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Rearrangement Approaches to Cyclic Skeletons. XIII.[1] Total Synthesis of Triquinane Sesquiterpenes, (±)-Modhephene, and (±)-Isocomene, on the Basis of Formal Substitution at Both Bridgeheads of a Bicyclo[2.2.2]oct-5-en-2-one[2]

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A reaction of 1,4-dimethoxybicyclo[2.2.2]oct-5-en-2-one and R^1MgX, followed by treatment with *p*-toluenesulfonic acid in benzene, gave the 5-methoxybicyclo[3.2.1]oct-6-en-2-one having a substituent (R^1) at the C-1 bridgehead. This ketone was converted into the 5-methoxybicyclo[3.2.1]oct-3-en-2-one. By treatment with $Li[CuR_2]$, a second bridgehead substituent (R) was introduced at the C-4 position of the conjugated ketone. The product was converted into the corresponding α,β-unsaturated ketone, and then treated with R^2Li or DIBAL-H ($R^2 = H$). Acid treatment of the resulting allyl alcohols gave the bicyclo[2.2.2]oct-5-en-2-one having substituents R, R^1, and R^2 at the C-1, 4, and 5 positions, respectively. This procedure was successfully applied to a formal total synthesis of (±)-modhephene, a propellane-type triquinane sesquiterpene, and that of (±)-isocomene, an angular triquinane sesquiterpene, on the basis of an oxa-di-π methane rearrangement of the bicyclo[2.2.2]oct-5-en-2-ones.

For the preparation of [*m*-*n*] fused-ring products, bicyclo[2.2.2]oct-5-en-2-ones (such as **2**) are potential bridged compounds. Photochemical reactions of the β,γ-unsaturated compounds give [5-5] fused-ring derivatives (**3**) through a [1,2]-acyl migration (oxa-di-π methane rearrangement).[3] Some [6-6] fused-ring systems (**4**) are derived from **2** through vinylation, followed by an oxy-Cope rearrangement.[4] In connection with our rearrangement approaches to [*m*-*n*] fused-ring natural products,[5] we were interested in the principal preparation of bicyclo[2.2.2]oct-5-en-2-ones.

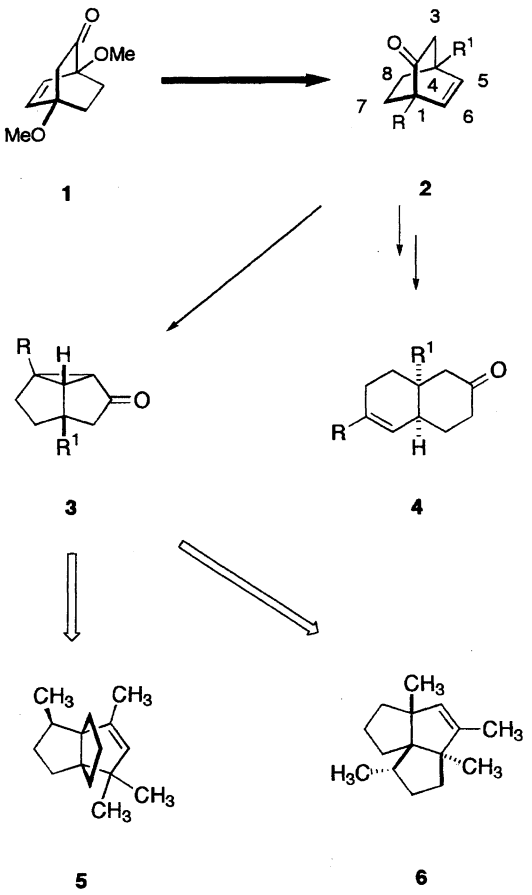
Straightforward routes to bicyclo[2.2.2]oct-5-en-2-ones seem to involve the Diels–Alder reaction of 1,3-cyclohexadienes and ketene equivalents.[6] There are many steps required, however, to prepare even a simple 1,3-cyclohexadiene selectively. Furthermore, the mode of substituents of the cycloaddition products depends upon the regioselectivity of the Diels–Alder reaction, which we cannot easily reverse.

In order to compensate for the weak points of simple Diels–Alder methodology, we have been investigating a formal bridgehead-substitution strategy (vide infra).[7] We wish to report herein a novel method used to introduce the desired substituents at both the C-1 and C-4 bridgeheads of a bicyclo[2.2.2]oct-5-en-2-one, that is, a transformation of **1** into **2** and its applications to the triquinane-sesquiterpene syntheses of two types. Modhephene (**5**) is an unusual sesquiterpene possessing a carbocyclic [3.3.3] propellane skeleton (Scheme 1).[8] Isocomene (**6**) is a representative sesquiterpene possessing an angular triquinane carbon framework.[9] Both of these are our synthetic targets, starting from **1**.

Results and Discussion

Scheme 2 shows the formal bridgehead substitution of 1-methoxybicyclo[2.2.2]oct-5-en-2-ones (**7**)[6] and retrosynthetic analysis for substitution at both bridgeheads of a bicyclo[2.2.2]oct-5-en-2-one. A ketone **7** was converted into an allyl alcohol (**9**) through a Lewis-acid catalyzed pinacol-type rearrangement, giving **8** followed by a reaction with an organolithium reagent. The treatment of **9** with TsOH (*p*-toluenesulfonic acid) gave the desired bridgehead-substitution product (**2**). We can select various alkyl groups, aryl groups, and even a hydrogen atom for the bridgehead substituent, that is, R. However, the handling of the C-4 substituent (R^1) has never been the subject of an investigation.

The acid treatment of **9** must give an allyl cation intermediate (**10**). We noticed the possibility of introducing the C-4 substituent R^1 by using another allyl alcohol (**12**) as the precursor of **10**. One of the precursors of the **12** must be an α,β-unsaturated ketone (**13**, $R \neq H$), which should be derived from **13** ($R = H$) through a 1,4-addition reaction of an organometallic reagent, such as $Li[CuR_2]$, followed by preparation of an unsaturated bond. If we choose a β,γ-unsaturated ketone **14** as the precursor of **13** ($R = H$), the ketone **14** should be derived from 1,4-dimethoxybicyclo[2.2.2]oct-5-en-2-one (**1**) through a pinacol-type rearrangement of the alcohol **15**.[10] The substituent, R^1 of **15**, can be introduced



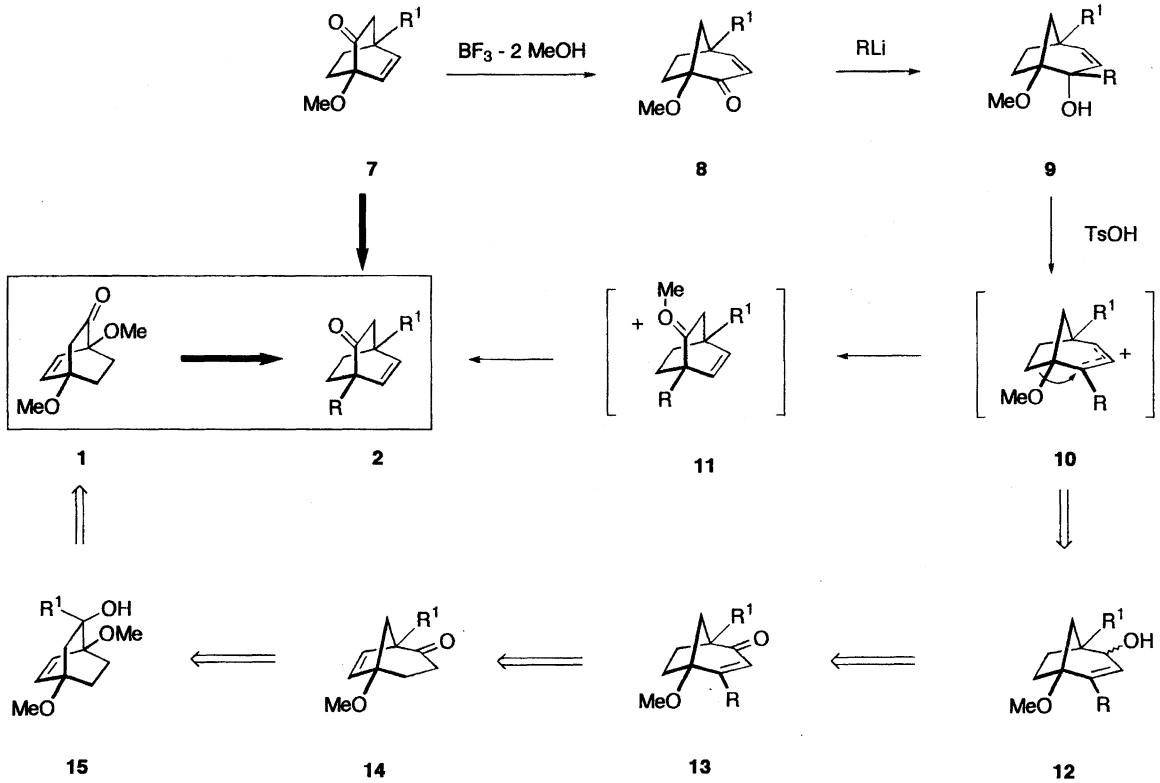
Scheme 1. An overview of this work.

by an organometallic reagent, such as a Grignard one. This overall transformation from **1** to **2** means that the desired substitution of both bridgehead methoxy groups is feasible.

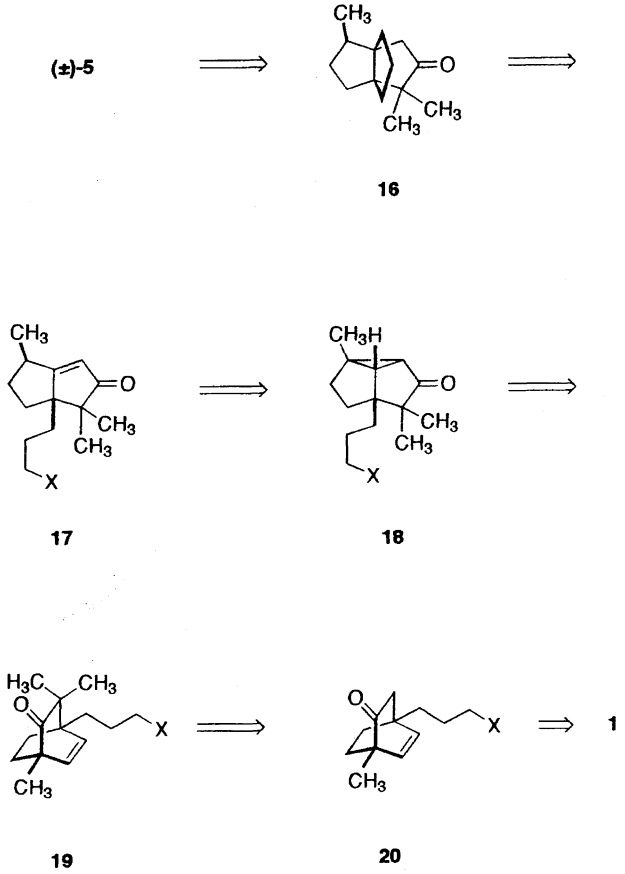
A Formal Total Synthesis of (±)-Modhephene (5). Scheme 3 shows our synthetic plan. (±)-Modhephene (**5**) has already been derived from a [3.3.3] propellane skeleton (**16**).[9m] If we select the oxa-di-π-methane rearrangement (such as **19** to **18**) followed by Birch reduction to obtain a diquinane system[11] and a radical cyclization to make the third cyclopentane ring of the propellane skeleton (such as **17** to **16**), we may use a protected 3-hydroxypropyl and methyl groups for the bridgehead substituents, R^1 and R, respectively.

