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Rearrangement Approaches to Cyclic Skeletons. I. Photochemical Rearrangement Approaches to (±)-Sesquicarene and (±)-Sirenin, [3—6] Fused-Ring Sesquiterpenes†

Tadao UYEHARA,* Jun-ichi YAMADA, Koichi OGATA, and Tadahiro KATO
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki-Aoba, Sendai 980
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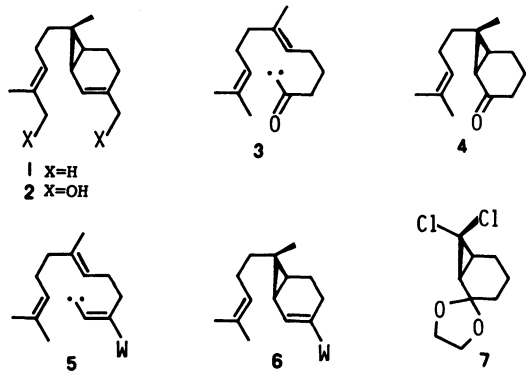
The 4-alkyl, 4-alkenyl, and 4-aryl derivatives of bicyclo[3.2.2]nona-3,6-dien-2-one (**9**) were prepared from **9** itself by ultrasound-promoted Barbier reaction followed by PCC oxidation. Photochemical transformation of the 4-(4-methyl-3-pentenyl) derivative of **9**, namely **13**, in THF–water gave *endo*-7-[*exo*-7-(4-methyl-3-pentenyl)bicyclo[4.1.0]hept-2-ene]acetic acid (**14**). Acid **14** was converted into *endo*-7-methyl-*exo*-7-(4-methyl-3-pentenyl)bicylo[4.1.0]heptan-2-one (**4**), a key intermediate of (±)-sesquicarene and (±)sirenin total syntheses. Furthermore, a highly stereospecific total synthesis of (±)-sesquicarene was acomplished by the photochemical transformation of the 1-methyl derivative of **13** prepared from 2-methyltropone (**21**).

Sesquiterpene analogues of 2-carene, such as sesquicarene (**1**)[3] and sirenin (**2**),[2] have attracted a good deal of synthetic attention.[3,4] The prominent step of the synthesis of **1** and/or **2** is the stereospecific elabolation of a 7,7-disubstituted bicyclo[4.1.0]heptane skeleton. Well established methods to prepare the bicyclo[4.1.0]-heptane system are based on intramolecular carbene additions, such as from the carbenes (**3**[3a,c—e,g—k] and **5**,W=CH_3,[3b,f,k] CO_2CH_3,[3l] and CN[3o]) to the cyclo-



propanes (**4** and **6**), respectively. Another practical one is stereoselective displacement of the *exo*-chlorine of the acetal (**7**) by the cuprate derived from 5-bromo-2-methyl-2-propene followed by stereospecific transmetallation and then methylation to give the ethylene acetal of **4**.[3n]

Our interest in rearrangement approaches to terpene skeletons has prompted us to develop a new route to these [3—6] fused-ring compounds. In this paper, we wish to report the approaches to racemic sesquicarene (**1**) and sirenin (**2**) based on the photochemical transformation of the bridged compounds into the 2-carene derivatives (*vide infra*).

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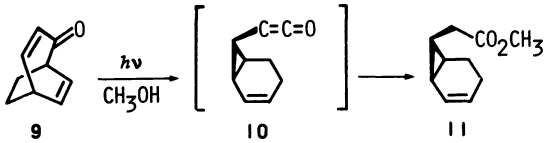
Results and Discussion

Bicyclo[3.2.2]nona-3,6-dien-2-one (**9**), derived from tropone (**8**) and ethylene as the 1,4-addition product,[5] is a photo-labile compound which was transformed into the methyl ester (**11**) by irradiation in methanol using a Hg-lamp through a Pyrex filter[6] (Scheme 1). This transformation is general not only for the bicyclo[3.2.2]nonadienones but also other bicyclo[3.2.x]dienones.[7,8] The process presumably involves the initial [3,3] sigmatropic rearrangement of **9** to the ketene intermediate (**10**) followed by addition of methanol.

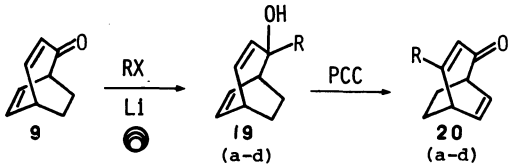


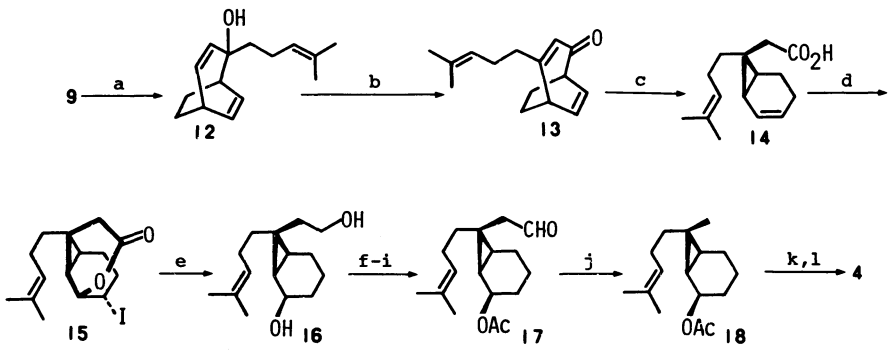
Scheme 1.

