic cleavage of the epoxy ring is useful. Therefore, we investigated the radical reaction of epoxydecalin thiocarbonylimidazolide **5**, which would efficiently generate the same alkoxy radical [B] via epoxymethyl radical [G] regardless of the nature of X. We report here the full details of this reaction.[7]

Results and Discussion

Epoxydecalin thiocarbonylimidazolides were prepared from bicyclic diketoester **6**, which was obtained by the Robinson annulation of methyl-3-oxo-4-pentenoate and 2-methylcyclohexane-1,3-dione.[8] First, we synthesized stereoisomers **14**, **18** and **19**, which contain an acetal group.



Scheme 2. (a) Ethylene glycol, TsOH, benzene, reflux, 2.5 h; (b) $NaBH_4$, MeOH, 0°C, 0.5 h; (c) TBDMS–Cl, imidazole, DMF, rt, 21 h; (d) DIBAH, toluene, −78°C, 2 h; (e) *m*CPBA, CH_2Cl_2, rt, 3 h; (f) 1,1′-thiocarbonyldiimidazole, Et_3N, $ClCH_2CH_2Cl$, reflux, 3.5 h; (g) $NaBH_4$, EtOH, −78°C, 4 h.

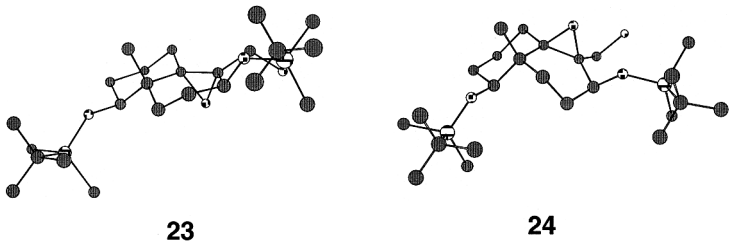


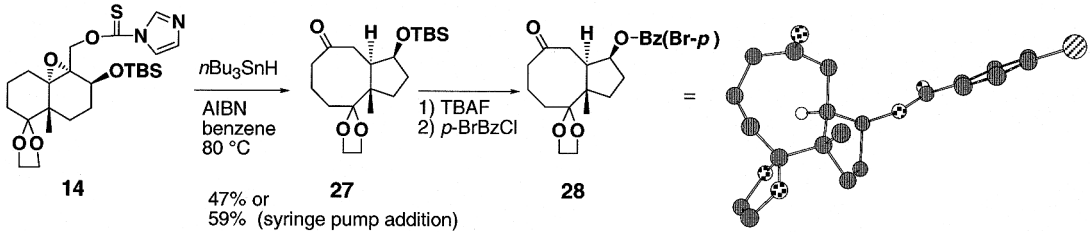
Figure 2. X-Ray structures of the epoxyalcohols **23** and **24**.

Selective monoacetalization of **6** gave **7**, which was reduced using $NaBH_4$ to give a mixture of alcohols **8** and **9** in a ratio of 2:1.[9] After separation by column chromatography, each alcohol was converted to silyl ethers **10** and **11**, respectively. Compound **10** was then converted to hydroxy epoxide **13** by DIBAH reduction followed by stereoselective epoxidation with *m*CPBA. The stereochemistry of **13** was determined by X-ray analysis (Fig. 1). Compound **13** was then converted to thiocarbonylimidazolide **14** using a conventional method.[10–12] The α-silyl ether **11** was also reduced to **15**, which was epoxidized by *m*CPBA to give two epoxides **16a** and **17**. These epoxides were separated and the stereochemistry of epoxide **16a** was determined to be α by X-ray analysis after it was converted to *p*-bromobenzoate **16b** (Fig. 1). Therefore, **17** was considered to be β-epoxide. Both epoxides were converted to radical precursors **18** and **19**.

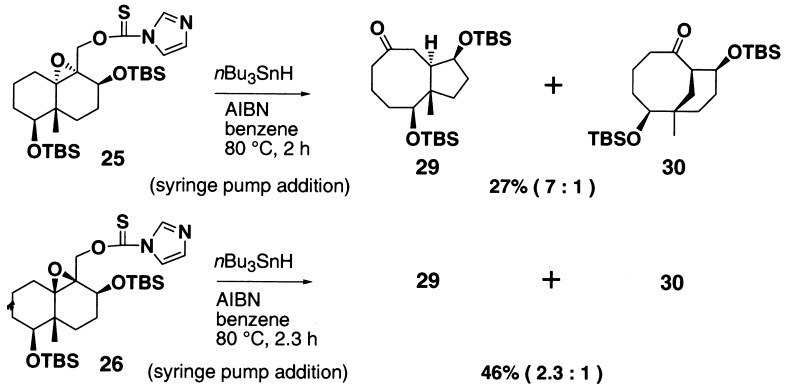
We also prepared bissilyl ethers **25** and **26**. Sodium borohydride reduction of **6** at −78°C gave two diols as a mixture of diastereoisomers, which were separated after conversion to bissilyl ethers **20** and **21** (**20**:**21**=2:1). β-Silyl ether **20** was then epoxidized by *m*CPBA to give two epoxides **23** and **24**. Their stereochemistries were determined by X-ray analysis (Fig. 2). Both **23** and **24** were converted to thiocarbonylimidazolides **25** and **26** as described above (Scheme 2).

When a mixture of **14**, *n*-Bu_3SnH (2 equiv.), and AIBN (catalytic amount) in benzene was heated for 0.5 h at 80°C, bicyclo[6.3.0]undecane derivative **27** was obtained in a yield of 47%, and its structure was confirmed by spectroscopic analysis and finally by X-ray crystallographic analysis after conversion to *p*-bromobenzoate **28**. The relative stereochemistry between the silyloxy group and the methyl group was retained, and the stereochemistry of the ring juncture was *trans* (Scheme 3). When a solution of *n*-Bu_3SnH and AIBN was also added slowly to a solution of **14** using a syringe pump for 1 h, the yield of **27** was improved (59%).

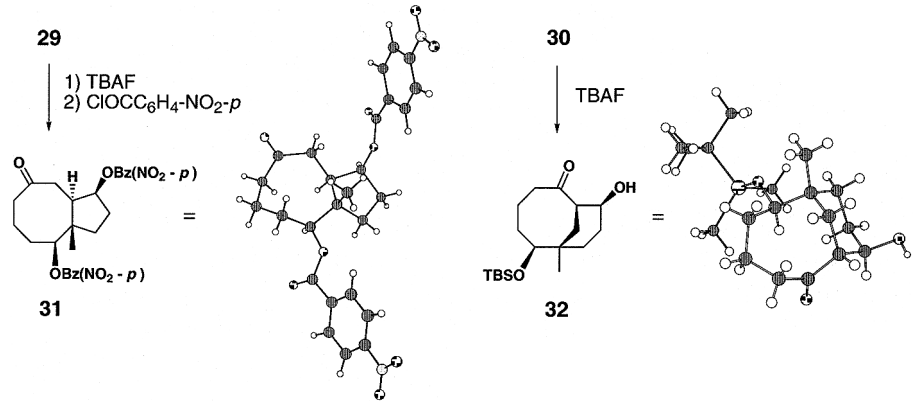
Next, we investigated the radical reaction of bissilyl ethers **25** and **26** by the slow addition of *n*-Bu_3SnH and AIBN using a syringe pump (Scheme 4). The α-epoxide **25** gave two products **29** and **30** in 27% yield, in a ratio of 7:1. Their structures were determined by X-ray crystallographic analyses after conversion to crystalline derivatives **31** and **32** (Scheme 5). The major product **29** had a *trans* bicyclo[6.3.0]undecane skeleton, while the minor product **30** had a bicyclo[5.3.1]undecane skeleton. X-Ray analysis showed



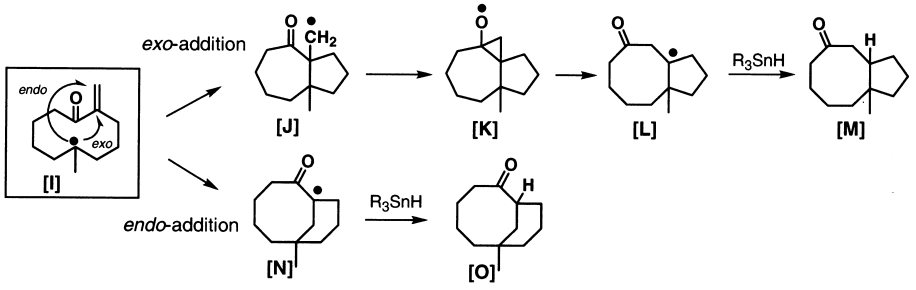
Scheme 3.



Scheme 4.