The ketone **1** was converted into a diquinane derivative (**21**) as shown in Scheme 4. The addition of 3-benzyloxypropylmagnesium bromide to **1** at room temperature gave the exo alcohol **15a** in 61% yield along with the endo isomer in 25% yield. The alcohol **15a** was converted into the ketone **14a** in 87% yield by treating with TsOH (10 mol%) in boiling benzene for 15 min. When an 8 : 5 mixture of **15a** and its *endo* isomer was treated under similar conditions, the ketone **14a** was obtained in 77% yield. The isomer **13a** was not detected in both reaction mixtures.[10]

Catalytic hydrogenation of **14a** using 5% Pt–C followed by treatment with potassium *t*-butoxide and then allyl chloroformate in THF gave the allyl enol carbonate. By treatment with a catalytic amount of palladium(II) acetate in boiling acetonitrile for 1 h, the α,β-unsaturated ketone **13a** was derived in 79% overall yield.[12] A reaction of **13a** and Li-



Scheme 2. Formal bridgehead substitution of 1-methoxybicyclo[2.2.2]oct-5-en-2-ones and retrosynthetic analysis for substitution at both bridgeheads of a bicyclo]2.2.2]oct-5-en-2-one.



Scheme 3. Retrosynthetic analysis for (±)-modhephene.

$[Cu(CH_3)_2]$ in ether at −78 °C gave a β-methyl ketone in 97% yield. Treatment of the ketone with LDA in THF −78 °C followed by TMSCl gave the trimethylsilyl enol ether. A reaction of the enol ether using NBS in THF at 0 °C formed a mixture of α-bromo ketones. Dehydrobromination of them using Li_2CO_3 as a base at 130 °C in DMF formed **13b** in 79% overall yield from **13a**.

The reduction of **13b** with DIBAL-H gave a mixture of allyl alcohols **12a**. By treatment with an equimolar amount of TsOH in boiling benzene for 30 min, a pinacol-type rearrangement of **12a** gave the ketone **20a** in 95% overall yield. The sequence from **1** for **20a**, the first formal substitution at both bridgeheads, was accomplished through 11 steps in 45% overall yield.

According to the synthetic plan (Scheme 3), the ketone **20a** was led to **19a** in 99% yield by treatment with potassium *t*-butoxide (4 molar amounts) and methyl iodide (5 molar amounts) in a mixture of THF and DMF. Since the benzyl protecting group of **19a** was somewhat labile to photochemical reaction conditions, the ether bond was cleaved by treatment with BBr_3 in CH_2Cl_2 at −78 °C. The resulting alcohol (**19b**, X = OH) was converted into a *t*-butyldimethylsilyl (TBS) ether **19c** (X = OTBS) by using TBSCl and imidazole in 92% overall yield.

By irradiation in acetone through a Pyrex filter using a 100-W Ushio Hg lamp under argon for 2 h, a tricyclic ketone **18a** was derived in 91% yield from the β,γ-unsaturated ketone **19c**. The dissolved metal reduction of **18a** with Li and *t*-BuOH in liquid ammonia–ether followed by pyridinium chlorochromate (PCC) oxidation gave a ketone **21** (2 : 5, diastereomeric ratio) in 92% yield (Scheme 4).

The ketone **21** was converted into α,β-unsaturated ketones (**17a** and **22a**) in 76% yield by a method similar to that for the preparation of **13a**. The stereochemistry of the C-8 methyl of **17a** and **22a** was not clarified at this stage. By treatment with acetic acid in THF–H_2O, the TBS ether of **17a** was cleaved to yield **17b**. Bromination of **17b** using a mixture CBr_4 and PPh_3 in CH_3CN at 0 °C gave **22c** and **23c** in 39 and 53% yields, respectively. The bromides (**22c** and **23c**) were obtained in 61 and 27% yields, respectively, by the treatment of an alcohol **22b** with CBr_4–PPh_3 in CH_3CN at −20 °C.

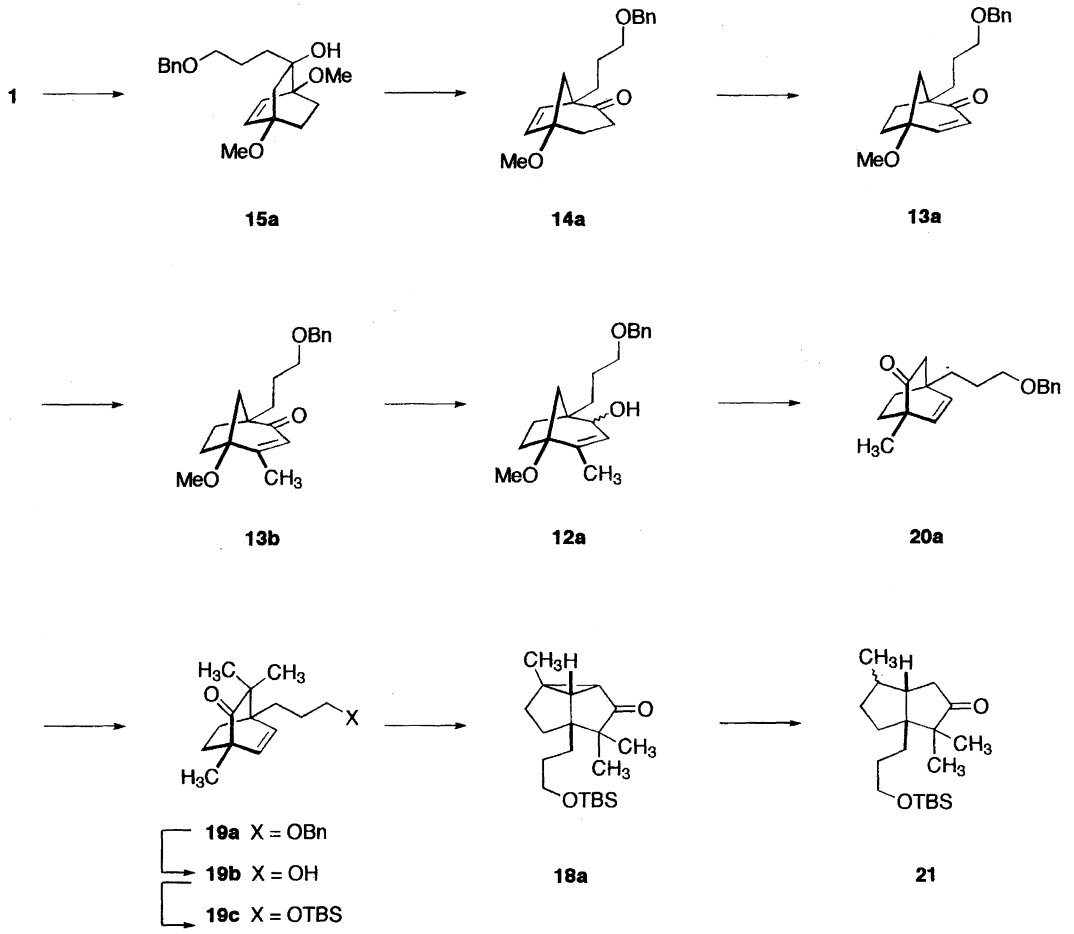
A radical cyclization reaction of **22c** using Bu_3SnH (1.5 molar amounts) and AIBN (0.1 molar amount) in benzene gave **24** in 69% yield after 2 h heating under reflux. The stereostructure of **24** was elucidated on the basis of NOE experiments (Fig. 1). The stereostructure of **22c** was deduced from that of **24**. Since **24** was an undesired isomer, we employed cyclization of the radical derived from **23c** for the preparation of **16** (Scheme 5).

By treatment with LDA in THF–HMPA, followed by protonation with aqueous ammonium chloride, **23a** was first derived from a mixture of **17a** and **22a** in 92 % yield in order to obtain **23c** selectively. By treatment with acetic acid in THF–H_2O, the TBS ether of **23a** was cleaved to give **23b** without migration of the double bond. In the presence of triethylamine, treatment of **23b** using a mixture of CBr_4 and PPh_3 in CH_3CN led to **23c** in 87% yield. A radical cyclization reaction of **23c** using Bu_3SnH (1.6 molar amount) and AIBN (0.1 molar amount) in benzene gave a 1.7 : 1 mixture of propellanones **16** and **24** in 67% yield after 2 h heating under reflux. The former was isolated by HPLC, and the structure of **16** was confirmed on the basis of its spectroscopic characteristics.

A Formal Total Synthesis of (±)-Isocomene (6). Scheme 6 shows our synthetic course based on oxa-di-π-methane rearrangement of **27c** into **28** followed by dissolving metal reduction to prepare a [5-5] fused-ring system, such as **29**. This drove us to select a protected 3-hydroxypropyl group and hydrogen for R^1 and R, respectively. An aldol cyclization reaction of **30** would give an angular triquinane **31**, from which a key intermediate **32**[8c] for (±)-isocomene (**6**) should be derived.

The first stage of the synthesis is the formal bridgehead substitution of **1** leading to **26** through **13a**. The route for the α,β-unsaturated ketone **13a** from **1** is shown in Scheme 4. Treatment of **13a** with methyllithium gave alcohols **25**. A pinacol-type rearrangement of **25** gave the ketone **26** in 91% overall yield from **13a**. Thus, the bridgehead substitution from **1** for **26** followed seven steps in 57% overall yield.

The enolate derived from **26** and LDA was treated with methyl iodide in the presence of HMPA to give stereoselectively the α-methyl ketone **27a** in 94% yield.[13] The stereochemistry of the 3-methyl group was confirmed on the basis of positive NOE between the signals due to the 3- and



Scheme 4. Preparation of a diquinane **21** through substitution at both bridgeheads of a bicyclo[2.2.2]oct-5-en-2-one **1**.