Since the conversion proceeds stereospecifically, we made a plan to prepare **4**, an established synthetic intermediate for both sesquicarene (**1**) and sirenin (**2**), starting from **8** and adopting the photochemical process. The synthetic route to **4** is outlined in Scheme 2.

Barbier reaction promoted by ultrasound irradiation[9] was taken to prepare the 1,2-addition product (**12**) selectively. Oxidation of the tertiary allylic alcohol (**12**) by pyridinium chlorochromate (PCC)[10] gave the α,β-unsaturated ketone (**13**) in a good yield.

Now, this two-step transformation is a general method for preparation of the C_4-substituted derivatives of **9** (**20**) from **9** itself *via* the allylic alcohol (**19**) as shown in Table 1. Run c shows that the oxidative transformation proceeded preferably on the C_3 bridge rather than on the side chain.





Scheme 2. Synthesis of *endo*-7-methyl-*exo*-7-(4-methyl-3-pentenyl)bicyclo[4.1.0]heptan-2-one (**4**)[a]. a) (a) $(CH_3)_2C{=}CHCH_2CH_2Br$, Li, THF, Ultrasounds, 45 min, 89%. (b) PCC, CH_2Cl_2, 87%. (c) *hv*, H_2O, THF, 88%. (d) I_2, $NaHCO_3$, H_2O–ether. (e) $LiAlH_4$, THF, reflux, 85% (from **14**). (f) TBDMS–Cl, DMAP, $N(CH_2CH_3)_3$, 76%. (g) Ac_2O, Py, 88%. (h) AcOH, THF, H_2O, 85%. (i) CrO_3–2Py, CH_2Cl_2, 83%. (j) $[Rh(PPh_3)_3]Cl$, PhCN, 145 °C, 5 min, 80%. (k) $LiAlH_4$, ether. (l) CrO_3–2Py, CH_2Cl_2, 84% (from **18**).

TABLE 1. ULTRASOUND-PROMOTED BARBIER REACTION FOLLOWED BY PCC OXIDATION OF BICYCLO[3.2.2]-NONA-3,6-DIEN-2-ONE (**9**), AN EFFICIENT TRANSFORMATION INTO THE C_4-SUBSTITUTED DERIVATIVES (**20a—d**)

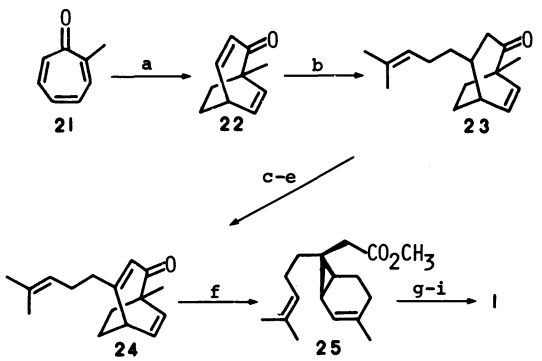
Run	Halide (RX)	Solvent	Sonication (min)	**19** (Yield/%)	**20** (Yield/%)
a	CH_3I	Ether	30	—	78[a]
b	$(CH_3)_2CHBr$	THF	30	90	88
c	$CH_2{=}CCH_3Br$	THF	25	—	59[a]
d	PhBr	THF	40	—[b]	33[a]

a) Overall yield from **9**. b) A crude mixture, obtained quantitatively, gave a satisfactory ^{1}H-NMR spectrum.

The photochemical transformation of **13** to the acid (**14**), the prominent step of the synthesis, was carried out in aqueous THF using a 100 W-high pressure mercury lamp through a Pyrex filter.

When **14** was treated with iodine in the presence of sodium hydrogencarbonate, the unstable iodo lactone (**15**) was obtained as the sole product. Formation of **15** means not only that the expected stereochemistry of the 7-position is proven but also that the new carbon–oxygen bond is formed at the desired position. However, we could not reduce the C–I bond of **15** to the C–H bond without change of the other functional group. When **15** was treated with tributyltin hydride in cyclohexane, the desired lactone was isolated only in 34% yield. Reduction of **15** with lithium aluminium hydride is thus far a useful way to remove the iodine and to obtain the diol (**16**).

In order to remove one carbon from the *syn* side chain, we wanted to adopt decarbonylation by chlorotris(triphenylphosphine)rhodium.[11] Thus, **16** was converted into the acetoxy aldehyde (**17**). We examined several routes to the aldehyde, and found that the secondary hydroxyl group of **16** is oxidized easily and that the primary one is not oxidized selectively before protection of the other.