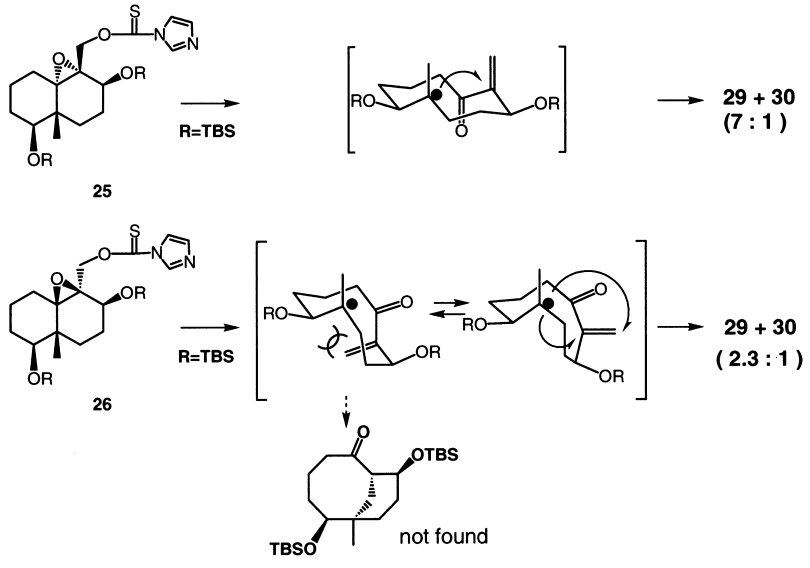
Scheme 5.



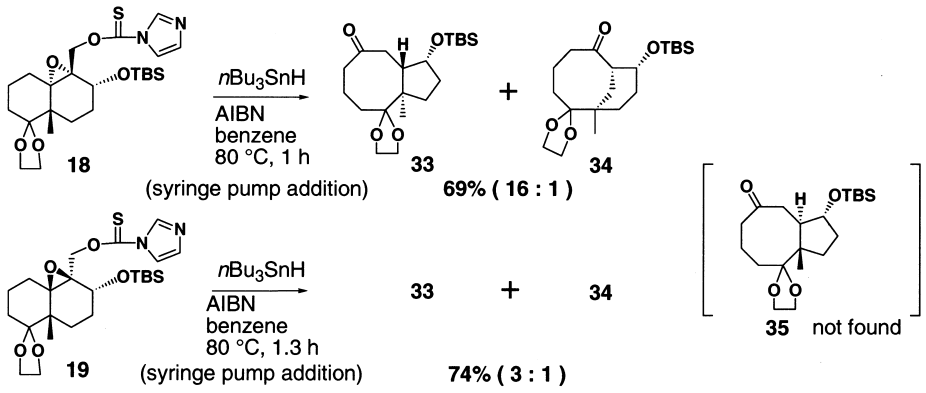
Scheme 6.

that both **29** and **30** retained the relative stereochemistry of substrate **25**. On the other hand, the reaction of *cis*-bissilyl ether **26** under the same conditions gave a mixture of **29** and **30** in 46% yield, but in a different ratio (2.3:1) (Scheme 6).

The formation of **28** and **29** could be explained by a mechanism established previously.[7] When the 10-membered carbon radical [I], which was generated from **5** via [G], is cyclized by *exo*-cyclization, bicyclo[5.3.0]-decanylmethyl radical [J] would be formed. Radical [J] is then converted to [M] via further ring expansion. On the other hand, if radical [I] is cyclized by *endo*-cyclization, new carbon radical [N] should be produced, which would be reduced to [O] (=**30**). Compound **30** is the first isolated product in these series of reactions. A question arises of why the ratio of the products, **29** and **30**, differs when isomeric **25** and **26** are reacted under the same conditions. Since they should generate the same radical intermediate [I], in which two stereo centers are lost except for the radical carbon, the same product should be produced in the same ratio. However, this is not the case. The difference in reactivity



Scheme 7.



Scheme 8.

between **25** and **26** may be attributed to the difference in their conformation in the 10-membered radical intermediate, as shown in Scheme 7.

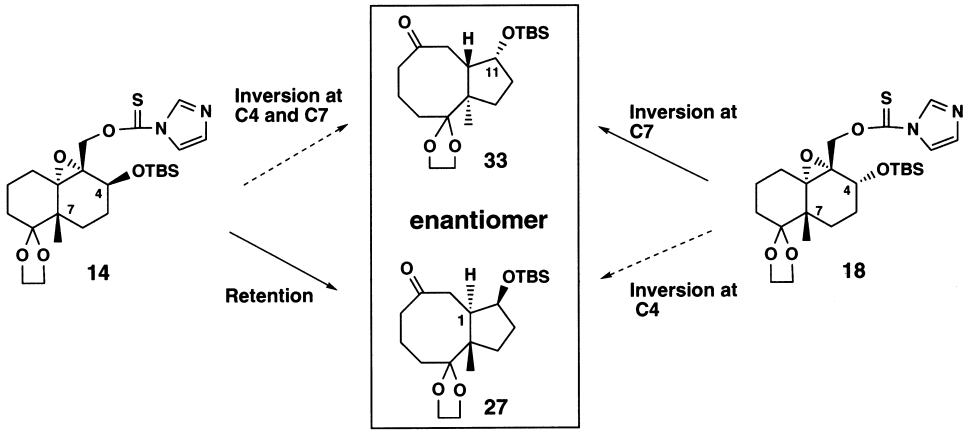
Thus, substrate **25**, whose conformation is *trans*-decaline, is converted to the radical intermediate while retaining its initial conformation. The resulting 10-membered carbon radical is cyclized mainly to **29** by a 5-*exo* cyclization mode. On the other hand, **26** has a *cis*-decaline conformation, which might have a different reactivity because of unfavorable interactions and the boat-like transition state for 5-*exo* cyclization as shown in Scheme 7.

Although the precise reason is not yet clear, this difference in reactivity, i.e. the *trans*-decaline substrate gave bicyclo-[6.3.0]undecanone more selectively than the *cis*-decaline substrate, was also observed in the reaction of **18** and **19**.

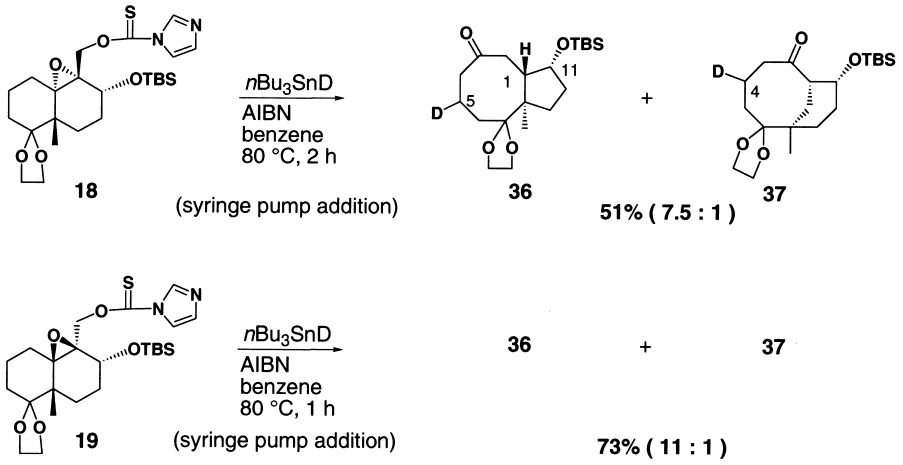
The radical reaction of **18** afforded bicyclo[6.3.0]undecanone **33** in 69% yield with higher selectivity (16:1) than the reaction of **19** (3:1). Although **18** is a diastereoisomer of **14**, product **33** was consistent with product **27**, which was obtained from **14**, with regard to their NMR and IR spectra. No isomeric product **35** has been detected so far (Schemes 8 and 9).

Therefore, an inversion of stereochemistry, at a single stereogenic center must occur to explain these results. Since the relative stereochemistry between the ring-juncture methyl and silyloxy group in **18** is *trans*, inversion of the stereocenter at C4 or C7 is required to give **33**. To clarify which stereocenter was inverted under these conditions, a deuterium trap experiment was carried out (Scheme 10).

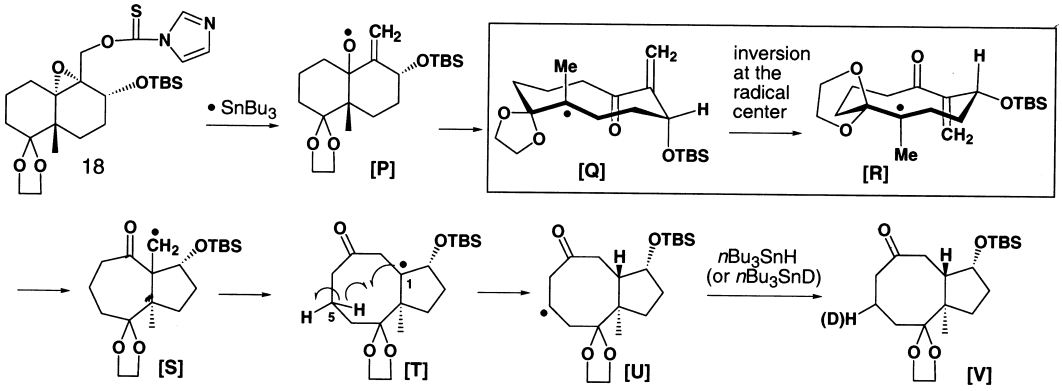
If the stereocenter at C4 in the product **18** is inverted, the carbon radical should be generated at C4 (at C11 of **33**). However, no incorporation of deuterium was observed at C1 or C11 in the product when **18** or **19** was reacted under the same conditions, except using *n*-Bu_3SnD. After careful studies using NMR and mass spectroscopy, a deuterium was incorporated at C5 in **36**.[13] Although inversion at C4 of **18** could not be ruled out completely, inversion at C7 is likely to occur. Scheme 11 shows this inversion mechanism in the reaction of **18** to give **33**. Ten-membered radical intermediate [Q], which was generated from **18** via the radical [P], could change its conformation with inversion at the radical center to give the radical [R]. *exo* Cyclization of the radical [R] followed by the ring expansion of [S] generated intermediate [T]. Intramolecular hydrogen abstraction afforded new carbon radical [U], which was quenched by *n*-Bu_3SnH or *n*-Bu_3SnD. The fact that three oxygen atoms face the same side of the 10-membered radical intermediate [Q] may contribute to preventing further cyclization and rather invert its conformation, although this would require an assessment of the TS energy of each step and the energy differences of each intermediate. Further studies along these lines are required to elucidate this radical process.