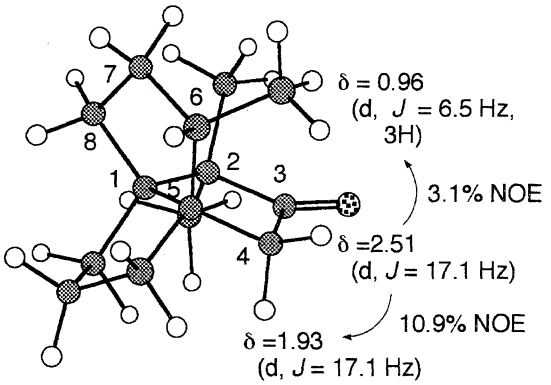


Fig. 1. A molecular model (MM2) and key interaction obtained from the NOE difference spectra of a propellanone **24**.

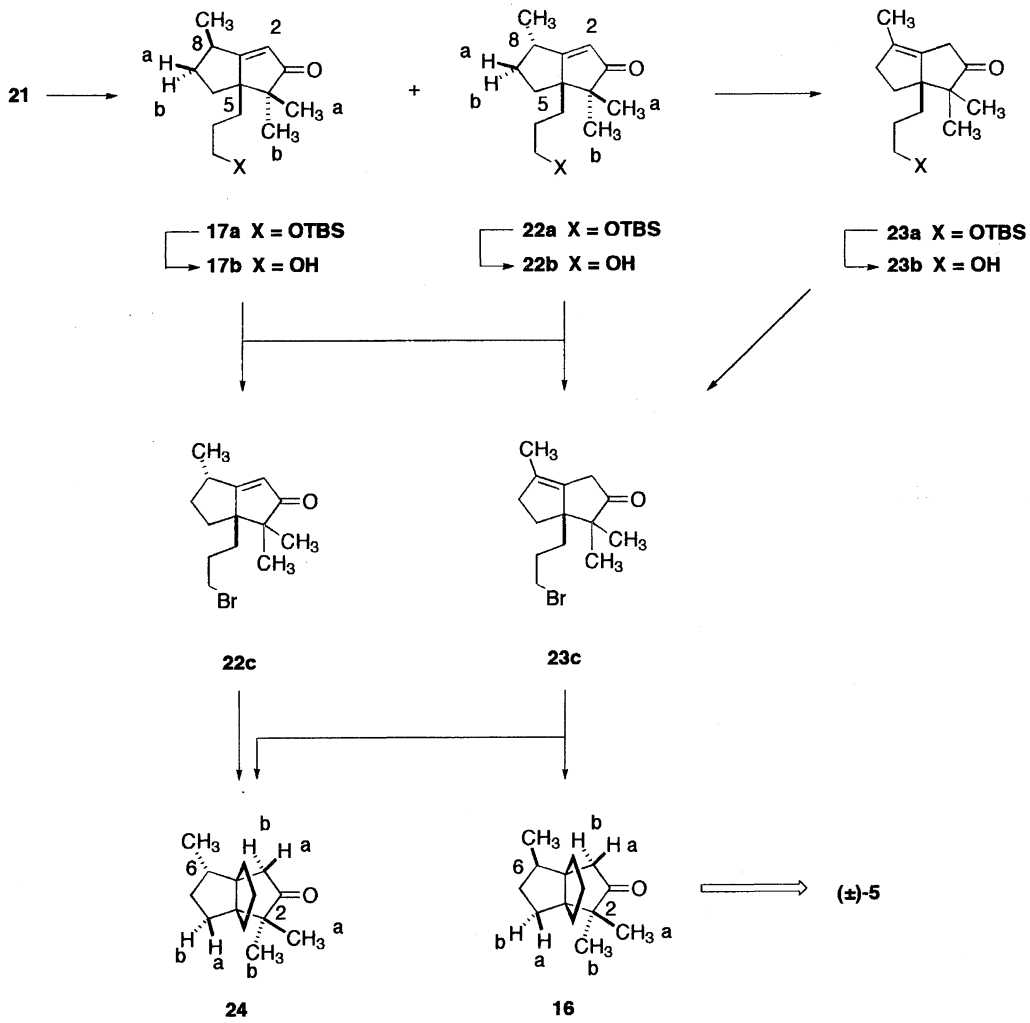
5-methyl groups. Before a photochemical transformation similar to that of **19c** into **18a**, the benzyl ether part of **27a** was cleaved by treatment with BBr_3 in CH_2Cl_2. The resulting alcohol **27b**, obtained in 94% yield, was transformed into **27c** by silylation in 92% yield.

A photochemical reaction of **27c** in acetone gave the tricyclic ketone **28** in 83% yield, which was due to an oxa-di-π-methane rearrangement. The stereochemistry of the 4-methyl group of **28** was estimated on the basis of NOE experiments. Enhancements at 1- and 4-methyl signals (δ = 1.31 and 1.10, respectively) were observed upon irradiation at 1.79 ppm, the center of the overlapping multiplets being due to three protons (H_2, H_8, and C_5–C<u>H</u>H–).

The cyclopropane was cleaved reductively to give **29a** in 75% yield. Cleavage of the silyl ether by treatment with tetrabutylammonium fluoride gave an alcohol **29b** in 99% yield. Oxidation of the alcohol with CrO_3–2Py[14] gave a keto aldehyde **30**. By treatment using KOH in methanol at room temperature, an intramolecular aldol reaction of **30** went on smoothly to give a mixture of **31a** in 83% yield.

The hydroxy group of **31a** was protected as a *t*-butyldimethylsilyl ether in 94% yield. The resulting mixture of **31b** was treated with LDA to generate the enolates. The lithium enolate were treated with 1,1,1,-trifluoro-*N*-phenyl-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide to give a mixture of the enol trifluoromethanesulfonates in 87% yield. A coupling reaction of the enol triflate with lithium dimethylcuprate(I) gave a mixture of the desired products in 65% yield. Cleavage of the silyl ether followed by PCC oxidation gave a ketone **32** in 74% overall yield. The spectroscopic characteristics of **32** are identical with those reported previously.[8c]

In conclusion, a practical method has been developed to introduce the desired substituents at both the C-1 and C-4 bridgeheads of a bicyclo[2.2.2]oct-5-en-2-one. A formal total synthesis of (±)-modhephene (**5**) and that of (±)-isocomene



Scheme 5. Preparation of synthetic intermediate **16** for (±)-modhephene.

(**6**) have been accomplished starting from the resulting bicyclic compounds possessing the desired substituents at both bridgeheads through an oxa-di-π methane rearrangement.

Experimental

General. NMR spectra were measured at 300 and 600 MHz in $CDCl_3$ using TMS [$(CH_3)_4Si$] as the internal standard. COSY and NOESY experiments were frequently employed for the assignment of stereostructures. THF and diethyl ether were distilled from diphenylketyl under argon immediately prior use. Dichloromethane was distilled from CaH_2 under argon immediately prior use. All reactions were monitored by analytical TLC using Merck precoated silica-gel $60F_{254}$ plates. Column chromatography was carried out with Merck silica gel 60 (70—230 mesh ASTM). Flash chromatography was carried out with Cica–Merck silica gel 60 (230—400 mesh ASTM). Semi-preparative HPLC was performed using a Merck Hiber® prepacked column RT (250×10 mm).

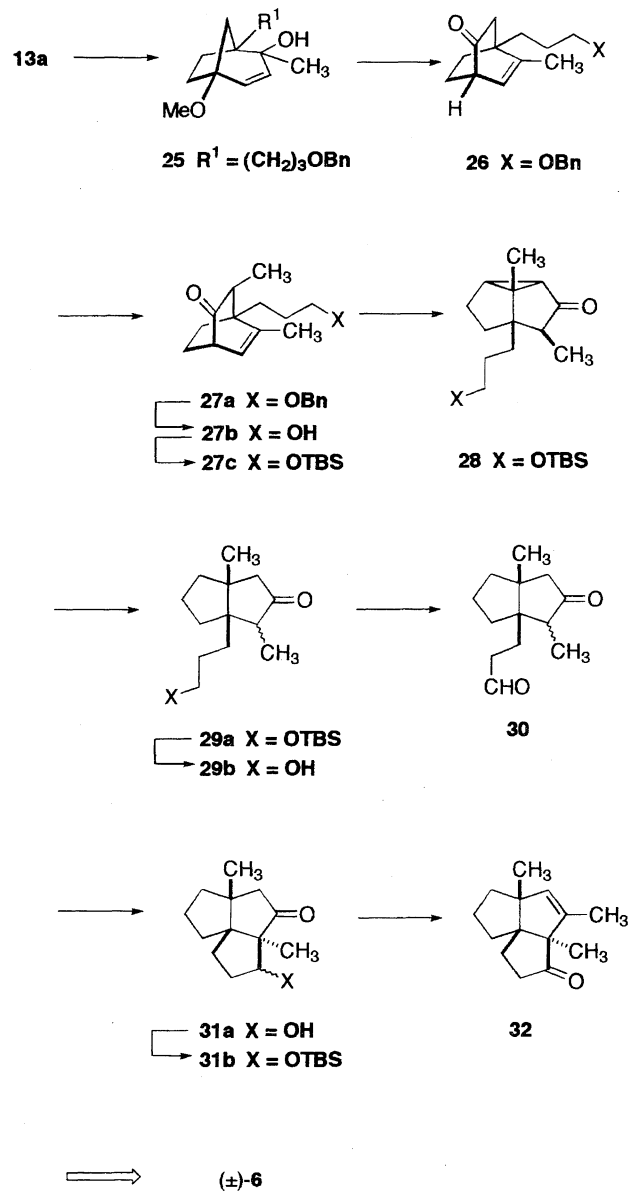
***exo*-2-(3-Benzyloxypropyl)-1,4-dimethoxybicyclo[2.2.2]oct-5-en-2-ol (15a) and *endo*-2-(3-Benzyloxypropyl)-1,4-dimethoxybicyclo[2.2.2]oct-5-en-2-ol.** (a) A solution of benzyl 3-bromopropyl ether was prepared from Mg (252 mg, 10.4 mmol) and 3-bromopropylbenzylether (2.336 g, 10.2 mmol) in THF (20.0 cm^3). To this solution was added dropwise a solution of 1,4-dimethoxybicyclo-[2.2.2]oct-5-en-2-one (**1**) (1.474 g, 8.09 mmol) in THF (5.0 cm^3) at room temperature. After stirring overnight, the reaction mixture was treated with a saturated aqueous NH_4Cl solution, and then extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil. Chromatography of this oil on silica gel (100 g, 3 : 1—1 : 1 hexane–ethyl acetate) gave **15a** (1.647 g, 4.95 mmol, 61%) and the *endo* isomer (675 mg, 2.05 mmol, 25%).

(b) A very similar reaction using 3-benzyloxypropylmagnesium bromide (39.0 mmol) and **1** (5.48 g, 30.1 mmol) gave an 8 : 5 mixture (9.82 g, 29.5 mmol, 98% yield) of **15a** and the *endo* isomer after chromatography.