Scheme 3. Synthesis of (±)-sesquicarene (**1**)[a]. a) (a) Ref. 13. (b) $(CH_3)_2C{=}CHCH_2CH_2MgBr$, CuI, THF, 66%. (c) LDA, THF, then TMS–Cl. (d) NBS, THF. (e) LiBr, Li_2CO_3, DMF, 81% (from **23**). (f) *hv*, MeOH, 66%. (g) $LiAlH_4$, ether. (h) CrO_3–2Py, CH_2Cl_2, 80%, (from **25**). (i) $[Rh(PPh_3)_3]Cl$, CH_3CN, 145 °C, 5 min, 43%.

With just one equivalent of Wilkinson's complex, heating of a benzonitrile solution of **17** at 145 °C for 5 min is the most suitable conditions for the decarbonylation to give the acetate (**18**). The yield of **18** decreased when heating time was extended, because of instability of **18** under the reaction conditions.

Reduction of **18** with lithium aluminium hydride followed by oxidation with Collins reagent gave the desired ketone (**4**). Thus, a new sythetic route from tropone (**8**) to (±)-sesquicarene (**1**) and that of (±)-sirenin (**2**) have been established formally.

Next, an analogous sequence has been used to prepare (±)-sesquicarene (**1**) itself (outlined in Scheme 3).

1-Methylbicyclo[3.2.2]nona-3,6-dien-2-one (**22**) is one of the 1,4-addition products of 2-methyltropone (**21**) and ethylene.[12] Regioselective addition of 4-methyl-3-pentenylmagnesium bromide to **21** was carried out in the presence of copper(I) iodide in tetrahydrofuran. The major product of the reaction

was the enone (**23**). The stereochemistry of the homoprenyl side chain is uncertain.

In order to convert **23** into the dienone (**24**), the enol trimethylsilyl ether of **23** was treated with *N*-bromosuccinimide,[13] and the resulting mixture of α-bromo ketones was dehydrobrominated by heating with lithium bromide and lithium carbonate in *N,N*-dimethylformamide.

Photochemical transformation of **24** into the 2-carene derivative (**25**) was carried out by irradiation of a methanolic solution of **24**.

The ester (**25**) was changed into the aldehyde (**26**) by lithium aluminium hydride reduction followed by Collins oxidation. The hydrocarbon (**1**) derived from **26** by heating vigorously with Wilkinson's complex in acetonitrile was identical spectroscopically with natural sesquicarene.

Thus, the photochemical transformation of bicyclo[3.2.2]nona-3,6-dien-2-ones to the [3—6] fused-ring compounds is applicable to the synthesis of sesquiterpene analogues of 2-carene.

Experimental

General. Melting and boiling points are uncorrected. IR spectra (in CCl_4, unless otherwise mentioned) were recorded on a Hitachi Model 215 spectrometer. NMR spectra (in CCl_4, unless otherwise noted) were obtained on Jeol JNM-PMX60, Varian EM-390 90 MHz, and Varian XL-200 NMR spectrometers, using tetramethylsilane as an internal standared. The mass spectral studies were conducted using a Hitachi M-52 spectrometer.

Photochemical reactions were carried out in an immersion well through a Pyrex filter using a Riko 100 W high pressure mercury lamp, under an inert atmosphere. A Shimmyodai 150 W ultrasonic cleaner was used for the Barbier reactions. Tetrahydrofuran (THF) and ether were distilled from benzophenone ketyl under argon, immediately prior to use. Dichloromethane was distilled from P_2O_5 and stored on 4A molecular sieves. Pyridine (from BaO), triethylamine, *N,N*-dimethylformamide (DMF, from BaO), and acetonitrile (from P_2O_5) were purified by distillation. Diisopropylamine was distilled from CaH_2 under argon immidiately prior to use. 4-Methyl-3-pentenyl bromide,[14] pyridinium chlorochromate (PCC),[15] Collins reagent,[16] and Wilkinson's complex[17] were prepared by using literature procedures.

All reactions were monitored by analytical TLC using E. Merck precoated silica gel $60F_{254}$ plates. E. Merck silica gel 60 (70—230 mesh ASTM, twenty to fifty times (w/w)) was used for column chromatography.

Ultrasound-Promoted Barbier Reactions of Bicyclo[3.2.2]nona-3,6-dien-2-one (9). Preparation of 2-(4-Methyl-3-pentenyl)-bicyclo[3.2.2]nona-3,6-dien-2-ol (12). In a 200 ml round bottomed flask with a septum inlet, equipped with a three way stopcock, were placed 1.341 g (9.99 mmol) of **9** and 2.477 g (15.0 mmol) of homoprenyl bromide, and then the system was flushed with argon. After addition of 50 ml of dry THF and 0.41 g (59 mmol) of lithium, the flask was partly submerged in the ice-water filled bath of an ultrasonic cleaner and sonicated for 45 min. The excess lithium and organolithium compounds were destroyed by stirring with methanol and then with water. The bulk of THF was removed and then the remaining pot residue was extracted with three portions of ether. The combined extracts were washed with water and with saturated aqueous NaCl, and then dried over $MgSO_4$. Romoval of the solvent afforded 2.22 g of a pale yellow oil, and which was purified by column chromatography (15:1 hexane, ethyl acetate) to give 1.951 g (89%) of **12** as a colorless oil. **12**: IR 3620 (w), 3475 (m), 1640 (w) and 710 cm^{-1}; NMR δ=6.33 (1H, dd, *J*=8.3 and 7.5 Hz), 5.95 (1H, dd, *J*=8.3 and 7.5 Hz), 5.70 (1H, dd, *J*=10.5 and 7.8 Hz), 5.08 (1H, dd, *J*=10.5 and 2.4 Hz), 5.00 (1H, tm, *J*=6.9 Hz), 1.65 (3H, bs), and 1.61 (3H, bs).