Scheme 9.



Scheme 10.



Scheme 11.

Conclusion

By radical rearrangement using epoxydecalin thiocarbonylimidazolide, we succeeded in synthesizing bicyclo[6.3.0]undecane derivatives. We also obtained bicyclo[5.3.1]undecane derivatives for the first time. Selectivity in this reaction was influenced by the stereochemistry of the epoxide and the functional group of the substrates, and the experimental conditions. We were also able to synthesize bicyclo[6.3.0]undecane derivatives with high selectivity. Due to the configuration of the substrates, we surmised that the radical center was inverted, and [1,5]-hydrogen transfer was likely based on an examination of tributyltindeuteride. Since these converted derivatives have many functional groups, they are important as synthetic intermediates of sesterterpenoides.

Experimental

Methyl (4a*S)-4a-methyl-2,5-dioxo-3,4,4a,6,7,8-hexahydronaphthalenecarboxylate (6).**[8] A solution of 2-methylcyclohexane-1,3-dione (421.5 mg, 3.4 mmol) and potassium fluoride (447 mg, 7.7 mmol) in MeOH (14 mL) was added using a syringe to a solution of methyl 3-oxo-4-pentenoate (535.0 mg, 4.2 mmol) in dry methanol (0.6 mL) and the mixture was stirred at room temperature for 27 h. After the solvent was evaporated in vacuo, the residue was dissolved in ether, and washed with 10% aq. Na_2CO_3 until the organic layer was colorless. Then the organic layer was further washed with brine and dried over $MgSO_4$. Evaporation of the solvent in vacuo afforded the residue, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give a yellow oil (**6**), 324.5 mg (41%). IR (film); 1730, 1705, 1670, 1615 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.84 (3H, s), 2.78–2.61 (3H, m), 2.56–2.43 (3H, m), 2.24–2.10 (3H, m), 1.84–1.69 (1H, m), 1.49 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 209.81 (C), 193.84 (C), 166.71 (C), 162.46 (C), 132.04 (C), 52.25 (CH_3), 50.16 (C), 37.08 (CH_2), 33.05 (CH_2), 28.94 (CH_2), 28.65 (CH_2), 23.24 (CH_3), 21.72 (CH_2); MS *m/z* (% int.); 236 (M^+, 13.3), 161 (100.0); HR-MS calcd for $C_{13}H_{16}O_4$ 236.1048; found 236.1056.

Methyl (4a*S)-4a-methyl-2,5-dioxo-3,4,4a,6,7,8-hexahydronaphthalenecarboxylate 5-ethylene acetal (7).** To a solution of **6** (997.0 mg, 4.22 mmol) in dry benzene (40 mL) was added a catalytic amount of *p*-TsOH and ethylene glycol (2.5 mL, 45.2 mmol). The reaction mixture was heated at reflux temperature, while water was azeotropically removed. Then additional portion of ethylene glycol (0.7 mL, 12.7 mmol) was added to the reaction mixture. After being stirred for 2.5 h, the mixture was poured into 5% $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with brine, and dried over

$MgSO_4$. Evaporation of the solvent in vacuo gave a residue, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give **7** (712.2 mg, 60%) as colorless oil. IR (film) 1720, 1670 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.01–3.91 (4H, m), 3.81 (3H, s), 2.52–2.44 (2H, m), 2.40–2.31 (2H, m), 1.90–1.65 (6H, m), 1.39 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 194.92 (C), 167.43 (C), 164.55 (C), 131.97 (C), 112.30 (C), 65.32 (CH_2), 65.06 (CH_2), 52.06 (CH_3), 44.84 (C), 33.51 (CH_2), 29.69 (CH_2), 28.47 (CH_2), 26.23 (CH_2), 21.31 (CH_2), 20.82 (CH_3); MS *m/z* (% int.) 280 (M^+, 10.2), 99 (100.0); HR-MS calcd for $C_{15}H_{20}O_5$ 280.1310; found 280.1328.

Methyl (2*S,4a*S**)-2-hydroxy-4a-methyl-5-oxo-2,3,4,4a,6,7,8-heptahydronaphthalenecarboxylate 5-ethylene acetal (8) and methyl (2*R**,4a*S**)-2-hydroxy-4a-methyl-5-oxo-2,3,4,4a,6,7,8-heptahydronaphthalenecarboxylate 5-ethylene acetal (9).** To a solution of **7** (34.1 mg, 0.12 mmol) in anhydrous methanol (1.6 mL) was added $NaBH_4$ (4.6 mg, 0.12 mmol) at 0°C under N_2. After being stirred for 0.5 h, the reaction was quenched by addition of aq. NH_4Cl, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent in vacuo gave a residue, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=3:1) to give **8** (15.5 mg, 46%) and **9** (7.8 mg, 23%) as colorless oil.

8: IR (film) 3450, 1720 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.49 (^1H ddd, *J*=7.7, 5.6, 1.8 Hz), 3.99–3.86 (4H, m), 3.77 (3H, s), 2.85–2.77 (1H, m), 2.22–1.42 (10H, m),1.30 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 169.54 (C), 149.59 (C), 130.05 (C), 113.10 (C), 67.25 (CH), 65.08 (CH_2), 64.94 (CH_2), 51.40 (CH_3), 44.88 (C), 30.02 (CH_2), 27.75 (CH_2), 26.61 (CH_2), 25.66 (CH_2), 23.39 (CH_3), 22.29 (CH_2); MS *m/z* (%, int.) 282 (M^+, 48.6), 99 (100.0); HR-MS calcd for $C_{15}H_{22}O_5$ 282.1466; found 282.1451.

9: IR (film) 3450, 1710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.35 (1H, brs), 4.04–3.89 (4H, m), 3.77 (3H, s), 3.03–2.95 (1H, m), 2.20–2.04 (2H, m), 1.92–1.53 (8H, m), 1.30 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 169.76 (C), 153.30 (C), 127.88 (C), 112.99 (C), 65.25 (CH_2), 64.99 (CH2), 64.61 (CH), 51.50 (CH_3), 45.52 (C), 29.86 (CH_2), 26.21 (CH_2), 26.08 (CH_2), 22.62 (CH_2), 21.96 (CH_2), 21.85 (CH_3); MS *m/z* (%, int.) 282 (M^+, 2.5), 99 (100.0); HR-MS calcd for $C_{15}H_{22}O_5$ 282.1466, found 282.1437.

Methyl (2*S,4a*S**)-4a-methyl-5-oxo-2-(1,1,2,2-tetramethyl-1-silapropoxy)-2,3,4,4a,6,7,8-heptahydronaphthalenecarboxylate 5-ethylene acetal (10).** To a solution of **8** (171.1 mg, 0.61 mmol) in dry DMF (0.3 mL) was added imidazole (62.0 mg, 0.91 mmol) and *t*-butyldimethylchlorosilane (182.9 mg, 1.2 mmol). After being stirred for 4.5 h at room temperature, ether was added and the organic layer was washed with water and brine, successively. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=5:1) to give **10** (200.0 mg, 83%) as colorless oil. IR (film) 1720 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.53 (1H, ddd, *J*=7.4, 5.4, 3.4 Hz), 3.97–3.86 (4H, m), 3.71 (3H, s), 2.40 (1H, d, *J*=2.5 Hz), 2.17–1.37 (9H, m), 1.28 (3H, s), 0.85 (9H, s), 0.06 (3H, s), 0.03 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 165.45 (C), 144.46 (C), 131.70 (C), 112.70 (C), 68.44 (CH), 65.03 (CH_2), 64.77 (CH_2), 50.96 (CH_3), 44.07 (C), 29.86 (CH_2), 28.78 (CH_2), 26.82 (CH_2), 25.68 (CH_2), 25.57 (CH_3×3), 22.65 (CH_3), 22.25 (CH_2), 17.68 (C), −3.73 (CH_3), −4.87 (CH_3); MS *m/z* (% int.) 396 (M^+, 2.2), 99 (100.0); HR-MS calcd for $C_{21}H_{36}O_5Si_1$ 396.2330, found 396.2324.