15a: Colorless oil; IR (neat) 3420 cm^{-1} (OH) ; ^{1}H NMR ($CDCl_3$) δ = 7.38—7.27 (5H, m, C_6H_5), 6.70 (2H, s, H_5 and H_6), 5.02 (2H, s, $OC\underline{H}_2C_6H_5$), 3.46 (2H, s, $C\underline{H}_2OCH_2C_6H_5$), 3.38 (3H, s, OCH_3), 3.33 (3H, s, OCH_3), and 2.18—1.55 (10H, m).

The *endo* Isomer of 15a: Colorless oil; IR (neat) 3490 cm^{-1} (OH) ; ^{1}H NMR ($CDCl_3$) δ = 7.38—7.28 (5H, m, C_6H_5), 6.36 (1H, d, $J_{5,6}$ = 9.3 Hz, H_5 or H_6), 6.28 (1H, d, $J_{6,5}$ = 9.3 Hz, H_6 or H_5), 4.52 (2H, s, $OC\underline{H}_2C_6H_5$), 3.52 (2H, s, $C\underline{H}_2OCH_2C_6H_5$), 3.41 (3H, s, OCH_3), 3.35 (3H, s, OCH_3), and 1.97—1.43 (10H, m).

1-(3-Benzyloxypropyl)-5-methoxybicyclo[3.2.1]oct-6-en-2-one (14a). (a) A solution consisting of an alcohol **15a** (1.492 g, 4.49 mmol), TsOH (monohydrate, 856 mg, 0.450 mmol) and dry benzene (9 cm^3) was heated at 80 °C (bath temperature) for 15 min. The reaction mixture was treated with a saturated aqueous



Scheme 6. Preparation of a synthetic intermediate **32** for (±)-isocomene.

$NaHCO_3$ solution and then extracted with three portions of ether. The combined extracts were washed with saturated brine and dried over $MgSO_4$ and concentrated to an oil. Chromatography of this oil on silica gel (80 g, 5 : 1 hexane–ethyl acetate) gave **14a** (1.176 g, 3.91 mmol, 87%).

(b) A solution consisting of an 8 : 5 mixture of **15a** and its *endo* isomer (9.81 g, 29.5 mmol), TsOH (monohydrate, 6.85 g, 36.0 mmol), and dry benzene (60 cm^3) was heated at 85 °C (bath temperature) for 30 min. Similar treatment to that descried above followed by chromatography on silica gel (270 g, 3 : 1 hexane–ethyl acetate) gave **14a** (6.80 g, 22.6 mmol, 77%).

14a: IR (neat) 1710 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.38—7.23 (5H, m), 6.16 (1H, d, J=5.4 Hz), 5.76 (1H, d, J=5.4 Hz), 4.50 (2H, s, $OC\underline{H}_2C_6H_5$), 3.50 (2H, t, J = 6.9 Hz, $C\underline{H}_2OCH_2C_6H_5$), 3.36 (3H, s, OCH_3), 2.59 (1H, ddd, J = 18.0, 9.6, and 8.4 Hz), 2.48—2.34 (2H, m), and 2.16—1.42 (7H, m). Found: C, 75.08; H, 8.11%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. Found: *m/z* 300.1719. Calcd for $C_{19}H_{24}O_3$: M, 300.1726.

1-(3-Benzyloxypropyl)-5-methoxybicyclo[3.2.1]oct-3-en-2-one (13a). To a solution of **14a** (6.77 g, 22.6 mmol) in ethyl acetate (160 cm^3) was added 5% Pt–C (100 mg). The mixture was stirred under hydrogen for 3 h, and then filtered through a silica-gel layer. Evaporation of the filtrate gave a colorless oil. Chromatography of the oil (6.78 g) on silica gel (200 g, 2 : 1 hexane–ethyl acetate) gave 1-(3-benzyloxypropyl)-5-methoxybicyclo[3.2.1]octan-2-one (6.65 g, 22.0 mmol, 98%): Colorless oil; IR (neat) 1710 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.38—7.23 (5H, m), 4.50 (2H, s, $OC\underline{H}_2C_6H_5$), 3.47 (2H, m, $C\underline{H}_2OCH_2C_6H_5$), 3.30 (3H, s, OCH_3), 2.51 (1H, dddd, J = 16.5, 12.0, 8.4, and 0.9 Hz), 2.40 (1H, ddd, J = 16.5, 7.2, and 1.8 Hz), and 2.16—1.59 (12H, m). Found: C, 75.45; H, 8.54%. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67%.

To a stirred solution of *t*-BuOK (169 mg, 1.51 mmol) in THF (2.5 cm^3) was added dropwise a solution of the saturated ketone (305 mg, 1.01 mmol) in THF (2.5 cm^3) at −78 °C under argon. The mixture was stirred for 30 min at −78 °C. To this solution was added dropwise allyl chloroformate (0.150 cm^3, 1.41 mmol) at −78 °C. This reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature. After confirming of the disappearance of the ketone by TLC, the resulting mixture was treated with a saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (427 mg). Chromatography of this oil on silica gel (12.5 g, 2 : 1 hexane–ethyl acetate) gave an allyl enol carbonate (343 mg, 0.887 mmol, 88%).

To a stirred solution of the allyl enol carbonate (343 mg, 0.887 mmol) in acetonitrile (8 cm^3) was added palladium(II) acetate (15.7 mg, 0.0699 mmol). The mixture was heated under reflux for 1 h under argon. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (75 g, 2 : 1 hexane–ethyl acetate) gave **13a** (245 mg, 0.816 mmol, 92%) as a colorless oil: IR (neat) 1680 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.37—7.23 (6H, m), 5.93 (1H, d, J = 9.9 Hz), 4.51 (2H, s, $OC\underline{H}_2C_6H_5$), 3.50 (2H, m, $C\underline{H}_2OCH_2C_6H_5$), 3.37 (3H, s, OCH_3), and 2.15—1.43 (10H, m). Found: C, 75.67; H, 8.25%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%.

1-(3-Benzyloxypropyl)-5-methoxy-4-methylbicyclo[3.2.1]oct-3-en-2-one (13b). To a suspension of copper(I) iodide (8.65 g, 45.4 mmol) in ether (90.0 cm^3) was added dropwise a solution of methyllithium (1.05 M in ether, 86.5 cm^3, 90.8 mmol, 1 M = 1 mol dm^{-3}) at −20 °C under argon. The mixture was stirred for 10 min at −20 °C and then cooled to −78 °C. To this solution was added dropwise a solution of **13a** (4.54 g, 15.1 mmol) in ether (45.0 cm^3) at −78 °C. This reaction mixture was allowed to reach room temperature, and was then stirred for 0.5 h. The resulting mixture was treated with a saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil. Chromatography of this oil on silica gel (150 g, 3 : 1 hexane–ethyl acetate) gave 1-(3-benzyloxypropyl)-5-methoxy-4-methylbicyclo-[3.2.1]octan-2-one (4.65 g, 14.7 mmol, 97%) as colorless oil: IR (neat) 1710 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.35—7.26 (5H, m), 4.50 (2H, s, $OC\underline{H}_2C_6H_5$), 3.49—3.45 (2H, m, $C\underline{H}_2OCH_2C_6H_5$), 3.25 (3H, s, OCH_3), 2.67 (1H, dd, J = 15.9 and 8.1 Hz, H_3), 2.45 (1H, ddq, J = 8.1, 6.9, and 0.9 Hz, H_4), 2.16 (1H, dt, J = 12.6 and 5.4 Hz), 2.08 (1H, dd, J = 15.9 and 0.9 Hz, H_3), 2.03—1.04 (10H, m), and 0.95 (3H, d, J = 6.9 Hz, 4-CH_3). Found: C, 75.76; H, 8.98%. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.98%. Found: *m/z* 316.2027. Calcd for $C_{19}H_{28}O_3$: M, 316.2038.

To a stirred solution of LDA (20.6 mmol) in THF (15 cm^3)

prepared under argon was added dropwise a solution of the β-methyl ketone (4.65 g, 14.7 mmol) in THF (35 cm^3) at −78 °C. The mixture was stirred for 30 min at −78 °C. To this solution was added TMSCl (2.85 cm^3, 22.1 mmol) at −78 °C. This mixture was stirred for 30 min, allowed to warm to room temperature, and treated with a saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (the silyl enol ether, 6.04 g).

To a solution of this oil in THF (150 cm^3) was added portionwise NBS (3.40 g, 19.1 mmol) at 0 °C. After confirmation of the disappearance of the silyl enol ether by TLC, the mixture was treated with saturated aqueous $NaHCO_3$ solution and then extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (an α-bromo ketone, 7.19 g).

To a preheated mixture of lithium carbonate (3.26 g, 44.1 mmol), lithium bromide (1.66 g, 19.1 mmol), and DMF (30.0 cm^3) at 130 °C under argon was added a solution of the bromo ketone in DMF (10.0 cm^3) with stirring. This mixture was heated at 130 °C for 1 h and then cooled to room temperature. The reaction mixture was diluted with water and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (4.81 g). Flash chromatography (150 g, 3 : 1 hexane–ethyl acetate) of this oil gave **13b** (3.76 g, 11.2 mmol, 81%): A colorless oil; IR (neat) 1670 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.38—7.26 (5H, m, C_6H_5), 5.80 (1H, q, J = 1.2 Hz, H_3), 4.51 (2H, s, $OC\underline{H}_2C_6H_5$), 3.50 (2H, m, $C\underline{H}_2OCH_2C_6H_5$), 3.29 (3H, s, OCH_3), 2.00 (3H, d, J = 1.2 Hz, 3-CH_3), 2.12—1.43 (10H, m). Found: *m/z* 314.1877. Calcd for $C_{20}H_{26}O_3$: M, 314.1882.

4-(3-Benzyloxypropyl)-1-methylbicyclo[2.2.2]oct-5-en-2-one (20a). To a solution of an enone **13b** (2.00 g, 6.36 mmol) in toluene (20.0 cm^3) was added dropwise a 1.5 M solution of DIBAL-H in toluene (6.80 cm^3, 10.2 mmol) at −78 °C with stirring. The mixture was stirred for 30 min at −78 °C and allowed to warm to room temperature. After confirmation of the disappearance of **13b** by TLC, a saturated aqueous NH_4Cl solution was added to the reaction mixture. After this mixture was stirred for 30 min, a white precipitate was filtered off and washed well with ether. The filtrate was extracted with three portions of ether. The combined ether layers were washed with saturated brine, dried over Na_2SO_4, and concentrated to an oil (**12a**, $R^1 = (CH_2)_3OBn$, $R^2 = CH_3$, 2.14 g).