2-Methylbicyclo[3.2.2]nona-3,6-dien-2-ol (19a). To a mixture 2.449 g (18.25 mmol) of **9**, 405 mg (58 mmol) of lithium and 73 ml of dry ether, prepared under argon, was added 3.88 g (27.3 mmol) of methyl iodide at 0 °C. After 30 min of sonication, the reaction mixture was allowed to stand at 0 °C for 15 min. The excess lithium and methyllithium were decomposed by methanol, and the ethereal solution was washed with water and then with saturated brine. After dried over $MgSO_4$, evaporation of the solvent left **19a** as a colorless oil, which was supplied without further purification to PCC oxidation. Distillation of a small portion (45—48 °C/0.2 Torr (1 Torr=133.322 Pa)) furnished an analytical sample. The major of **19a**: NMR δ=6.33 (1H, bt, *J*=7.5 Hz), 5.95 (1H, bt, *J*=7.5 Hz), 5.68 (1H, dd, *J*=10.8 and 8.0 Hz), 5.02 (1H, dd, *J*=10.8 and 2.4 Hz), and 1.18 (3H, s).

2-Isopropylbicyclo[3.2.2]nona-3,6-dien-2-one (19b). (As General Procedure.) A mixture of 490 mg (3.65 mmol) of **9**, 90 mg (3.9 eq) of lithium, 680 mg (0.52 ml, 1.5 eq) of isopropyl bromide, and 18 ml (5 ml/1 mmol of **9**) of THF was sonicated for 30 min at 0 °C. After stirring with methanol and then water, the solution was extracted with three portions of ether. The combined extracts were washed with water and saturated brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the remaining oil (636 mg) was chromatographed on silica gel (10:1 hexane, ethyl acetate) to yield 583 mg (90%) of **19b**. The major of **19b**: NMR δ=6.32 (1H, bt, *J*=7.5 Hz), 5.89 (1H, bt, *J*=7.5 Hz), 5.70 (1H, dd, *J*=10.8 and 8.0 Hz), 5.17 (1H, dd, *J*=10.8 and 2.4 Hz), 0.92 (3H, d, *J*=6.9 Hz), and 0.9 (3H, d, *J*=6.9 Hz).

PCC Oxidation of Bicyclo[3.2.2]nona-3,6-dien-2-ols (12 and 19). 4-(4-Methyl-3-pentenyl)bicyclo[3.2.2]nona-3,6-dien-2-one (13). (As General Procedure.) To a solution of 3.214 g (14.91 mmol) of PCC in 22 ml of CH_2Cl_2 was added a solution of 1.627 g (7.45 mmol) of **12** in 75 ml of CH_2Cl_2 at room temperature, and the mixture was stirred for 2.5 h. After addition of 30 ml of ether, the solution was decanted from the black solids. The residue was washed in turn with several portions of ether. The combined etherial extracts were washed succesively with 5% aqueous NaOH, 1 M HCl (1 M=1 mol dm^{-3}), saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed (15:1 hexane, ethyl acetate) to give 1.407 g (87%) of **13** as a pale yellow oil. **13**: IR 1665 (s) and 1635 (m) cm^{-1}; NMR δ=6.38 (1H, ddd, *J*=8.1, 7.4, and 1.4 Hz), 6.05 (1H, ddd, *J*=8.1, 7.4, and 1.4 Hz), 5.40 (1H,

bs), 5.05 (1H, bm), 3.37 (1H, dm, J=7.4 Hz), 3.08 (1H, dm, J=7.4 Hz), 1.68 (3H, s), and 1.62 (3H, s); MS, m/z (rel intensity), 216 (M^+, 14), 188 (80), 142 (52), and 69 (100). The 2,4-DNP derivative of **13**: C, 63.73; H, 6.10; N, 14.05%. Calcd for $C_{21}H_{24}N_4O_4$: C, 63.62; H, 6.10; N, 14.13%.