Methyl (2*R,4a*S**)-4a-methyl-5-oxo-2-(1,1,2,2-tetramethyl-1-silapropoxy)-2,3,4,4a,6,7,8-heptahydronaphthalenecarboxylate 5-ethylene acetal (11).** To a solution of **9** (157.4 mg, 0.56 mmol) in dry DMF (0.1 mL) was added imidazole (76.2 mg, 1.1 mmol) and *t*-butyldimethylchlorosilane (168.3 mg, 1.1 mmol). After being stirred for 45 min at room temperature, ether was added and organic layer was washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=5:1) to give **11** (192.7 mg, 87%). IR (film) 1720 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.49 (1H, dd, *J*=6.3, 4.1 Hz), 4.01–3.89 (4H, m), 3.71 (3H, s), 2.64–2.58 (1H, m), 2.20–2.10 (1H, m), 2.01–1.94 (1H, m), 1.85–1.58 (7H, m), 1.17 (3H, s), 0.91 (9H, s), 0.05 (3H, s), −0.002 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.31 (C), 148.05 (C), 130.03 (C), 113.29 (C), 66.02 (CH), 65.23 (CH_2), 65.03 (CH_2), 51.24 (CH_3), 44.88 (C), 30.50 (CH_2), 28.54 (CH_2), 26.69 (CH_2), 25.75 (CH_3×3), 24.05 (CH_2), 22.30 (CH_3), 22.25 (CH_2), 17.96 (C), −4.69 (CH_3), −4.82 (CH_3); MS *m/z* (% int.) 396 (M^+, 93.3), 73 (100.0); HR-MS calcd for $C_{21}H_{36}O_5Si_1$ 396.2330, found 396.2301.

[(1*S,3*R**,4*S**,7*S**)-3-Hydroxymethyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]-undecane]-8-one 8-ethylene acetal (13).** A solution of DIBAH (1.0 M toluene solution, 0.70 mL) was added to a solution of **10** (200.0 mg, 0.51 mmol) in dry toluene (20 mL). The mixture was stirred at −78°C for 3.3 h, and then at room temperature for 1.5 h. The solution was diluted with ether and the reaction was quenched by addition of saturated NH_4Cl. After two layers were separated, the aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. Thus obtained crude **12** (190.0 mg) was dissolved in CH_2Cl_2 (15 mL) and *m*-CPBA (70%, 190.8 mg, 0.77 mmol) was added to the solution at −14°C. The solution was allowed to warm to room temperature for 2.5 h. The reaction was quenched by addition of saturated sodium thiosulfate and saturated sodium hydrogen carbonate, successively, and the product was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo.The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=3:1) to give **13** (181.7 mg, 94%). Recrystallization of the residue from ether–pentane afforded a colorless plate, mp 76–79°C. IR (film) 3550, 1460, 1390, 1370, 1360 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.10 (1H, t, *J*=2.5 Hz), 4.06–3.75 (4H, m), 3.71 (1H, dd, *J*=12.4, 6.4 Hz), 3.39 (1H, t, *J*=11.2 Hz), 2.56 (1H, dd, *J*=11.2, 2.5 Hz), 1.90 (1H, ddd, *J*=17.8, 13.4, 4.5 Hz), 1.82–1.55 (6H, m), 1.42–1.26 (2H, m), 1.18 (3H, s), 0.95 (1H, dt, *J*=13.4, 9.4, 4.0 Hz), 0.81 (9H, s), 0.08 (3H, s), 0.03 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 112.75 (C), 70.91 (CH), 65.72

(CH_2), 65.02 (CH_2), 64.30 (C), 63.02 (CH_2), 42.36 (C), 30.60 (CH_2), 27.89 (CH_2), 26.09 (CH_3×3), 25.21 (CH), 21.58 (CH_2), 20.81 (CH_3), 19.99 (CH_2), 18.21 (C), −3.94 (CH_3), −4.86 (CH_3); MS *m*/*z* (% int.) 384 (M^+, 0.05), 99 (100.0); HR-MS calcd for $C_{20}H_{36}O_5Si_1$ 384.2330, found 384.2348.

(1*S,3*R**,4*S**,7*S**)-3-(Imidazolylthioxomethoxy)methyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]undecan-8-one 8-ethylene acetal (14).** To a solution of **13** (128.2 mg, 0.34 mmol) in anhydrous 1,2-dichloroethane (1.7 mL), was added 1,1′-thiocarbonyldiimidazole (90%, 132.2 mg, 0.68 mmol). After being refluxed for 3.5 h, the reaction mixture was partitioned between water and CH_2Cl_2. Then the separated aqueous layer was further extracted with CH_2Cl_2. The combined extracts were treated with cold 1N HCl, washed with saturated $NaHCO_3$ and brine, successively. Dried solvent was evaporated in vacuo to give a residue, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=3:1) affording **14** (115.7 mg, 70%). IR (film) 1520, 1460, 1380, 1330, 1280 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.27 (1H, s), 7.56 (1H, s), 6.98 (1H, s), 4.85 (1H, d, *J*=11.4 Hz), 4.64 (1H, d, *J*=11.4 Hz), 4.06–3.86 (4H, m), 3.79 (1H, t, *J*=5.9 Hz), 1.99–1.64 (7H, m), 1.49–1.32 (2H, m), 1.27 (3H, s), 1.10 (1H, d, *J*=12.9 Hz), 0.74 (9H, s), 0.06 (3H, s), −0.09 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.64 (C), 136.39 (CH), 130.61 (CH), 117.58 (CH), 111.95 (C), 72.54 (CH2), 70.16 (C), 67.19 (CH), 65.30 (CH_2), 64.61 (CH_2), 62.64 (C), 41.89 (C), 29.93 (CH_2), 27.20 (CH_2), 25.68 (CH_2), 25.48 (CH_3×3), 20.95 (CH_2), 20.23 (CH_3), 19.54 (CH_2), 17.56 (C), −4.23 (CH_3); MS *m*/*z* (% int.) 494 (M^+, 0.2), 99 (100.0); HR-MS calcd for $C_{24}H_{38}N_2O_5S_1Si_1$ 494.2269, found 494.2298.

[(1*S,3*R**,4*R**,7*S**)-3-Hydroxymethyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]-undecane]-8-one 8-ethylene acetal (16a) and [(1*R**,3*S**,4*R**,7*S**)-3-hydroxymethyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]undecane]-8-one 8-ethylene acetal (17).** A solution of DIBAH (1.0 M, toluene solution, 0.70 mL) was added to a solution of **11** (192.7 mg, 0.49 mmol) in dry toluene (17 mL). The mixture was stirred at −78°C for 2.3 h, and then at room temperature for 1.5 h. The reaction was quenched by addition of ether and saturated NH_4Cl and the product was extracted with ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude **15** (159.9 mg) was dissolved in CH_2Cl_2 (13 mL). To this solution, *m*CPBA (70%, 160.7 mg, 0.65 mmol) was added at −8°C. The solution was allowed to warm to room temperature for 3.5 h. Then the reaction was quenched by addition of saturated sodium thiosulfate and saturated sodium hydrogen carbonate. The product was extracted three times with CH_2Cl_2. The organic layers were washed by brine, dried over $MgSO_4$ and concentrated in vacuo.The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=3:1) to give **16a** (83.2 mg, 44%) and **17** (44.2 mg, 23%).

16a: IR (film) 3470, 1460, 1360, 1250 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.07 (1H, dd, *J*=6.9, 5.8 Hz), 3.99–3.86 (4H, m), 3.61 (1H, t, *J*=10.0 Hz), 2.49 (1H, d, *J*=10.0 Hz), 1.93–1.78 (3H, m), 1.76–1.58 (6H, m), 1.13 (3H, s) 0.93 (9H, s), 0.15 (3H, s), 0.10 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 113.87 (C), 70.91 (CH_2), 69.81 (C), 67.9 (C), 64.72 (CH_2), 64.39 (CH_2), 63.27 (CH), 42.16 (C), 29.86 (CH_2), 27.53 (CH_2), 25.84 (CH_2), 25.75 (CH_3×3), 24.16 (CH_2), 20.95 (CH_2), 19.37 (CH_3), 17.92 (C), −4.32 (CH_3), −4.72 (CH_3); MS *m*/*z* (% int.) 384 (M^+, 0.37), 99 (100.0); HR-MS calcd for $C_{20}H_{36}O_5Si_1$ 384.2330, found 384.2316.

17: IR ($CHCl_3$) 3500, 1460, 1370, 1340, 1280 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.17 (1H, dd, *J*=6.8, 2.3 Hz), 4.06–3.78 (4H, m), 3.80 (1H, t, *J*=5.9 Hz), 3.63 (1H, d, *J*=12.0 Hz), 2.12 (1H, ddd, *J*=18.0, 12.0, 4.9 Hz),1.89–1.62 (7H, m), 1.59–1.49 (2H, m), 1.14 (3H, s), 0.89 (9H, s), 0.09 (3H, s), 0.08 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 112.30 (C), 69.63 (C), 66.20 (CH), 65.43 (CH_2), 64.88 (C), 64.73 (CH_2), 61.51 (CH_2), 42.27 (C), 30.37 (CH_2), 27.33 (CH_2), 25.83 (CH_3×3), 24.10 (CH_2), 21.68 (CH_2), 20.47 (CH_3), 19.79 (CH_2), 18.01 (C), −4.01 (CH_3), −4.78 (CH_3); MS *m*/*z* (% int.) 384 (M^+, 0.02), 99 (100.0); HR-MS calcd for $C_{20}H_{36}O_5Si_1$ 384.2330, found 384.2333.