A solution consisting of the oil, *p*-toluenesulfonic acid (TsOH, 1.46 g, 7.68 mmol), and dry benzene (13.0 cm^3) was heated under reflux for 30 min. The reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution, and then extracted with three portions of ether. The combined extracts were washed with saturated brine and dried over $MgSO_4$ and concentrated to an oil (1.84 g). Chromatography of this oil on silica gel (55 g, 4 : 1 hexane–ethyl acetate) gave **20a** (1.72 g, 6.04 mmol, 95% from **13b**): colorless oil; IR (neat) 1720 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.42—7.25 (5H, m, C_6H_5), 6.24 (1H, d, J = 8.1 Hz, H_5), 5.87 (1H, d, J = 8.1 Hz, H_6), 4.53 (2H, s, $OC\underline{H}_2C_6H_5$), 3.52 (2H, t, J = 6.0 Hz, $C\underline{H}_2OCH_2C_6H_5$), 1.97 (1H, dd, J = 18.0 and 2.4 Hz, H_{3endo}), 1.93 (1H, d, J = 18.0 Hz, H_{3exo}), 1.77—1.41 (8H, m), and 1.21 (3H, s, 1-CH_3). Found: *m/z* 284.1783. Calcd for $C_{19}H_{24}O_2$: M, 284.1776.

4-(3-Benzyloxypropyl)-1,3,3-trimethylbicyclo[2.2.2]oct-5-en-2-one (19a). To a stirred solution of *t*-BuOK (1.71 g, 15.2 mmol) in THF (23.0 cm^3) was added dropwise a solution of a keotne **20a** (865 mg, 3.04 mmol) in THF (8.0 cm^3) at −78 °C under argon. The mixture was stirred for 30 min at −78 °C. To this solution was added dropwise methyl iodide (1.24 cm^3, 18.5 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was treated with a saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (941 mg). Flash chromatography of this oil on silica gel (150 g, 8 : 1 hexane–ethyl acetate) gave **19a** (563 mg, 2.74 mmol, 84%) and a mixture of monomethylated ketones (370 mg). Methylation of the latter under the very similar conditions gave an additional **19a** (377 mg, 15%).

19a: Colorless oil; IR (neat) 3430 (OH) and 1720 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.40—7.26 (5H, m, C_6H_5), 6.25 (1H, d, J=8.4 Hz, H_5), 5.77 (1H, d, J = 8.4 Hz, H_6), 4.54 (2H, s, $OC\underline{H}_2C_6H_5$), 3.54 (2H, t, J = 6.3 Hz, $C\underline{H}_2OCH_2C_6H_5$), 1.75—1.44 (8H, m), 1.20 (3H, s, 1-CH_3), 1.01 (3H, s, 3-CH_3), and 0.99 (3H, s, 3-CH_3). Found: C, 80.44; H, 9.32%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%. Found: *m/z* 312.2089. Calcd for $C_{21}H_{28}O_2$: M, 312.2089.

4-(3-Hydroxypropyl)-1,3,3-trimethylbicyclo[2.2.2]oct-5-en-2-one (19b). To a solution of a benzyl ether **19a** (875 mg, 2.80 mmol) in CH_2Cl_2 (10.0 cm^3) was added BBr_3 (1.33 M CH_2Cl_2 solution, 3.16 cm^3, 4.20 mmol) at −78 °C under argon. The mixture was stirred for 30 min at −78 °C, and then allowed to warm to room temperature. The resulting mixture was treated with a saturated aqueous $NaHCO_3$ solution (20 cm^3), and then extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (1.07 g). Chromatography of this oil on silica gel (32 g, 3 : 2 hexane–ethyl acetate) gave **19b** (583 mg, 2.62 mmol, 94%): Colorless needles; mp 43.2—44.5 °C; IR (neat) 3430 (OH) and 1720 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 6.26 (1H, d, J = 8.1 Hz, H_5), 5.79 (1H, d, J = 8.1 Hz, H_6), 3.73 (2H, t, J = 6.0 Hz, $C\underline{H}_2OH$), 1.78—1.43 (9H, m), 1.20 (3H, s, 1-CH_3), 1.02 (3H, s, 3-CH_3), and 1.00 (3H, s, 3-CH_3). Found: C, 70.85; H, 10.16%. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%. Found: *m/z* 222.1624. Calcd for $C_{14}H_{22}O_2$: M, 222.1620.

4-[3-(*t*-Butyldimethylsiloxy)propyl]-1,3,3-trimethylbicyclo-[2.2.2]oct-5-en-2-one (19c). To a solution of **19b** (2.33 mg, 10.5 mmol) and imidazole (1.88 g, 27.6 mmol) in DMF (10.0 cm^3) prepared under argon was added dropwise a solution of *t*-butyldimethylsilyl chloride (2.56 g, 17.0 mmol) in DMF (30 cm^3) under argon. This reaction mixture stirred for 1.5 h at room temperature, and then diluted with ether (50 cm^3) and water (50 cm^3). This mixture was extracted with three portions of ether. The combined extracts were washed successively with water, 5% aqueous HCl, water, an aqueous $NaHCO_3$ solution, and saturated brine, dried over $MgSO_4$, and concentrated to an oil (4.11 g). Chromatography of this oil on silica gel (120 g, 10 : 1 hexane–ethyl acetate) gave a ketone **19c** (3.47 g, 10.3 mmol, 98%): Colorless needles; mp 37.8—38.4 °C; IR (neat) 1720 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 6.25 (1H, d, J = 8.4 Hz, H_5), 5.77 (1H, d, J = 8.4 Hz, H_6), 3.67 (2H, t, J = 6.0 Hz, $C\underline{H}_2OSi$), 1.75—1.39 (9H, m), 1.19 (3H, s, 1-CH_3), 1.01 (3H, s, 3-CH_3), 0.99 (3H, s, 3-CH_3), 0.91 (9H, s, *t*-BuSi), and 0.07 (6H, s, $Si(CH_3)_2$). Found: C, 71.18; H, 10.83%. Calcd for $C_{20}H_{36}O_2Si$: C, 71.37; H, 10.78%. Found: *m/z* 336.2480. Calcd for $C_{20}H_{36}O_2Si$: M, 336.2485.

5-[3-(*t*-Butyldimethylsiloxy)propyl]-4,4,8-trimethyltricyclo-[3.3.0.$0^{2,8}$]octan-3-one (18a). A solution of a ketone **19c** (1.59 g, 4.73 mmol) in acetone (470 cm^3) was divided into three portions. Each portion was placed in an immersion well equipped with a Pyrex filter and irradiated for 1.5 h with a 100-W Ushio Hg lamp under argon. The combined acetone solutions were concentrated under vacuum. Chromatography of the remaining oil on silica gel (50 g, 10 : 1 hexane–ethyl acetate) gave a tricyclic ketone **18a** (1.43

g, 4.30 mmol, 91%) as a colorless oil; IR (neat) 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 3.61 (2H, t, J = 5.7 Hz, $C\underline{H}_2OSi$), 1.94 (1H, d, J = 5.4 Hz, H_2), 1.88 (1H, d, J = 5.4 Hz, H_1), 1.83—1.45 (8H, m), 1.23 (3H, s, 8-CH_3), 1.03 (3H, s, 4-CH_3), 0.90 (9H, s, *t*-BuSi), 0.86 (3H, s, 4-CH_3), and 0.07 (6H, s, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 219.1 (C-3), 63.6 (C-3′), 55.2 (C-5), 54.1 (C-4), 44.3 (C-1), 42.1 (C-2), 38.7 (C-8), 38.6, 31.5, 31.0, 29.3, 25.9 ($(\underline{C}H_3)_3CSi$), 24.6 (4-CH_3), 22.3 (8-CH_3), 18.3 $(CH_3)_3\underline{C}Si$), 17.6 (4-Me), and −5.4 $Si(CH_3)_2$). Found: *m/z* 336.2491. Calcd for $C_{20}H_{36}O_2Si$: M, 336.2485.

5-(3-*t*-Butyldimethylsilyloxypropyl)-4,4,8-trimethylbicyclo-[3.3.0]octan-3-one (21). To liquid ammonia (70 cm^3) was added with mechanical stirring a solution of tricyclic ketone **18a** (620 mg, 1.84 mmol), 2-methyl-2-propanol (3.70 cm^3) in ether (13.0 cm^3) at −78 °C under argon. Lithium (57.8 mg, 8.33 mmol) was added to the mixture. The resulting blue solution was stirred for 5 h, and then treated with methanol (5.0 cm^3). Ammonia was evaporated, and the remaining solid was dissolved by treatment with water (20.0 cm^3). The mixture was extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (630 mg). Chromatography of this oil on silica gel (22.5 g, 10 : 1 hexane–ethyl acetate) gave **21** (458 mg) and a mixture of alcohols (159 mg) due to over-reduction. PCC oxidation (151 mg of PCC) of the alcohols gave **21** (117 mg). Thus, **21** (575 mg) were derived as a 2 : 5 mixture of the stereoisomers in 92% yield from **18a**.

(5*RS*,8*SR*)-and (5*RS*,8*RS*)-5-[3-(*t*-Butyldimethylsiloxy)propyl]-4,4,8-trimethylbicyclo[3.3.0]oct-1-en-3-ones (17a and 22a, respectively). To a stirred solution of *t*-BuOK (1.03 g, 9.14 mmol) in THF (15 cm^3) was added dropwise a solution of ketones **21** (1.97 g, 5.80 mmol) in THF (15 cm^3) at −78 °C under argon. The mixture was stirred for 30 min at −78 °C. To this solution was added dropwise allyl chloroformate (0.924 cm^3, 8.71 mmol) at −78 °C. This reaction mixture was stirred at −78 °C for 30 min, and then allowed to warm to room temperature. After confirmation of the disappearance of **21** by TLC, the resulting mixture was treated with a saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (2.73 g). Chromatography of this oil on silica gel (85 g, 10 : 1 hexane–ethyl acetate) gave the enol carbonate (2.15 g, 4.86 mmol, 84%).

To a stirred solution of the allyl enol carbonate (2.15 g, 4.86 mmol) in acetonitrile (45 cm^3) was added palladium(II) acetate (88.0 mg, 0.390 mmol). The mixture was heated under reflux for 1 h under argon. The solvent was removed under reduced pressure and the residue (1.71 g) was purified by flash chromatography on silica gel (200 g, 10 : 1 hexane–ethyl acetate) gave a 1 : 2.3 mixture of **17a** and **22a** (1.49 g, 4.42 mmol, 91%) as a colorless oil. The ketones were separated by repeated flash chromatography.

17a: Colorless oil; IR (neat) 1710 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 5.78 (1H, d, J = 1.5 Hz, H_2), 3.51 (2H, m, $-C\underline{H}_2OSi$), 2.88—2.74 (1H, m, H_8), 2.27—2.14 (1H, m, H_7), 1.80—1.35 (6H, m), 1.27 (3H, d, J = 7.2 Hz, 8-CH_3), 1.25—1.17 (1H, m), 1.12 (3H, s, 4-CH_3), 0.94 (3H, s, 4-CH_3), 0.86 (9H, s, *t*-Bu–Si), and 0.01 (6H, s, $-OSi(CH_3)_2-$). Found: *m/z* 336.2505. Calcd for $C_{20}H_{36}O_2Si$: M, 336.2485.