*4-Methylbicyclo[3.2.2]nona-3,6-dien-2-one (**20a**)*: Bp 82—84 °C/0.9 Torr; IR 1665 (s) and 1635 (m) cm^{-1}; NMR δ=6.37 (1H, ddd, J=8.4, 7.2, and 1.5 Hz), 6.02 (1H, ddd, J=9.0, 7.2, and 1.5 Hz), 5.42 (1H, m), 3.33 (1H, b, $W_{1/2}$=14.3 Hz), 3.07 (1H, b, $W_{1/2}$=14.3 Hz), and 2.01 (3H, d, J=1.5 Hz); MS, m/z (rel intensity) 148 (M^+, 100) and 133 (86). Found: C, 80.78; H, 8.34%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

*4-Isopropylbicyclo[3.2.2]nona-3,6-dien-2-one (**20b**)*: Bp 57—59 °C/0.3 Torr; IR 1660 (s), and 1630 (m) cm^{-1}; NMR δ=6.32 (1H, ddd, J=8.7, 7.1, and 1.4 Hz), 6.04 (1H, ddd, J=8.7, 7.1, and 1.4 Hz), 5.36 (1H, m), 3.33 (1H, dm, J=7.1 Hz), 3.16 (1H, dm, J=7.1 Hz), 2.42 (1H, septet, J=6.7 Hz), and 1.12 (6H, d, J=6.7 Hz); MS m/z (rel intensity) 176 (M^+, 51) and 133 (100). Found: C, 82.05; H, 9.32%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. The 2,4-DNP derivative of **20b**: mp 146.7—148.9 °C. Found: C, 60.73; H, 5.77; N, 15.77%. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.72%.

*4-(2-Methyl-2-propenyl)bicyclo[3.2.2]nona-3,6-dien-2-one (**20c**)*: Bp 58—60 °C/0.1 Torr; IR 1660 (s) and 1635 (m) cm^{-1}; NMR δ=6.38 (1H, ddd, J=8.9, 7.1, and 1.2 Hz), 6.10 (1H, ddd, J=8.9, 7.4, and 1.2 Hz), 5.63 (1H, m), 5.37 (1H, bs), 5.16 (1H, bs), 3.63 (1H, dm, J=7.4 Hz), 3.38 (1H, dm, J=7.4 Hz), and 2.1—1.7 (7H, m); MS, m/z (rel intensity) 174 (M^+, 100) and 130 (46). The 2,4-DNP derivative of **20c**: mp 159.2—160.8 °C. Found: C, 61.21; H, 5.33; N, 15.81%. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12; N, 15.81%.

*4-Phenylbicyclo[3.2.2]nona-3,6-dien-2-one (**20d**)*: Mp 73.8—74.6 °C; IR 1660 (s) and 1630 (m) cm^{-1}; NMR δ=7.5—7.1 (5H, m), 6.50 (1H, ddd, J=8.9, 7.1, and 1.2 Hz), 5.81 (1H, dd, J=2.3 and 1.5 Hz), 3.73 (1H, dm, J=7.1 Hz), 3.46 (1H, dm, J=7.1 Hz), and 2.4—1.7 (4H, m); MS, m/z (rel intenaity), 210 (M^+, 100), 192 (51), 167 (61), and 105 (62). Found: C, 85.67; H, 6.71%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

*Photochemical Transformation of **13** into* endo-*7-[*exo-*7-(4-Methyl-3-pentenyl)bicyclo[4.1.0]hept-2-ene]acetic Acid (**14**).* To a solution of 1.002 g (4.63 mmol) of **13** in 350 ml of THF was added 35 ml of water, and the mixture was irradiated for 4 h. After removal of the bulk of the solvents, to the residue was added 10% aqueous NaOH. The basic solution was extracted once with ether, and acidified with 6 M HCl. After addition of saturated aqueous NaCl, the aqueous phase was extracted with two portions of ether. The extracts were combined, and dried over $MgSO_4$. Removal of the solvent gave 998 mg of a yellow oil, which was purified by column chromatography (3:1 hexane, ethyl acetate) to yield 955 mg (88%) of **14**: IR 1705 (s) cm^{-1}; NMR δ=9.0 (1H, b), 5.87 (1H, dm, J=10.5 Hz), 5.66 (1H, dm, J=10.5 Hz), 5.07 (1H, tm, J=6.9 Hz), 2.42 (1H, d, J=16.5 Hz), 2.43 (1H, d, J=16.5 Hz), 1.67 (3H, bs), and 1.62 (3H, bs). The methyl ester of **14**: bp 70 °C/0.15 Torr. Found: C, 77.10; H, 9.62%. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74%.

*Iodolactonization of **14**. Preparation of 7-Iodo-2-(4-methyl-3-pentenyl)-5-oxabicyclo[4.4.0.0^{2,10}]decan-4-one (**15**).* To a solution of 681.6 mg (2.91 mmol) of **14** in 19 ml of saturated aqueous $NaHCO_3$ was added a solution of 740 mg (2.92 mmol) of iodine in 25 ml of ether over a period of 20 min at room temperature in the dark. After 1 h of stirring, the mixture was diluted with water and ether, and extracted with several portions of ether. The ethereal extracts were combined, washed with 5% aqueous $Na_2S_2O_3$ and with saturated brine, and then dried over $MgSO_4$. Evaporation of the solvent without heating from outside gave 1.156 g of a pale yellow oil, which was supplied directly to the $LiAlH_4$ reduction. Flush column chromatography of a small portion furnished an analytical sample of **15**: NMR δ=5.22 (H_8, dd, J=8.7 and 3.5 Hz), 5.00 (1H, tm, J=6.9 Hz), 4.35 (H_7, q, J=3.5 Hz), 2.60 (H_3, d, J=19.1 Hz), 2.28 (H_3, d, J=19.1 Hz), 1.67 (3H, bs) and 1.61 (3H, bs).