[(1*S,3*R**,4*R**,7*S**)-8,8-Ethylenedioxy-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]-undec-3-yl]methyl 4-bromobenzoate (16b).** Mp 124–126°C. IR (film) 2920, 1710, 1580, 1450, 1350, 1260 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.87 (2H, d, *J*=2.0 Hz), 7.61 (2H, d, *J*=2.0 Hz), 4.69 (1H, d, *J*=11.5 Hz), 4.26 (1H, dd, *J*=6.0, 2.2 Hz), 4.12 (1H, d, *J*=11.5 Hz), 4.06–3.79 (5H, m), 2.17 (1H, ddd, *J*=13.0, 6.0 Hz), 1.97–1.25 (8H, m), 1.19 (3H, s), 0.90 (9H, s), 0.07 (3H, s), 0.06 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 218.10 (C), 165.20 (C), 131.90 (CH×2), 131.02 (CH×2), 112.21 (C), 77.01(C), 69.90 (C), 65.45 (CH_2), 64.99 (CH), 64.79 (CH_2), 64.22 (CH_2), 63.36 (C), 42.24 (C), 30.32 (CH_2), 27.27 (CH_2), 25.81 (CH_3×3), 24.89 (CH_2), 21.70 (CH_2), 20.53 (CH_3), 19.81 (CH_2), 18.01 (C), −4.08(CH_3), −4.85 (CH_3); MS *m*/*z* (% int.); 566 (M^+, 0.82), 353 (100.0); HR-MS calcd for $C_{27}H_{39}N_2O_6Br_1Si_1$ 566.1698, found 566.1670.

(1*S,3*R**,4*R**,7*S**)-3-(Imidazolylthioxomethoxy)methyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]undecan-8-one 8-ethylene acetal (18).** To a solution of **16a** (83.0 mg, 0.22 mmol) in anhydrous 1,2-dichloroethane (1.1 mL), was added 1,1′-thiocarbonyldiimidazole (90%, 85.6 mg, 0.43 mmol). After being refluxed for 3 h, the mixture was cooled to room temperature. The product was partitioned between water and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with cold 1N HCl, saturated $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give **18** (87.8 mg, 82%) as colorless oil. IR (film) 1530, 1460, 1380, 1320, 1280, 1220 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.28 (1H, s), 7.58 (1H, s), 7.05 (1H, s), 5.06 (1H, d, *J*=11.4 Hz), 4.33 (1H, d, *J*=11.4 Hz), 4.18 (1H, dd, *J*=6.1, 2.3 Hz), 4.04–3.79 (4H, m), 2.15 (1H, dt, *J*=13.0, 6.0 Hz), 2.02–1.55 (10H, m), 1.37 (1H, d, *J*=11.1 Hz), 1.20 (3H, s), 1.03

(1H, dt, *J*=13.0, 9.0, 4.8 Hz), 0.88 (9H, s), 0.05 (3H, s), 0.01 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.13 (C), 136.36 (CH), 131.07 (CH), 117.78 (CH), 111.97 (C), 72.53 (CH_2), 69.83 (C), 65.45 (CH_2), 65.41 (CH), 64.77 (CH_2), 62.74 (C), 42.22 (C), 30.19 (CH_2), 27.15 (CH_2), 25.73 (CH_3×3), 25.00 (CH_2), 21.72 (CH_2), 20.60 (CH_3), 19.74 (CH_2), 17.94 (C), −4.04 (CH_3), −4.87 (CH_3); MS *m*/*z* (% int.); 494 (M^+, 0.44), 99 (100.0); HR-MS calcd for $C_{24}H_{38}N_2O_5S_1Si_1$ 494.2269, found 494.2299.

(1*R,3*S**,4*R**,7*S**)-3-(Imidazolylthioxomethoxy)methyl-7-methyl-2-oxa-4-(1,1,2,2-tetramethyl-1-silapropoxy)tricyclo[5.4.0.0<1,3>]undecan-8-one 8-ethylene acetal (19).** To a solution of **17** (44.2 mg, 0.12 mmol) in anhydrous 1,2-dichloroethane (1.0 mL) was added 1,1′-thiocarbonyldiimidazole (90%, 45.6 mg, 0.23 mmol). After being refluxed for 2.5 h, the solution was diluted with water and extracted CH_2Cl_2. After the mixture was washed with cold 1N HCl, saturated $NaHCO_3$ and brine, the solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give **19** (31.7 mg, 56%) as colorless oil. IR (film) 1530, 1460, 1390, 1330, 1280, 1240 (broad) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.42 (1H, s), 7.71 (1H, s), 7.02 (1H, s), 4.84 (1H, d, *J*=11.5 Hz), 4.76 (1H, d, *J*=11.5 Hz), 4.14 (1H, t, *J*=5.4 Hz), 4.04–3.92 (4H, m), 2.02–1.92 (2H, m), 1.79–1.47 (8H, m), 1.17 (3H, s), 0.80 (9H, s), 0.03 (3H, s), −0.03 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.75 (C), 136.85 (CH), 130.71 (CH), 118.11 (CH), 113.64 (C), 73.19 (CH_2), 69.28 (C), 68.73 (CH), 66.05 (C), 64.92 (CH_2), 64.55 (CH_2), 42.13 (C), 29.29 (CH_2), 26.67 (CH_2), 26.38 (CH_2), 25.57 (CH_3×3), 23.57 (CH_2), 20.40 (CH_3), 19.11 (CH_2), 17.79 (C), −4.48 (CH_3), −4.94 (CH_3); MS *m*/*z* (% int.) 494 (M^+, 0.4), 73 (100.0); HR-MS calcd for $C_{24}H_{38}N_2O_5S_1Si_1$ 494.2243, found 494.2269.

Methyl (3*S,6*S**,7*S**)-3,7-bis(1,1,2,2-tetramethyl-1-silapropoxy)-6-methylbicyclo[4.4.0]dec-1-ene-2-carboxylate (20) and methyl (3*R**,6*S**,7*S**)-3,7-bis(1,1,2,2-tetramethyl-1-silapropoxy)-6-methylbicyclo[4.4.0]dec-1-ene-2-carboxylate (21).** A solution of **6** (304.0 mg, 1.3 mmol) in ethanol (17 mL) was stirred at −78°C in the presence of $NaBH_4$ (73.0 mg, 1.9 mmol) under N_2. After being stirred for 4 h, saturated NH_4Cl was added to the solution and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was dissolved in dry DMF (0.5 mL) and imidazole (422.1 mg, 6.2 mmol) and *t*-butyldimethylchlorosilane (934.5 mg, 6.2 mmol) were added to the solution. After being stirred for 21 h at room temperature, ether was added and organic layer was washed three times with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/benzene=1:1) to give **20** (136.6 mg, 23%) and **21** (69.7 mg, 12%).

20: IR (film) 2950, 2850, 1720, 1470, 1350 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.49 (1H, dddd, *J*=8.6, 5.3, 1.8 Hz), 3.70 (3H, s), 3.23 (2H, dd, *J*=10.2, 5.4 Hz), 2.29 (1H, d, *J*=11.9 Hz), 2.06 (1H, ddd, *J*=11.9, 9.1, 2.0 Hz), 1.87–1.49 (7H, m), 1.07 (3H, s), 0.86 (9H, s), 0.83 (9H, s), 0.01 (6H, s), 0.00 (6H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.09 (C), 145.76 (C), 131.44 (C), 78.69 (CH), 68.75 (CH), 51.28 (CH_3), 41.48 (C), 32.94 (CH_2), 30.81 (CH_2), 28.58 (CH_2), 27.59 (CH_2), 25.83 (CH_3×3), 25.75 (CH_3×3), 23.81 (CH_2), 18.03 (C), 17.90 (C), 17.70 (CH_3), −3.90 (CH_3), −4.19 (CH_3), −4.87 (CH_3), −5.16 (CH_3); MS *m*/*z* (% int.), 468 (M^+, 0.8), 279 (100); MS *m*/*z* (% int) 469 (M^++1, 19), 428 (57), 411 (52), 369 (84), 337 (80); HR-MS calcd for $C_{25}H_{49}O_4Si_2$ (M^++1) 469.3167; found 469.3169.

21: IR (film) 2950, 2850, 1720, 1460, 1360, 1250 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.51 (d, *J*=2.0 Hz, 1H), 3.63 (s, 3H), 3.13 (dd, *J*=10.7, 5.1 Hz, 1H), 2.34 (dd, *J*=10.7, 9.9 Hz, 1H), 1.87–1.42 (m, 5H), 1.33–0.98 (m, 4H), 0.88 (s, 3H), 0.85 (s, 9H), 0.82 (s, 9H), 0.02 (s, 6H), −0.02 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 175.72 (C), 149.34 (C), 129.73 (C), 79.48 (CH), 73.85 (CH), 51.11 (CH_3), 38.92 (C), 35.71 (CH_2), 30.76 (CH_2), 25.84 (CH_3×3), 25.66 (CH_3×3), 25.06 (CH_2), 24.01 (CH_2), 23.46 (CH_2), 18.05 (C), 17.06 (C), 10.64 (CH_3), −3.95 (CH_3), −4.08 (CH_3), −4.61(CH_3), −4.87 (CH_3).