22a: Colorless oil; IR (neat) 1710 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 5.74 (1H, d, J = 2.1 Hz, H_2), 3.49 (2H, t, J = 6.0 Hz, $C\underline{H}_2OSi$), 2.90—2.77 (1H, m, H_8), 2.43—2.28 (1H, m, H_{7a}), 1.88—1.77 (1H, m, H_{7b}), 1.62—1.21 (6H, m), 1.18 (3H, d, J = 6.6 Hz, 8-CH_3), 1.10 (3H, s, 4a-CH_3), 0.97 (3H, s, 4b-CH_3), 0.86 (9H, s, *t*-Bu–Si), and 0.01 (6H, s, $Si(CH_3)_2$). Found: *m/z* 336.2505. Calcd for $C_{20}H_{36}O_2Si$: M, 336.2485.

(5*RS*, 8*SR*)- 5- (3- Hydroxypropyl)- 4, 4, 8- trimethylbicyclo-[3.3.0]oct-1-en-3-one (17b). To a stirred solution of **17a** (108 mg, 0.320 mmol) in THF (1.0 cm^3) and water (1.0 cm^3) was added dropwise acetic acid (3.0 cm^3) at room temperature. The mixture was stirred for 1 h, treated carefully with a saturated aqueous $NaHCO_3$ solution, and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (118 mg). Chromatography of the oil on silica gel (10 g, 2 : 3 hexane–ethyl acetate) gave **17b** (63.8 mg, 0.290 mmol, 90%): Colorless oil; IR (neat) 3440 (OH), 1690 (C=O), and 1630 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 5.77 (1H, d, J = 1.2 Hz, H_2), 3.53 (2H, t, J = 6.6 Hz, $C\underline{H}_2OH$), 2.88—2.72 (1H, m), 2.05—1.85 (1H, broad, OH), 1.80—1.52 (3H, m), 1.42 (1H, ddd, J = 14.4, 12.0, and 5.4 Hz, H_6), 1.25 (3H, s, J = 7.2 Hz, 8-CH_3), 1.35—1.13 (3H, m), 1.09 (3H, s, 4-CH_3), and 0.92 (3H, s, 4-CH_3).

(5*RS*, 8*RS*)- 5- (3- Hydroxypropyl)- 4, 4, 8- trimethylbicyclo-[3.3.0]oct-1-en-3-one (22b). The silyl ether **22a** (122 mg, 0.363 mmol) was treated with acetic acid (3.06 cm^3) in THF (1.2 cm^3) and water (1.2 cm^3) for 1 h at room temperature. A similar work-up to that for **17b** yielded **22b** (66.3 mg, 0.298 mmol, 83%): Colorless oil; IR (neat) 3430 (OH), 1690 (C=O), and 1630 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 5.75 (1H, d, J = 1.2 Hz, H_2), 3.54 (2H, t, J = 6.6 Hz, $C\underline{H}_2OH$), 2.89—2.78 (1H, m), 2.40—2.31 (1H, m), 1.89—1.20 (8H, m), 1.17 (3H, s, J = 6.9 Hz, 8-CH_3), 1.10 (3H, s, 4-CH_3), and 0.97 (3H, s, 4-CH_3).

Bromination of 17b. To a stirred solutions of **17b** (63.8 mg, 0.287 mmol) in acetonitrile (2.0 cm^3) were added carbon tetrabromide (126 mg, 0.381 mmol) and triphenylphosphine (99.7 mg, 0.381 mmol) rapidly at 0 °C. After stirring 15 min, the reaction mixture was concentrated under vacuum, washed with hexane, and the resulting solid was removed by filtration. The filtrate was concentrated and purified by chromatography on silica gel (5 g, 7 : 1 hexane–ethyl acetate) to give **22c** (32.0 mg, 0.112 mmol, 39%) and **23c** (43.5 mg, 0.152 mmol. 53%).

22c: Colorless oil; IR (neat) 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 5.70 (1H, d, J = 2.1 Hz, H_2), 3.27—3.22 (2H, m, CH_2Br), 2.85—2.70 (1H, m), 2.39—2.25 (1H, m), 1.85—1.27 (7H, m), 1.13 (3H, d, J = 6.9 Hz, 8-CH_3), 1.04 (3H, s, 4-CH_3), and 0.92 (3H, s, 4-CH_3).

23c: Colorless oil; IR (neat) 1750 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 3.36 (2H, t, J = 6.6 Hz, CH_2Br), 2.83 (1H, d, J = 21.6 Hz, H_2), 2.68—2.49 (2H, m, H_2 and H_7), 2.35—2.23 (1H, m, H_7), 2.00 (1H, ddd, J = 13.5, 10.5, and 7.5 Hz, H_6), 1.93—1.70 (5H, m), 1.70 (3H, d, J = 0.9 Hz, 8-CH_3), 1.62—1.51 (2H, m), 1.15 (1H, ddd, J = 16.5, 12.6, and 3.9 Hz, $C\underline{H}H(CH_2)_2Br$), 1.00 (3H, s, 4-$CH_3$), and 0.85 (3H, s, 4-$CH_3$). Found: C, 58.74; H, 7.39%. Calcd for $C_{14}H_{21}OBr$: C, 58.96; H, 7.42%. Found: *m/z* 284.0777. Calcd for $C_{14}H_{21}OBr$: M, 284.0776.

Bromination of 22b. A similar procedure to that for **17b** was employed. An alcohol **22b** (66.3 mg, 0.298 mmol) in acetonitrile (2.0 cm^3) was treated with carbon tetrabromide (129 mg, 0.390 mmol) and triphenylphosphine (102 mg, 0.390 mmol) at −20 °C for 15 min. This mixture was treated with a saturated aqueous $NaHCO_3$ solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil. Chromatography of the oil on silica gel (7.5 g, 7 : 1 hexane–ethyl acetate) gave **22c** (51.8 mg, 0.182 mmol, 61%) and **23c** (23.0 mg, 0.0806 mmol, 27%).

Radical Cyclization of 22c: Preparation of (1*RS*,5*SR*,6*SR*)-2.2.6-Trimethyltricyclo[3.3.3.0^{1,5}]undecan-3-one (24). A solution of **22c** (51.3 mg, 0.180 mmol), tributyltin hydride (0.0750

cm^3, 0.270 mmol), and AIBN (3.0 mg, 0.018 mmol) in benzene (6.0 cm^3) was heated under reflux for 1.5 h. A similar work-up to that employed previously followed by chromatography of the remaining oil (295 mg) on silica gel (10 g, 10 : 1 hexane–ethyl acetate) gave **24** (25.1 mg, 0.124 mmol, 69%): Colorless oil; IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 2.51 (1H, d, J = 17.1 Hz, H_{4b}), 1.95 (1H, dddd, J = 13.5, 6.7, and 1.6 Hz, H_{8b}), 1.93 (1H, d, J = 17.1 Hz, H_4), 1.82—1.76 (2H, m), 1.77—1.71 (1H, m, H_6), 1.62—1.50 (3H, m), 1.45—1.41 (1H, m), 1.25 (1H, J = 13.5, 12.5, and 6.4 Hz, H_{8a}), 1.17—1.09 (2H, m), 1.05 (3H, s, 2a-CH_3), 0.99 (3H, s, 2b-CH_3), and 0.96 (3H, d, J = 6.5 Hz, 6-CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 222.61 (C-3), 62.43, 56.57, 50.51, 43.05 (C-6), 42.56 (C-4), 41.36, 37.44, 35.25, 35.15 (C-8), 24.44, 23.25 (2a-CH_3), 21.89 (2b-CH_3), and 15.19 (6-CH_3). Found: *m/z* 206.1667. Calcd for $C_{14}H_{22}O$: M, 206.1671.

1-[3-(*t*-Butyldimethylsiloxy)propyl]-2,2,6-trimethylbicyclo-[3.3.0]oct-5-en-3-one (23a). To a stirred solution of LDA (10.2 mmol) and HMPA (1.02 cm^3, 5.85 mmol) in THF (10.0 cm^3) prepared under argon was added dropwise a solution of a mixture of the ketones (**17a** and **22a**, 1.51 g, 4.50 mmol) in THF (10 cm^3) at −78 °C. The mixture was stirred for 30 min at −78 °C and then allowed to warm to room temperature. This mixture was treated with saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (1.58 g). Chromatography of the oil on silica gel (50 g, 10 : 1 hexane–ethyl acetate) gave **23a** (1.39 g, 4.14 mmol, 92%): Colorless oil; IR (neat) 1750 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 3.54 (2H, t, J = 6.3 Hz, CH_2OSi), 2.80 (1H, dq, J = 20.7 and 0.6 Hz, H_4), 2.68—2.46 (2H, m, H_4 and H_7), 2.32—2.18 (1H, m, H_7), 2.01—1.88 (1H, m, H_8), 1.68 (3H, s, J = 0.6 Hz, 6-CH_3), 1.64—1.25 (4H, m), 1.10—0.99 (1H, m), 0.97 (3H, s, 2-CH_3), 0.87 (9H, s, *t*-BuSi), 0.84 (3H, s, 2-CH_3), and 0.02 (6H, s, $Si(CH_3)_2$). Found: *m/z* 336.2491. Calcd for $C_{20}H_{36}O_2Si$: M, 336.2485.

1-(3-Hydroxypropyl)-2,2,6-trimethylbicyclo[3.3.0]oct-5-en-3-one (23b). To a stirred solution **23a** (919 mg, 2.73 mmol) in THF (8.20 cm^3) and water (8.20 cm^3) was added dropwise acetic acid (25.0 cm^3) at room temperature. The mixture was stirred for 1 h, treated carefully with saturated aqueous $NaHCO_3$ solution, and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (0.938 g). Chromatography of the oil on silica gel (30 g, 10 : 1 hexane–ethyl acetate) gave **23b** (606 mg, 2.73 mmol, > 99%): Colorless oil; IR (neat) 3450 and 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 3.60 (2H, t, J = 6.3 Hz, $C\underline{H}_2OH$), 2.83 (1H, d, J = 21.0 Hz, H_2), 2.71—2.49 (2H, m, H_2 and H_7), 2.28 (1H, m, H_7), 1.99 (1H, ddd, J = 17.4, 14.1, and 7.5 Hz, H_6), 1.69 (3H, s, 6-CH_3), 1.66—1.40 (4H, m), 1.37—1.27 (1H, broad s, OH), 1.06 (1H, m), 0.99 (3H, s, 4-CH_3), and 0.85 (3H, s, 4-CH_3). Found: *m/z* 222.1632. Calcd for $C_{14}H_{22}O_2$: M, 222.1620.