*Reduction of Iodo lactone **15**. Preparation of* endo-*7-(2-Hydroxyethyl)*-exo-*7-(4-methyl-3-pentenyl)bicyclo[4.1.0]heptan-2-ol (**16**).* To a mixture of 280 mg (7.38 mmol) of $LiAlH_4$ and 5 ml of dry THF was added a solution of 1.156 g of **15**, obtained from 681.6 mg (2.91 mmol) of **14**, in 30 ml of dry THF at 0 °C. The reaction mixture was heated under reflux for 2 h. After cooling to 0 °C, the resulting suspension was treated by successive dropwise addition of a few ml of ethyl acetate, 0.3 ml of water, 0.3 ml of 15% aqueous NaOH, and 0.9 ml of water, and then allowed to warm to room temperature with stirring. The THF solution was filtered, and concentration of the filtrate *in vacuo* afforded 622.6 mg of a colorless oil. Purification of the product by column chromatography (1:1 hexane, ethyl acetate) gave 587.9 mg (85% from **14**) of **16**: IR 3250 (m), 1070 (m), and 1040 (m) cm^{-1}; NMR δ=5.49 (2H, bs), 5.01 (1H, tm, J=6.9 Hz), 4.06 (1H, b, $W_{1/2}$=21 Hz), 3.75 (2H, m), 1.65 (3H, s), and 1.58 (3H, s); MS, m/z (rel intensity) 230 (M^+, 2), 139 (100), and 138 (85). The diacetate of **16**: C, 70.75; H, 9.46%. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38%.

*Transformation of Diol **16** into* endo-*7-(2-Oxoethyl)*-exo-*7-(4-methyl-3-pentenyl)bicyclo[4.1.0]heptan*-trans-*2-yl Acetate (**17**).* In order to protect the primary hydroxyl group selectively, to a solution of 304.7 mg (1.28 mmol) of **16**, 145.1 mg (0.2 ml, 1.1 eq) of triethylamine, and a small amount of 4-dimethylaminopyridine in 10 ml of dry CH_2Cl_2 was added a solution of 242.5 mg (1.2 eqive) of *t*-butyldimethylsilyl chloride in 10 ml of dry CH_2Cl_2 under argon. After standing for 24 h at room temperature, the sulution was washed with saturated aqueous NH_4Cl, and dried over $MgSO_4$. Removal of the solvent gave 456.7 mg of the oily products, which were purified by chromatography (15:1 hexane, ethyl acetate) to give 341.4 mg (76%) of the monosilyl ether of **16**: NMR δ=4.98 (1H, tm, J=6.9 Hz), 4.22 (1H, m), 3.70 (2H, m), 3.19 (1H, m), 1.63 (3H, bs), 1.57 (3H, bs), 0.93 (9H, s), and 0.10 (6H, s).

To protect the secondary hydroxyl group, 1 ml of acetic anhydride was added to 314.4 mg (0.97 mmol) of the monosilyl ether in 3 ml of dry pyridine. After standing overnight at room temperature, evaporation of the solvent *in vacuo* gave 375.3 mg of the residue, which was chromatographed (15:1 hexane, ethyl acetate) to afford 333.1 mg (88%) of the acetate: IR 1735 (s) and 1020 (m) cm^{-1}. Found: C, 69.96; H, 10.77%. Calcd for $C_{23}H_{42}O_3Si$: C, 70.00; H, 10.73%.

In order to remove the silyl group, 332.2 mg (0.84 mmol) of the acetate was treated with a mixture of 1.7 ml of THF, 1.7 ml of water, and 5.1 ml of acetic acid[18] for 19 h at room temperature. The mixture was diluted with ether, and washed successively with water (four times), saturated aqueous $NaHCO_3$, and saturated brine, and then dried over $MgSO_4$. The solvent was removed *in vacuo*, and the remaining was purified by chromatography (2:1 hexane, ethyl acetate). Thus obtained was 198.5 mg (85%) of the hydroxy

hydride (50 mg, 1.32 mmol) in ether (20 ml) at 0 °C. The acetate: IR 1735 (s) and 1015 (s) cm^{-1}, NMR δ=5.25 (1H, qm, J=7.5 Hz), 5.01 (1H, tm, J=6.9 Hz), 3.67 (2H, m), 2.01 (3H, s), 1.66 (3H, bs), and 1.61 (3H, bs).

To a solution of 1.54 g 5.96 mmol) of Collins reagent in 24 ml of dry CH_2Cl_2 was added a solution of 278.5 mg (0.99 mmol) of the hydroxy acetate in 7 ml of CH_2Cl_2. After 7 min stirring at room temperature, the solution was decanted, and the black residue was washed with several portions of ether. The organic layers were combined, and washed successively with 5% aqueous NaOH, 5% HCl, saturated aqueous $NaHCO_3$, and saturated brine, and then dried over $MgSO_4$. Evaporation of the solvent gave 265.6 mg of an oil, which was purified by column chromatography (10:1 hexane, ethyl acetate) to give 229.7 mg (83%) of the unstable aldehyde, **17**: IR 2720 (w), 1740 (s), 1730 (s), and 1245 (s) cm^{-1}; NMR δ=9.72 (1H, t, J=2.3 Hz), 5.25 (H_2, m, $W_{1/2}$=18.8 Hz), 4.97 (1H, tm, J=6.9 Hz), 2.47 (2H, d, J=2.3 Hz), 1.95 (3H, s), 1.64 (3H, bs), and 1.57 (3H, s); MS, m/z (rel intensity) 278 (M^+, 1), 137 (79), 136 (100), 121 (52), and 82 (74).