[(1*S,3*R**,4*S**,7*R**,8*S**)-4,8-Bis(1,1,2,2-tetramethyl-1-silapropoxy)-7-methyl-2-oxatricyclo[5.4.0.0<1,3>undec-3-yl]methan-1-ol (23) and [(1*R**,3*S**,4*S**,7*R**,8*S**)-4,8-bis(1,1,2,2-tetramethyl-1-silapropoxy)-7-methyl-2-oxatricyclo[5.4.0.0<1,3>]undec-3-yl]methan-1-ol (24).** A toluene solution of DIBAH (1.0 M, 1.2 mL) was added to a solution of **20** (190.9 mg 0.41 mmol) in toluene (30 mL). The mixture was stirred at −78°C for 2 h, and then at room temperature for 1.5 h. The solution was added ether and saturated NH_4Cl and extracted with ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (6 mL) and *m*CPBA (70%, 74.4 mg, 0.30 mmol) was added to the solution at −11°C. The reaction mixture was gradually warmed to room temperature for 3 h. The reaction was quenched by addition of saturated solutions of sodium thiosulfate and sodium hydrogen carbonate, and the product was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=10:1) to give **23** (58.1 mg, 31%) and **24** (26.8 mg, 14%).

23: Mp 122–125°C (methanol, colorless needle); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.13 (1H, dd, *J*=5.5, 4.5 Hz), 3.85 (1H, d, *J*=10.7 Hz), 3.64 (1H, d, *J*=10.7 Hz), 3.46 (1H, dd, *J*=10.7, 4.6 Hz), 1.85–1.42 (8H, m), 1.26–1.15 (3H, m), 1.00 (3H, s), 0.91 (9H, s), 0.82 (9H, s), 0.084 (3H, s), 0.065 (3H, s), 0.00 (3H, s), −0.02 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 75.52 (CH), 69.63 (C), 69.01 (CH), 68.02 (C), 61.53 (CH_2), 40.37 (C), 30.28 (CH_2), 29.86(CH_2), 26.58 (CH_2), 25.84 (CH_3×3), 25.79 (CH_3×3), 25.62 (CH_2), 20.78 (CH_2), 18.09 (C), 18.01 (C), 16.46 (CH_3), −3.81 (CH_3), −3.95 (CH_3), −4.67 (CH_3), −4.89 (CH_3); MS *m*/*z* (% int.) 456 (M^+, 0.06), 75 (100.0); HR-MS calcd for $C_{24}H_{48}O_4Si_2$ (M^+) 456.3089; found 456.3100.

24: Mp 61–62°C (methanol, colorless needle); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.98 (1H, t, *J*=9.1 Hz), 3.96 (1H, dd, *J*=13.3, 3.7 Hz), 3.49 (1H, dd, *J*=13.3, 3.7 Hz), 3.45

(1H, t, J=11.3 Hz), 2.70 (1H, dd, J=11.3, 2.6 Hz), 1.92–1.76 (2H, m), 1.73–1.37 (6H, m), 1.24–1.13 (2H, m), 1.09 (3H, s), 0.91 (9H, s), 0.86 (9H, s), 0.15 (3H, s), 0.12 (3H, s), 0.03 (3H, s), −0.01 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 77.76 (CH), 71.82 (C), 71.25 (CH), 65.53 (C), 63.42 (CH_2), 39.99 (C), 30.73 (CH_2), 28.29 (CH_2), 28.26 (CH_2), 26.11 (CH_3×6), 24.99 (CH_2), 20.68 (CH_2), 18.30 (C), 18.23 (C), 16.14 (CH_3), −3.67 (CH_3), −3.87 (CH_3), −4.58 (CH_3), −4.82 (CH_3); MS m/z (% int.) 456 (M^+, 0.02), 75 (100.0); HR-MS calcd for $C_{24}H_{48}O_4Si_2$ (M^+) 456.3089; found 456.3095.

{[(1*S,3*R**,4*S**,7*R**,8*S**)-4,8-Bis(1,1,2,2-tetramethyl-1-silapropoxy)-7-methyl-2-oxatricyclo[5.4.0.0<1,3>]undec-3-yl]methoxy}-2-imidazolinylmethane-1-thione (25).** To a solution of **23** (87.4 mg, 0.19 mmol) in anhydrous 1,2-dichloroethane (1.2 mL), was added 1,1′-thiocarbonyldiimidazole (90%, 76.0 mg, 0.38 mmol). After being refluxed for 1.3 h, the solution then diluted with water and extracted with CH_2Cl_2. Combined organic layers were treated with cold 1N HCl, washed with saturated $NaHCO_3$ and brine, successively. The solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=5:1) to give **25** (97.0 mg, 89%) as yellow oil. IR (film) 1470, 1390, 1330, 1280 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.24 (1H, s), 7.55 (1H, s), 7.01 (1H, s), 5.07 (1H, d, J=11.4 Hz), 4.33 (1H, d, J=11.4 Hz), 4.05 (1H, t, J=4.7 Hz), 3.41 (1H, dd, J=10.7, 4.5 Hz), 1.84 (1H, dt, J=14.2, 4.4 Hz), 1.65–1.49 (5H, m), 1.46–1.04 (4H, m), 0.99 (3H, s), 0.81 (9H, s), 0.80 (9H, s), 0.00 (3H, s), −0.006 (3H, s), −0.02 (3H, s), −0.04 (3H, s); MS m/z (% int.); 566 (M^+, 0.15) 73 (100.0); HR-MS calcd for $C_{28}H_{50}N_2O_4S_1Si_2$ 566.3027; found 566.3021.

{[(1*R,3*S**,4*S**,7*R**,8*S**)-4,8-Bis(1,1,2,2-tetramethyl-1-silapropoxy)-7-methyl-2-oxatricyclo[5.4.0.0<1,3>]undec-3-yl]methoxy}-2-imidazolinylmethane-1-thione (26).** To a solution of **24** (77.0 mg, 0.17 mmol) in anhydrous 1,2-dichloroethane (1.0 mL), was added 1,1′-thiocarbonyldiimidazole (90%, 66.9 mg, 0.34 mmol). After being refluxed for 3.6 h, the mixture was diluted with water and extracted with CH_2Cl_2. Combined organic layers were treated with cold 1N HCl, washed with saturated $NaHCO_3$ and brine, successively. The solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=5:1) to give **26** (70.1 mg, 73%) as yellow oil. IR (film) 1470 and 1390 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.30 (1H, s), 7.59 (1H, s), 7.01 (1H, s), 4.85 (1H, d, J=11.2 Hz), 4.69 (1H, d, J=11.2 Hz), 4.02 (1H, t, J=7.9 Hz), 3.50 (1H, dd, J=9.9, 4.5 Hz), 1.92–1.34 (9H, m), 1.29–1.24 (4H, m), 1.10 (3H, s), 0.85 (9H, s), 0.77 (9H, s), 0.04 (3H, s), 0.02 (3H, s), 0.00 (3H, s), −0.04 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.83 (C), 136.72 (CH), 130.80 (CH), 117.78 (CH), 76.67 (CH), 73.09 (CH_2), 71.22 (C), 67.63 (CH), 64.07 (C), 39.72 (C), 30.23 (CH_2), 27.81 (CH_2), 27.71 (CH_2), 25.81 (CH_3×3), 25.62 (CH_3×3), 20.40 (CH_2), 17.99 (C), 17.74 (C), 15.74 (CH_3), −3.99 (CH_3), −4.03 (CH_3), −4.89 (CH_3); MS m/z (% int.) 509 (M^+, 9.1), 73 (100.0); HR-MS calcd for $C_{24}H_{41}N_2O_4S_1Si_2$ ($M-C_4H_9$) 509.2323; found 509.2359.

Radical rearrangement of 14

To a solution of **14** (113.1 mg, 0.23 mmol) in refluxing benzene (1.0 mL), was added a benzene solution (1.0 mL) of AIBN (5.0 mg, 0.030 mmol) and *n*-Bu_3SnH (0.12 mL, 0.46 mmol) using a syringe pump (1.0 mL/h) for 1 h. The reaction mixture was refluxed for 1 h. After the mixture was cooled to room temperature, the mixture was treated with 1N HCl and extracted with ether. Combined organic layers were sequentially washed with saturated aqueous $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and evaporated in vacuo.The residue was purified by column chromatography on silica gel (benzene/ethyl acetate=20:1) to give (1*R**,8*S**,11*S**)-8-methyl-11-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[6.3.0]undecane-3,7-dione 7-ethylene acetal, **27** (50.0 mg, 59%) as colorless oil.