Selective Synthesis of 1-(3-Bromopropyl)-2,2,6-trimethylbicyclo[3.3.0]oct-5-en-3-one (23c). To a stirred solution of **23b** (73.5 mg, 0.331 mmol) in acetonitrile (2.0 cm^3) was added triethylamine (0.0700 cm^3, 0.502 mmol) at room temperature. The mixture was stirred for 10 min. To the resulting mixture were added carbon tetrabromide (154 mg, 0.464 mmol) and triphenylphosphine (122 mg, 0.465 mmol) rapidly. After stirring 15 min, the reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated. The residue was treated with hexane and the solid was removed by filtration. The filtrate was concentrated and purified by chromatography on silica gel (10 g, 10 : 1 hexane–ethyl acetate) to give **23c** (82.0 mg, 0.288 mmol, 87%).

Radical Cyclization of 23c: Preparation of (1*RS*,5*SR*,6*RS*)- and (1*RS*,5*SR*,6*SR*)-2.2.6-Trimethyltricyclo[3.3.3.0^{1,5}]undecan-3-ones (16 and 24, Respectively). A solution of **23c** (58.7 mg, 0.206 mmol), tributyltin hydride (0.0930 cm^3, 0.336 mmol), and AIBN (3.5 mg, 0.021 mmol) in benzene (7.0 cm^3) was heated under reflux for 2 h. After confirmation of the disappearance of **23c** by TLC, ethyl bromide (1 cm^3) was added to the mixture. The mixture was heated under reflux for 1 h. The solvent was removed under vacuum at room temperature. Chromatography of the remaining oil (295 mg) on silica gel (50 g, 10 : 1 hexane–ethyl acetate) gave a 1.7 : 1 mixture of **16** and **24** (28.5 mg, 0.138 mmol, 67%). Analytical samples were purified by HPLC (200 : 1 hexane–ethyl acetate).

16: Colorless oil; IR (neat) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 2.39 (1H, d, J = 17.7 Hz, H_4), 2.19 (1H, d, J = 17.7 Hz, H_4), 1.88 (1H, dddd, J = 12.9, 6.3, 5.3, and 1.0 Hz, H_{8b}), 1.77—1.58 (5H, m), 1.45—1.32 (4H, m), 1.32—1.24 (1H, m, H_{8a}), 1.03 (3H, s, 2a-CH_3), 1.01 (3H, s, 2b-CH_3), and 0.98 (3H, d, J = 6.5 Hz, 6-CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 223.46 (C-3), 63.04, 56.33, 51.24, 49.35 (C-4), 46.85 (C-6), 38.11 (C-8), 35.62, 34.44, 33.28, 26.53, 23.98 (2b-CH_3), 22.32 (2a-CH_3), and 14.32 (6a-CH_3). Found: *m/z* 206.1669. Calcd for $C_{14}H_{22}O$: M, 206.1671.

4-(3-Benzyloxypropyl)-5-methylbicyclo[2.2.2]oct-5-en-2-one (26). To a solution of an enone **13a** (4.68 g, 15.6 mmol) in THF (70.0 cm^3) was added dropwise a 1.03 M solution of methyllithium in ether (27.4 cm^3, 28.2 mmol) at −78 °C with stirring. The mixture was stirred for 30 min at −78 °C and allowed to warm to room temperature. After confirming of the disappearance of **13a** by TLC, a saturated aqueous NH_4Cl solution was added to the reaction mixture. This mixture was extracted with three portions of ether. The combined ether layers were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (**25**, 5.07 g).

A solution consisting of the oil, *p*-toluenesulfonic acid (TsOH, 0.304 g, 1.60 mmol), and dry benzene (35.0 cm^3) was heated under reflux for 15 min. The reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution, and then extracted with three portions of ether. The combined extracts were washed with saturated brine and dried over $MgSO_4$ and concentrated to an oil (4.48 g). Chromatography of this oil on silica gel (130 g, 4 : 1 hexane–ethyl acetate) gave **26** (3.84 g, 13.5 mmol, 91%): Colorless oil; IR (neat) 1720 cm^{-1} (C=O) ; ^{1}H NMR ($CDCl_3$) δ = 7.40—7.20 (5H, m, C_6H_5), 5.85 (1H, dq, J = 6.6 and 1.5 Hz, H_6), 4.52 (2H, s, $OC\underline{H}_2C_6H_5$), 3.52 (2H, t, J = 6.0 Hz, $C\underline{H}_2OCH_2C_6H_5$), 1.98 (1H, q, J = 18.0 Hz, H_3), 1.90—1.79 (2H, m), 1.82 (3H, d, J = 1.5 Hz, 5-CH_3), 1.74—1.53 (6H, m), and 1.26 (1H, ddd, J = 12.0, 7.2, and 3.0 Hz, H-8). Found: *m/z* 284.1774. Calcd for $C_{19}H_{24}O_2$: M, 284.1776.

***endo*-4-(3-Benzyloxypropyl)-3,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (27a).** To a solution of LDA prepared from diisopropylamine (0.640 cm^3, 4.50 mmol) and butyllithium (2.60 cm^3, 4.20 mmol) in THF (3.0 cm^3) was added dropwise a solution of a ketone **26** (0.850 g, 2.99 mmol) in THF (1.5 cm^3) at −78 °C with stirring. The mixture was stirred for 30 min at −78 °C. To this solution were added HMPA (1.83 cm^3, 10.5 mmol) and methyl iodide (0.32 cm^3, 4.8 mmol), and the resulting mixture was allowed to warm to room temperature. After confirming of the disappearance of **26** by TLC, a saturated aqueous NH_4Cl solution was added to the reaction mixture. This mixture was extracted with three portions of ether. The combined ether layers were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (0.893 g). Chromatography of this oil on silica gel (30 g, 4 : 1 hexane–ethyl acetate) gave **27a**

(X = $OCH_2C_6H_5$) (0.841 g, 2.82 mmol, 94%): Colorless oil; IR (neat) 1720 cm^{-1} (C=O) ; ^1H NMR ($CDCl_3$) δ = 7.40—7.20 (5H, m, C_6H_5), 5.82 (1H, dq, J = 6.6 and 1.2 Hz, H_6), 4.54 (2H, s, $OCH_2C_6H_5$), 3.52 (2H, t, J = 6.0, Hz, $C\underline{H}_2OCH_2C_6H_5$), 2.90 (1H, m), 1.90 (1H, q, J = 18.0 Hz, H_3), 1.80 (3H, d, J = 1.5 Hz, 5-CH_3), 1.85—1.52 (7H, m), 1.33—1.18 (1H, m, H-8), and 0.96 (3H, d, J = 7.2 Hz, 3-CH_3). Positive NOE between 1.80 (d) and 0.96 (d). Found: *m/z* 298.1938. Calcd for $C_{20}H_{26}O_2$; M, 298.1933.

***endo*-4-(3-Hydroxypropyl)-3,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (27b).** To a solution of a benzyl ether **27a** (3.86 g, 12.9 mmol) in CH_2Cl_2 (50.0 cm^3) was added BBr_3 (1.06 M CH_2Cl_2 solution, 19.6 cm^3, 20.6 mmol) at −78 °C under argon. The mixture was stirred for 5 h at −78 °C and then treated with a saturated aqueous $NaHCO_3$ solution. The mixture was extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (4.75 g). Chromatography of this oil on silica gel (250 g, 2 : 3 hexane–ethyl acetate) gave **27b** (2.54 g, 12.2 mmol, 94%): Colorless oil; IR (neat) 3430 (OH) and 1720 cm^{-1} (C=O) ; ^1H NMR ($CDCl_3$) δ = 5.84 (1H, dq, J = 6.3 and 1.5 Hz, H_6), 3.80—3.68 (2H, m, $C\underline{H}_2OH$), 3.00 (1H, m, H_1), 1.91 (1H, q, J = 7.2 Hz, H_3), 1.81 (3H, d, J = 1.5 Hz, 5-CH_3), 1.85—1.52 (5H, m), 1.32—1.20 (1H, m, H-8), and 0.97 (3H, d, J = 7.2 Hz, 3-CH_3). Found: *m/z* 208.1465. Calcd for $C_{13}H_{20}O_2$: M, 208.1463.

***endo*-4-[3-(*t*-Butyldimethylsiloxy)propyl]-3,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (27c).** To a solution of **25b** (358 mg, 1.72 mmol) and imidazole (313 mg, 4.60 mmol) in DMF (5.0 cm^3) prepared under argon was added dropwise a solution of *t*-butyldimethylsilyl chloride (422 mg, 2.80 mmol) in DMF (5 cm^3) under argon. This reaction mixture was stirred for 2.5 h at room temperature, and then diluted with ether (50 cm^3) and water (50 cm^3). This mixture was extracted with three portions of ether. The combined extracts were washed successively with water, 5% aqueous HCl, water, an aqueous $NaHCO_3$ solution, and saturated brine, dried over $MgSO_4$, and concentrated to an oil (616 mg). Chromatography of this oil on silica gel (25 g, 9 : 1 hexane–ethyl acetate) gave a TBS ether **27c** (509 mg, 1.58 mmol, 92%): Colorless oil; IR (neat) 1720 cm^{-1} (C=O) ; ^1H NMR ($CDCl_3$) δ = 5.89 (1H, dq, J = 6.6 and 1.5 Hz, H_6), 3.68 (2H, m, CH_2O), 3.02—2.96 (1H, m, H_1), 1.90 (1H, q, J = 7.2 Hz, H_3), 1.80 (3H, d, J = 1.5 Hz, 5-CH_3), 1.83—1.68 (2H, m), 1.61—1.41 (5H, m), 1.30—1.20 (1H, m, H_8), 0.96 (3H, d, J = 7.2 Hz, 3-CH_3), 0.91 (9H, s, *t*-BuSi), and 0.07 (6H, s, $Si(CH_3)_2$). Found: *m/z* 332.2339. Calcd for $C_{19}H_{34}O_2Si$: M, 332.2328.