Decarbonylation of **17**. *Preparation of* endo-*7-Methyl*-exo-*7-(4-methyl-3-pentenyl)bicyclo[4.1.0]heptan-2-yl Acetate* (**18**). A flask containing of a mixture of 153.8 mg (0.55 mmol) of **17**, 509.7 mg (0.55 mmol) of Wilkinson's complex and 2 ml of benzonitrile, prepared under argon, was immersed in a preheated oil bath at 145 °C for 5 min with stirring. The bulk of benzonitrile was removed by Kugelrohr distillation (100 °C/3 Torr) and the residure was stirred with ethanol, and then filtered. Concentration of the filtrate gave 362.4 mg of an oil, chromatography (15:1 hexane, ethyl acetate) of which gave 110.5 mg (80%) of **18**: bp 70 °C/1.5 Torr; IR 1740 (s) and 1245 (s) cm^{-1}; NMR δ=5.21 (H_2, m), 5.02 (1H, tm, J=6.9 Hz), 1.99 (3H, s), 1.68 (3H, s), 1.61 (3H, s), and 1.14 (3H, s); MS, m/z (rel intensity) 250 (M^+, 2), 190 (52), 147 (78), 121 (100), and 82 (75). Found: C, 76.55; H, 10.49%. Calcd for $H_{16}H_{26}O_2$: C, 76.75; H, 10.47%.

Preparation of endo-*7-Methyl*-exo-*7-(4-methyl-3-pentenyl)bicyclo[4.1.0]heptan-2-one* (**4**). To a suspension of 20 mg (0.527 mmol) of $LiAlH_4$ in 2 ml of dry ether was added a solution of 79.3 mg (0.317 mmol) of **18** in 10 ml of ether at 0 °C. After 20 min stirring, to the reaction mixture were added successively one drop of water, one drop of 15% aqueous NaOH, and three drops of water. After stirring untill a granular precipitate was formed, $MgSO_4$ was added to the mixture and filtered. Concentration of the filtrate gave 66.4 mg of the alcohol. An analytical sample was purified by chromatography (10:1 hexane, ethyl acetate). Treatment of the crude alcohol (66.4 mg) with 500 mg of Collins reagent in 10 ml of dry CH_2Cl_2 at room temperature for 5 min, followed by work-up as described above gave 61.3 mg of the crude product. Chromatography on silica gel (15:1 hexane, ethyl acetate) gave 55.1 mg (84%) of pure **4**: IR 1685 (s) cm^{-1}; NMR δ=5.00 (1H, tm, 6.9 Hz), 1.66 (3H, bs), 1.60 (3H, bs), and 1.10 (3H, s). Found: C, 81.31; H, 10.84%. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75%.

1,4-Addition of 4-Methyl-3-pentenylmagnesium Bromide to 1-Methylbicyclo[3.2.2]nona-3,6-dien-2-one (**22**). 4-Methyl-3-pentenylmagnesium bromide was prepared from 1.07 g (6.55 mmol) of homoprenyl bromide and 140 mg (6 mmol) of magnesium in 17 ml of dry THF. The solution of the Grignard reagent was added to a mixture of 507.8 mg (3.28 mmol) of **22** and 140 mg (0.66 mmol) of copper(I) iodide in 2 ml of dry THF at −24 °C *via* a double ended needle. The mixture was allowed to warm to room temperature with stirring, and cooled to 0 °C, and then treated with 6 ml of 10% H_2SO_4. After filtration through a Celite layer, the filtrate was extracted with several portions of ether. The combined extracts were washed successively with water, saturated aqueous $NaHCO_3$, and saturated brine, and the dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue (861 mg) was purified by chromatography (15:1 hexane, ethyl acetate) to give 505.3 mg (66%) of 1-methyl-4-(4-methyl-3-pentenyl)-bicyclo[3.2.2]non-6-en-2-one (**23**) as a colorless oil. **23**: IR 1700 (s) cm^{-1}; NMR δ=6.11 (1H, dd, J=9.3 and 7.2 Hz), 5.80 (1H, d, J=9.3 Hz), 5.00 (1H, tm, J=6.9 Hz), 1.67 (3H, bs), 1.60 (3H, bs), and 1.11 (3H, s); MS, m/z (rel intensity) 232 (M^+, 100) and 161 (55). The 2,4-DNP derivative of **23**: mp 108—109 °C (dec). Found: C, 63.89; H, 6.91; N, 13.71%. Calcd for $C_{22}H_{28}N_4O_4$: C, 64.06; H, 6.84; N, 13.51%.