27: IR (film) 1700, 1460, 1360, 1250 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.23 (1H, t, J=4.3 Hz), 4.02–3.83 (4H, m), 2.85–2.78 (1H, m), 2.64 (1H, dd, J=15.0, 12.1 Hz), 2.55 (1H, dd, J=4.6, 1.6 Hz), 2.26 (1H, dd, J=15.0, 1.6 Hz), 2.20 (1H, dd, J=12.1, 5.3 Hz), 1.92–1.66 (6H, m), 1.64–1.54 (2H, m), 1.12 (3H, s), 0.87 (9H, s), 0.03 (3H, s), 0.01 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 215.05 (C), 113.93 (C), 78.63 (CH), 65.12 (CH_2), 64.22 (CH_2), 51.44 (C), 45.15 (CH), 43.17 (CH_2), 38.79 (CH_2), 35.05 (CH_2), 33.53 (CH_2), 30.59 (CH_2), 25.77 (CH_3×3), 20.86 (CH_2), 19.20 (CH_3), 17.89 (C), −4.39 (CH_3), −4.58 (CH_3); MS m/z (% int.) 368 (M^+, 0.35), 99 (100.0); HR-MS calcd for $C_{20}H_{36}O_4Si_1$ 368.2381, found 368.2378.

(1*R,8*S**,11*S**)-7,7-Ethylenedioxy-8-methyl-3-oxobicyclo-[6.3.0]undecane-11-yl 4-bromobenzoate (28).** To a THF solution (0.7 mL) of **27** (50.0 mg, 0.14 mmol), was added *n*-Bu_4NF (1 M solution in THF, 0.61 mL) and the mixture was stirred for 20 h at room temperature. The mixture was then treated with aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to give a residue. The residue was dissolved in anhydrous pyridine (1.0 mL). To this solution, were added dimethylaminopyridine (20.6 mg, 0.17 mmol) and *p*-bromobenzoyl chloride (124.2 mg, 0.57 mmol). After being stirred for 54 h, the reaction mixture was treated with 5% HCl and extracted with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and evaporated in vacuo.The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=3:1) to give **28** as white solid. Recrystallization from benzene-*n*-hexane afforded pure **28** (25.9 mg, 71%). Mp 177–178°C (benzene–*n*-hexane, colorless plate); IR ($CHCl_3$) 1710, 1590, 1480, 1390, 1280, 1270 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (2H, d, J=8.5 Hz), 7.58 (2H, d, J=8.6 Hz), 5.57 (1H, ddd, J=8.4, 6.1, 2.3 Hz), 4.00–3.92 (4H, m), 2.90 (1H, ddd, J=12.4, 6.1, 2.8 Hz), 2.89–2.85 (1H, m), 2.60 (1H, dd, J=16.3, 12.4 Hz), 2.42 (1H, dd, J=16.3, 2.6 Hz), 2.25–2.20 (1H, m), 2.17 (1H, ddd, J=14.5, 9.8, 6.1 Hz), 1.99 (1H, ddd, J=13.2, 9.8, 6.7 Hz), 1.90–1.74 (5H, m), 1.66 (1H, ddd, J=13.2, 8.6, 5.8 Hz), 1.21 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.51 (C), 155.81 (C), 131.82 (CH×4), 114.41 (C), 113.29 (C), 92.15 (C), 81.24 (CH), 65.25 (CH_2), 64.39 (CH_2), 51.99 (C), 43.89 (CH), 42.14 (CH_2), 38.46 (CH_2),

34.81 (CH_2), 30.70 (CH_2), 30.42 (CH_2), 21.59 (CH_2), 18.16 (CH_3); MS *m*/*z* (% int.) 437 (M^+, 0.02), 99 (100.0); HR-MS calcd for $C_{19}H_{21}O_5Br_1$ ($M^+-C_2H_4$) 408.0572, found 408.0597.

Radical rearrangement of 25

To a solution of **25** (115.4 mg, 0.204 mmol) in refluxing benzene (1.0 mL), was added a benzene solution (1 mL) of AIBN (8.5 mg, 0.052 mmol) and *n*-Bu_3SnH (0.07 mL, 0.25 mmol) using a syringe pump (0.8 mL/h). The reaction mixture was refluxed for 2 h and cooled to room temperature. The mixture was treated with 1N HCl and extracted with ether. The combined organic layers were successively washed with saturated solutions of $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (benzene) to give (1*R**,7*S**,8*S**,11*S**)-7,11-bis(1,1,2,2-tetramethyl-1-silapropoxy)-8-methylbicyclo[6.3.0]undecan-3-one (**29**, 21.5 mg, 24%) and (1*S**,6*S**,7*S**,10*S**)-6,10-bis-(1,1,2,2-tetramethyl-1-silapropoxy)-7-methylbicyclo[5.3.1]-undecan-2-one (**30**, 3.0 mg, 3%).

29: IR ($CHCl_3$) 1690, 1460, 1260 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.21 (1H, ddd, *J*=8.5, 6.0, 2.2 Hz), 3.31 (1H, d, *J*=8.2 Hz), 2.76 (1H, ddd, *J*=11.6, 10.8, 6.3 Hz), 2.54 (1H, dd, *J*=17.3, 11.9 Hz), 2.23–2.15 (2H, m), 1.97 (1H, ddd, *J*=11.9, 6.0, 2.5 Hz), 1.94–1.80 (2H, m), 1.78–1.65 (3H, m), 1.57 (1H, dddd, *J*=13.8, 11.1, 8.7, 2.4 Hz), 1.52–1.48 (1H, m), 1.42 (1H, ddd, *J*=19.0, 18.7, 9.2 Hz), 0.97 (3H, s), 0.85 (9H, s), 0.84 (9H, s), 0.00 (3H, s), −0.005 (3H, s), −0.02 (3H, s), −0.03 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 215.22 (C), 81.02 (CH), 77.92 (CH), 49.20 (C), 48.05 (CH), 42.24 (CH_2), 40.04 (CH_2), 38.26 (CH_2), 33.03 (CH_2), 31.78 (CH_2), 25.84 (CH_3×3), 25.79 (CH_3×3), 23.26 (CH_2), 17.98 (C), 17.89 (C), 14.40 (CH_3), −4.03 (CH_3), −4.52 (CH_3), −4.79 (CH_3); MS *m*/*z* (% int.) 440 (M^+, 0.21), 73 (100.0); HR-MS calcd for $C_{20}H_{39}O_3Si_2$ ($M^+-C_4H_9$) 383.2436, found 383.2466.

30: IR ($CHCl_3$) 1690, 1460, 1440, 1380, 1360, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.44 (1H, s), 3.33 (1H, d, *J*=7.1 Hz), 2.71 (1H, ddd, *J*=14.5, 11.2, 3.9 Hz), 2.26 (1H, brs), 2.17–2.08 (2H, m), 2.03–1.89 (3H, m), 1.86–1.67 (2H, m), 1.54–1.38 (4H, m), 0.89 (9H, s), 0.85 (9H, s), 0.81 (3H, s), 0.05 (3H, s), 0.01 (3H, s), −0.005 (3H, s), −0.04 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.37 (C), 72.54 (CH), 64.44 (CH), 54.67 (CH), 40.22 (CH_2), 38.11 (C), 33.67 (CH_2), 30.32 (CH_2), 28.65 (CH_2), 28.43 (CH_2), 25.79 (CH_3×6), 25.51 (CH_2), 22.73 (CH_3), 17.87 (C), −4.03 (CH_3), −4.76 (CH_3); MS *m*/*z* (% int.) 440 (M^+, 0.19), 75 (100.0); HR-MS calcd for $C_{20}H_{39}O_3Si_2$ ($M^+-C_4H_9$) 383.2436, found 383.2434.

Radical rearrangement of 26

To a solution of **26** (97.0 mg, 0.172 mmol) in refluxing benzene (1.0 mL), was added a benzene solution (1 mL) of AIBN (3.4 mg, 0.021 mmol) and *n*-Bu_3SnH (0.09 mL, 0.34 mmol) using a syringe pump (0.7 mL/h) for 1.5 h. After being refluxed for 50 min, the reaction mixture was cooled to room temperature. The mixture was treated with 1N HCl and extracted with ether. The combined organic layers were successively washed with saturated solutions of $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (benzene/*n*-hexane=1:1) to give **29** (24.0 mg, 32%) and **30** (10.4 mg, 14%).

(1*R,2*S**,8*R**,9*S**)-8-Methyl-7,11-bis(4-nitrophenylcarbonyloxy)bicyclo[6.3.0]undecan-3-one (31).** To a THF solution (0.5 mL) of **29** (63.8 mg, 0.15 mmol), was added *n*-Bu_4NF (1 M solution in THF, 0.6 mL) and the mixture was stirred for 4.5 h at room temperature. The mixture was then treated with aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to give a residue. The residue was dissolved in anhydrous pyridine (0.2 mL), and *p*-nitrobenzoyl chloride (34.6 mg, 0.19 mmol) was added to the solution. After being stirred for 4 h, the reaction mixture was treated with saturated $NaHCO_3$ and the product was extracted with ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give **31**, which was recrystallized from ethyl acetate, mp 230–232°C (colorless plate). The structure of **31** was confirmed by X-ray analysis.