5- [3- (*t*- Butyldimethylsiloxy)propyl]1, 4- dimethyltricyclo-[3.3.3.$0^{2,8}$]octan-3-one (28). A solution of a ketone **27c** (495 mg, 1.49 mmol) in acetone (150 cm^3) was placed in an immersion well equipped with a Pyrex filter and irradiated for 1.5 h with a 100-W Ushio Hg lamp under argon. The solution was concentrated under a vacuum. Chromatography of the remaining oil (540 mg) on silica gel (25 g, 9 : 1 hexane–ethyl acetate) gave a tricyclic ketone **28** (0.409 mg, 1.27 mmol, 83%) as a colorless oil: IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ = 3.67—3.58 (2H, m, CH_2O), 2.02 (1H, ddd, J = 13.7, 10.4, and 6.0 Hz, H_7), 1.93—1.87 (2H, m, H_4 and H_6), 1.84—1.77 (3H, m, H_2, H_8, and C_5-C$\underline{H}$H), 1.64 (1H, dd, J = 12.1 and 7.0, H_6), 1.54 (1H, dddd, J = 13.7, 10.9, 7.0 and 1.0 Hz, H_7), 1.51—1.44 (2H, m, C_5–CH$\underline{H}$C$\underline{H}$H), 1.42—1.37 (1H, m, C_5–CH_2CH$\underline{H}$), 1.31 (3H, s, 1-CH_3), 1.10 (3H, d, J = 7.5 Hz, 4-CH_3), 0.90 (9H, s, *t*-Bu–Si), and 0.06(6H, s, $OSi(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ = 218.5 (C-3), 63.5 (CH_2O), 55.4 (C-4), 55.1 (C-2), 52.1 (C-1 or C-5), 45.3 (C-6), 44.3 (C-5 or C-1), 43.2 (C-2 or C-8), 38.5 (C-8 or C-2), 29.7 (C_5–$CH_2\underline{C}H_2$), 29.5 (C_5–$\underline{C}H_2$), 25.6 ($C(\underline{C}H_3)_3$), 24.6 (C-7), 18.3 ($Si\underline{C}(CH_3)_3$), 16.6 (1-CH_3), 15.4 (4-CH_3), and −0.53 ($Si(\underline{C}H_3)_2$). Found: *m/z* 332.2339. Calcd for $C_{19}H_{34}O_2Si$: M, 332.2328.

5- [3- (*t*- Butyldimethylsiloxy)propyl]1, 4- dimethylbicyclo-[3.3.0]octan-3-one (29a). To liquid ammonia (50 cm^3) was added with mechanically stirring a solution of a tricyclic ketone **28** (400 mg, 1.24 mmol), 2-methyl-2-propanol (2.50 cm^3) in ether (8.0 cm^3) at −78 °C under argon. Lithium (44.0 mg, 6.34 mmol) was added to the mixture. The resulting blue solution was stirred for 5 h and then treated with methanol (3.5 cm^3). Ammonia was evaporated, and the remaining solid was dissolved by treatment with water (20.0 cm^3). The mixture was extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (417 mg). Chromatography of this oil on silica gel (12.5 g, 10 : 1 hexane–ethyl acetate) gave a mixture of ketones **29a** (299 mg, 0.92 mmol, 75%). IR (neat) 1740 cm^{-1} (C=O). Found: *m/z* 324.2489. Calcd for $C_{19}H_{36}O_2Si$: M, 324.2484. The major isomer: ^1H NMR ($CDCl_3$) δ = 3.61 (2H, t, J = 5.7 Hz, CH_2O), 2.33—2.10 (2H, m), 1.77—1.39 (11H, m), 1.10 (3H, s, 1-CH_3), 1.04 (3H, d, J = 6.9 Hz, 4-CH_3), 0.90 (9H, s, *t*-BuSi), and 0.06 (6H, s, $Si(CH_3)_2$).

4- Hydroxy- 5, 8- dimethyltricyclo[6.3.0.$0^{1,5}$]undecan- 6- one (31a). To a stirred solution of **29a** (131 mg, 0.404 mmol) in THF (1.0 cm^3) was added dropwise a solution of tetrabutylammonium fluoride (1.0 M, 0.48 cm^3). The mixture was stirred for 1 h, treated carefully with a saturated aqueous NaCl solution, and extracted with three portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated to an oil (138 mg). Chromatography of the oil on silica gel (12.5 g, 2 : 3 hexane–ethyl acetate) gave (**29b**) (X=OH, 84.1 mg, 0.400 mmol, 99%): Colorless oil; IR (neat) 3430 (OH) and 1740 cm^{-1} (C=O). Found: *m/z* 208.1475. Calcd for $C_{13}H_{20}O_2$: M, 208.1463. The major isomer: ^1H NMR ($CDCl_3$) δ = 3.66 (2H, t, J = 6.3 Hz, $C\underline{H}_2OH$), 2.27—2.12 (1H, m), 1.78—1.30 (12H, m), 1.11 (3H, s, 1-CH_3), and 0.92 (3H, d, J = 6.9 Hz, 4-CH_3).

To a solution of pyridine (0.825 cm^3) in CH_2Cl_2 (10 cm^3) was added portionwise chromium trioxide (510 mg, 5.10 mmol) at 0 °C. After 15 min stirring, to the mixture was added a solution of **29b** (107 mg, 0.510 mmol) in CH_2Cl_2 (3 cm^3). The mixture was stirred for 1 h at room temperature and then treated with ether and 5% aqueous NaOH solution. The mixture was extracted with three portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated to an oil **30** (99.4 mg). This oil was treated with KOH (112 mg, 2.00 mmol) in methanol (2 cm^3) at room temperature for 30 min. The mixture was diluted with a saturated aqueous NH_4Cl solution and extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (109 mg). Chromatography of the oil on silica gel (3 g, 2 : 1 hexane–ethyl acetate) gave **31a** (X = OH, 87.7 mg, 0.421 mmol 83%): Colorless needles; mp 159.4—162.8 °C; IR (neat) 3450 (OH) and 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ = 3.83—3.77 (2H, m), 2.72 (1H, broad, OH), 2.56—1.36 (12H, m), 1.31 (3H, s), and 1.12 (3H, s). Found: *m/z* 208.1475. Calcd for $C_{13}H_{20}O_2$: M, 208.1463.

5,6,8-Trimethyltricyclo[6.3.0.$0^{1,5}$]undec-6-en-4-one (32). To a solution of **31a** (52.0 mg, 0.250 mmol) and imidazole (49.0 mg, 0.720 mmol) in DMF (1.0 cm^3) prepared under argon was added dropwise a solution of *t*-butyldimethylsilyl chloride (101 mg, 0.670 mmol) in DMF (1.0 cm^3) under argon. This reaction mixture was stirred for 4 h at 50 °C, and diluted with ether (10 cm^3) and water (30 cm^3). This mixture was extracted with three portions of ether. The combined extracts were washed successively with water, 5%

aqueous HCl, water, an aqueous $NaHCO_3$ solution, and saturated brine, dried over $MgSO_4$, and concentrated to an oil (113 mg). Chromatography of this oil on silica gel (3.0 g, 15 : 1 hexane–ethyl acetate) gave a TBS ether **31b** (76.3 mg, 0.235 mmol, 94%): Colorless oil; IR (neat) 1735 cm^{-1} (C=O). Found: *m/z* 322.2351. Calcd for $C_{19}H_{34}O_2Si$: M, 322. 2328.

To a solution of LDA prepared from diisopropylamine (0.130 cm^3, 0.900 mmol) and butyllithium (1.6 M in hexane, 0.530 cm^3, 0.840 mmol) in THF (1.0 cm^3) was added dropwise a solution of the ketone **31b** (194 mg, 0.600 mmol) in THF (2.0 cm^3) at −78 °C with stirring. The mixture was stirred for 30 min at −78 °C. To this solution were added a solution of 1,1,1-trifluoro-*N*-phenyl-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide (260 mg, 0.720 mmol) in THF (2.0 cm^3). The mixture was allowed to warm to 0 °C, stirred for 5 h, allowed to warm to room temperature, and then stirred for 16 h. After confirming of the disappearance of **31b** by TLC, the solvents were removed under a vacuum. The remaining oil (0.649 g) was chromatographed on silica gel (22.5 g, 15 : 1 hexane–ethyl acetate) to give a mixture of the enol trifluoromethanesulfonate (0.238 g, 0.524 mmol, 87%). Found: *m/z* 320.2546. Calcd for $C_{20}H_{36}OSi$: M, 320.2538.

A solution of lithium dimethylcuprate(I) was prepared from copper(I) iodide (4.29 g, 22.5 mmol), methyllithium (1.04 M in ether, 43.3 cm^3), and ether (30.0 cm^3) at −20 °C, and then the resulting solution was allowed to warm to 0 °C. To this solution was added a solution of the enol triflate (1.98 g, 4.37 mmol) in ether (10 cm^3). This mixture was stirred for 2 h at 0 °C and then for 3.5 h at room temperature. After confirming of the disappearance of the triflate by TLC, a saturated aqueous NH_4Cl solution was added to the reaction mixture. This mixture was extracted with three portions of ether. The combined ether layers were washed with saturated brine, dried over $MgSO_4$, and concentrated to an oil (1.55 g). Chromatography of this oil on silica gel (45 g, hexane) gave a mixture of TBS ethers (917 mg, 2.86 mmol, 65%).

To a stirred solution of the TBS ether (86.2 mg, 0.269 mmol) in THF (1.0 cm^3) was added dropwise a solution of tetrabutylammonium fluoride (1.0 M, 1.08 cm^3). The mixture was stirred for 51 h, treated carefully with a saturated aqueous NaCl solution, and extracted with three portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated to an oil (88.1 mg). Chromatography of the oil on silica gel (5 g, 4 : 1 hexane–ethyl acetate) gave a mixture of alcohols (54.2 mg, 0.263 mmol, 98%; colorless needles; mp 87.5—90.7 °C).

A mixture of PCC (647 mg, 3.00 mmol) and CH_2Cl_2 (15.0 cm^3) was stirred for 10 min at room temperature. To this mixture was added a solution of a mixture of the alcohols (421 mg, 2.00 mmol) in CH_2Cl_2 (5.0 cm^3) and stirred for 3.5 h at room temperature. After confirming of the disappearance of the alcohols by TLC, ether was added to the reaction mixture. The ethereal solution was decanted and the precipitate was washed with ether. The combined ethereal solutions were filtered through Cerite® and concentrated. Chromatography of a remaining oil (435 mg) on silica gel (10 g, 10 : 1 hexane–ethyl acetate) gave a ketone **32** (317 mg, 1.55 mmol, 76%): Mp 84.2—85 °C; IR (KBr) 1730 cm^{-1} (C=O); ^1HNMR ($CDCl_3$) δ = 5.07 (1H, q, J = 1.2 Hz, H_7), 2.43 (1H, ddd, J = 18.0, 14.1, and 9.0 Hz, H_3), 2.11 (1H, ddd, J = 18.0, and 8.1, and 0.9 Hz, H_3), 2.06 (1H, ddd, J = 13.5, 9.0, and 0.90 Hz, H_2), 1.87 (1H, ddd, J = 9.9, 5.4, and 1.8 Hz), 1.60 (3H, d, J = 1.2 Hz, 6-CH_3), 1.70—1.20 (6H, m), 1.15 (3H, s, 5-CH_3), and 1.05 (3H, s, 8-CH_3; ^{13}CNMR ($CDCl_3$) δ = 220.3 (C-4), 138.4 (C-6), 131.6 (C-7), 65.2 (C-5), 59.7 (C-1), 56.4 (C-8), 42.0, 38.4, 36.9 (C-3), 28.5 (C-2), 23.8, 22.3 (8-CH_3), 15.4 (5-CH_3), and 12.6 (6-CH_3). Found: *m/z* 204.1530. Calcd for $C_{14}H_{20}O$: M, 204.1514.

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