(1*S,6*S**,7*S**,10*S**)-10-Hydroxy-7-methyl-6-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[5.3.1]undecan-2-one (32).** To a THF solution (0.15 mL) of **30** (20.0 mg, 0.05 mmol), was added *n*-Bu_4NF (1 M solution in THF, 0.4 mL) and the mixture was stirred for 19 h at room temperature. The mixture was then treated with aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo to give a residue. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate=2:1) to give **32**, which was recrystallized from benzene–*n*-hexane (4 mg, 27%). Mp 117–119°C (benzene–*n*-hexane, colorless plate); IR ($CHCl_3$) 3400, 1680, 1440, 1350, 1240 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.53 (1H, d, *J*=2.1 Hz), 3.35 (1H, d, *J*=7.1 Hz), 2.74 (1H, ddd, *J*=15.2, 11.2, 4.0 Hz), 2.44–2.42 (1H, m), 2.22–2.15 (2H, m), 2.03–1.68 (3H, m), 1.59–1.25 (5H, m), 0.85 (9H, s), 0.84 (3H, s), −0.01 (3H, s), −0.04 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 216.10 (C), 72.75 (CH), 64.62 (CH), 53.92 (CH), 40.55 (CH_2), 38.64 (C), 34.15 (CH_2), 30.67 (CH_2), 28.87 (CH_2×2), 26.28 (CH_3×3), 25.77 (CH_2), 23.13 (CH_3), 18.33 (C), −3.57 (CH_3), −4.52 (CH_3).

Radical rearrangement of 18

To a solution of **18** (87.8 mg, 0.18 mmol) in refluxing benzene (0.9 mL), was added a benzene solution (1.0 mL) of AIBN (5.0 mg, 0.030 mmol) and *n*-Bu_3SnH (0.10 mL, 0.36 mmol) using a syringe pump (1.0 mL/h), the reaction mixture was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was treated with 1N HCl and extracted with ether. The combined organic layers were successively washed with saturated solutions of $NaHCO_3$ and brine. The solution was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (benzene/ethyl acetate=20:1) to give (1*S**,8*R**,11*R**)-8-methyl-11-(1,1,2,2-tetramethyl-1-

silapropoxy)bicyclo[6.3.0]undecane]-3,7-dione 7-ethylene acetal (**33**, 42.3 mg, 65%) and (1*R**,7*R**,10*R**)-7-methyl-10-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[5.3.1]undecane]-2,6-dione 6-ethylene acetal (**34**, 2.8 mg, 4%).

33: IR (film) 1685, 1460, 1350, 1250 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.22 (1H, t, J=4.6 Hz), 3.97–3.82 (4H, m), 2.84–2.79 (1H, m), 2.63 (1H, dd, J=15.0, 12.6 Hz), 2.54 (1H, dd, J=4.6, 1.6 Hz), 2.28 (1H, dd, J=15.0, 1.6 Hz), 2.18 (1H, dd, J=12.6, 6.1 Hz), 1.97–1.53 (8H, m), 1.10 (3H, s), 0.86 (9H, s), 0.01 (3H, s), 0.00 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 215.09 (C), 113.95 (C), 78.65 (CH), 65.13 (CH_2), 64.22 (CH_2), 51.46 (C), 45.19 (CH), 43.90 (CH_2), 38.83 (CH_2), 35.07 (CH_2), 33.56 (CH_2), 30.63 (CH_2), 25.79 (CH_3×3), 20.87 (CH_2), 19.28 (CH_3), −4.56 (CH_3); MS *m*/*z* (% int.) 368 (M^+, 0.73), 99 (100.0); HR-MS calcd for $C_{20}H_{36}O_4Si_1$ 368.2381, found 368.2443.

34: IR ($CHCl_3$) 1690, 1460, 1370, 1250 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.19 (1H, dd, J=4.1, 2.5 Hz), 4.07–3.97 (4H, m), 2.93 (1H, dddd, J=11.9, 9.3, 6.6, 2.5 Hz), 2.71–2.56 (3H, m), 2.28 (1H, d, J=13.7 Hz), 1.98 (1H, ddd, J=12.9, 9.3, 3.6 Hz), 1.87–1.45 (5H, m), 1.34–1.22 (2H, m), 1.04 (3H, s), 0.88 (9H, s), 0.03 (3H, s), 0.02 (3H, s); MS *m*/*z* (% int.) 368 (M^+, 1.8), 113 (100.0); HR-MS calcd for $C_{20}H_{36}O_4Si_1$ 368.2381, found 368.2362.

Radical rearrangement of 19

To a solution of **19** (31.7 mg, 0.064 mmol) in refluxing benzene (0.3 mL), was added a benzene solution (0.3 mL) of AIBN (3.0 mg, 0.018 mmol) and *n*-Bu_3SnH (0.035 mL, 0.13 mmol) using a syringe pump for 20 min (1.0 mL/h), and the reaction mixture was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was treated with 1N HCl and extracted with ether. The combined organic layers were washed successively with saturated solutions of $NaHCO_3$ and brine. The solution was dried over $MgSO_4$ and evaporated in vacuo.The residue was purified by column chromatography on silica gel (benzene/ethyl acetate=20:1) to give **33** (13.3 mg, 56%) and **34** (4.2 mg, 18%).

Radical rearrangement of 18 using tri-*n*-butyltin deuteride

To a solution of **18** (57.9 mg, 0.12 mmol) in refluxing benzene (0.9 mL), was added a benzene solution (0.6 mL) of AIBN (5.0 mg, 0.030 mmol) and *n*-Bu_3SnD (0.06 mL, 0.23 mmol) using a syringe pump (1.0 mL/h), and the reaction mixture was refluxed for 2 h. After being cooled to room temperature, the reaction mixture was treated with 1N HCl and extracted with ether. The combined extracts were washed with saturated solutions of $NaHCO_3$ and brine, successively. The solution was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (benzene/ethyl acetate=20:1) to give [5-$^2H_1$]-5H-(1*S**,8*R**,11*R**)-8-methyl-11-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[6.3.0]undecane]-3,7-dione (**36**, 19.4 mg, 45%) and **37** (2.6 mg, 6%).

36: IR ($CHCl_3$) 1690, 1470, 1460, 1360, 1250 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.23 (1H, t, J=4.6 Hz), 4.01–3.83 (4H, m), 2.85–2.78 (1H, m), 2.64 (1H, dd, J=15.0, 12.2 Hz), 2.55 (1H, dd, J=4.5, 1.5 Hz), 2.26 (1H, dd, J=15.0, 1.5 Hz), 2.21 (1H, dd, J=12.2, 4.1 Hz), 1.91–1.53 (7H, m), 1.11 (3H, s), 0.87 (9H, s), 0.02 (3H, s), 0.01 (3H, s); ^{13}C NMR (68 MHz, $CDCl_3$) δ 215.09 (C), 113.95 (C), 78.65 (CH), 65.14 (CH_2), 64.02 (CH_2), 51.46 (C), 45.19 (CH), 43.19 (CH_2), 38.75 (CH_2), 35.07 (CH_2), 33.56 (CH_2), 30.54 (CH_2), 25.79 (CH_3×3), 20.54 (CHD, triplet), 19.28 (CH_3), 17.92 (C), −4.37 (CH_3), −4.56 (CH_3); MS *m*/*z* (% int.) 369 (M^+, 1.2), 100 (100.0); HR-MS calcd for $C_{20}H_{35}D_1O_4Si_1$ 369.2444, found 369.2439.

37: IR ($CHCl_3$) 1690, 1460, 1380, 1250 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.19 (1H, ddd, J=5.8, 4.3, 1.5 Hz), 4.02–3.85 (4H, m), 2.97–2.87 (1H, m), 2.67–2.59 (3H, m), 2.28 (1H, d, J=13.7 Hz), 1.98 (1H, ddd, J=12.9, 9.4, 3.5 Hz), 1.89–1.34 (m, 4H), 1.31–1.09 (2H, m), 1.04 (3H, s), 0.88 (9H, s), 0.03 (3H, s), 0.02 (3H, s); MS *m*/*z* (% int.) 369 (M^+, 0.75), 60 (100.0); HR-MS calcd for $C_{20}H_{35}D_1O_4Si_1$ 369.2444, found 369.2454.

Radical rearrangement of 19 using tri-*n*-butyltin deuteride

To a refluxing solution of **19** (35.4 mg, 0.072 mmol) in dry benzene (0.4 mL), was added a benzene solution (0.4 mL) of AIBN (4.0 mg, 0.024 mmol) and *n*-Bu_3SnD (0.04 mL, 0.14 mmol) using a syringe pump (1.0 mL/h), and the reaction mixture was refluxed for 1.0 h. After being cooled to room temperature, the reaction mixture was treated with 1N HCl and extracted with ether. The ether layer was washed with saturated solutions of $NaHCO_3$ and brine, successively. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (benzene/ethyl acetate=20:1) to give **36** (17.7 mg, 67%) and **37** (1.5 mg, 6%).

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13. In the ^{13}C NMR spectra of **36**, only the C5 signal at 20.96 ppm observed for **29** was disappeared and a new triplet signal was observed at 20.54 ppm. The same spectra were also obtained from **36** which was produced from **19**. A deuterium was incorporated at somewhere except C1 and C10 in **37**. However, we could not determine the precise position because of limited amount of **37** and the position shown in Scheme 10 was estimated from a mechanistic point of view. A reason for the difference in the product ratio between the reactions using *n*-Bu_3SnH and *n*-Bu_3SnD is unclear now.