Preparation of 1-Methyl-4-(4-methyl-3-pentenyl)-bicyclo[3.2.2]nona-3,6-dien-2-one (**24**). To a solution of 252.7 mg (0.35 ml, 2.5 mmol) of diisopropylamine in 8 ml of dry THF, prepared under argon, was added 1.7 ml (2.55 mmol) of 1.5 M hexane solution of n-BuLi at −72 °C. After 20 min of stirring, to the LDA solution was added a solution of 505.3 mg (2.18 mmol) of **23** *via* a double ended needle. The solution was kept at −72 °C for 15 min, and then at 0 °C for 30 min. To the solution was added 513.6 mg (0.6 ml, 4.73 mmol) of chlorotrimethylsilane *via* a syringe at 0 °C. After stirring at room temperature for 30 min, the solvent and the volatile components of the mixture was removed by a rotary evaporator, and the residue was diluted with 8 ml of dry THF. *N*-Bromosuccinimide (390 mg, 2.2 mmol) was added to a solution at 0 °C, and the mixture was stirred for 1 h, and then diluted with ether. The ethereal solution was washed with a 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated brine, and with saturated brine.

After dried over $MgSO_4$, evaporation of the solvent gave 868.7 mg of a yellow oil, which was dissolved in 6 ml of dry DMF. To the solution were added 570 mg (6.6 mmol) of LiBr and 810 mg (11.0 mmol) of Li_2CO_3, and the mixture was heated at 100 °C for 4 h under an argon atmosphere. Dilution with water followed by extraction with three portions of ether and the usual work-up gave 668.9 mg of a brown oil. Purification by chromatography (15:1 hexane, ethyl acetate) gave 405.7 mg (81%) of **24**: IR 1660 (s) and 1630 (s) cm^{-1}; NMR δ=6.34 (1H, dd, J=9.3 and 7.5 Hz), 5.62 (1H, d, J=9.3 Hz), 5.42 (1H, bs), 5.03 (1H, bm), 3.07 (1H, bm), 1.69 (3H, bs), and 1.20 (3H, s); MS, m/z (rel intensity) 230 (M^+, 45), 202 (48), 147 (90), and 69 (100). The 2,4-DNP derivative of **24**: mp 117—118 °C. Found: C, 64.29; H, 6.48; N, 13.88%. Calcd for $C_{22}H_{26}N_6O_4$: C, 64.38; H, 6.38; N, 13.65%.

Photochemical Transformation of **24** *into the 2-Carene Derivative* **25**. After 3 h irradiation of a solution of 460.2 mg (2.0 mmol) of **24** in 300 ml of methanol, evaporation of the solvent gave 586.2 mg of an orange oil. Column chromatography of the crude oil (20:1 hexane, ethyl acetate) gave 346.7 mg (66%) of pure **25**: IR 1735 (s) cm^{-1}; NMR δ=5.49 (1H, bs), 5.01 (1H, J=6.9 Hz), 3.59 (3H, s), 2.26 (1H, d, J=15.9 Hz), 2.07 (1H, d, J=15.9 Hz), 1.65 (6H, bs), and 1.59 (3H, bs); MS, m/z (rel intensity) 262 (M^+, 53), 177 (100), 145 (73), and 119 (100). Found: C, 77.52; H, 10.23%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; 9.99%.

Conversion of **25** *into (±)-Sesquicarene* (**1**). Ester **25**

(193.3 mg, 0.74 mmol) was reduced by lithium aluminium usual work-up as described previously gave the corresponging alcohol (172.8 mg). Oxidation of the alcohol by Collins reagent (1.15 g, 4.45 mmol) in CH_2Cl_2 (23 ml) at room temperature for 10 min, followed by the usual work-up and purification by chromatography (10:1 hexane, ethyl acetate), gave the aldehyde (**26**) (136.7 mg, 80%). **26**: IR 2710 (m) and 1725 (s) cm^{-1}; NMR δ=9.58 (1H, t, J=2.3 Hz), 5.53 (1H, bs), 5.00 (1H, tm, J=6.9 Hz), 2.21 (1H, dd, J=16.5 and 2.3 Hz), 2.17 (1H, dd, J=16.5 and 2.3 Hz), 1.65 (6H, bs), and 1.59 (3H, bs); MS, m/z (rel intensity) 232 (M^+, 66), 147 (100), 119 (52), and 93 (45). The 2,4-DNP derivative of **26**: mp 140—142 °C. Found: C, 64.13; H, 6.95; N, 13.31%. Calcd for $C_{22}H_{28}N_4O_4$: C, 64.06; H, 6.84; N, 13.58%.

A flask containing a mixture of 74.5 mg (0.32 mmol) of the aldehyde, 296.3 mg (0.32 mmol) of Wilkinson's complex, and 2 ml of acetonitrile was immersed in a preheated (145 °C) oil bath for 5 min. After removal of the solvent by a rotary evaporator, to the residue was added pentane and the mixture was filtered. Concentration of the filtrate followed by chromatography (pentane) gave 28.2 mg (43%) of pure *(±)-sesquicarene* (**1**): IR (neat) 2980 (s), 2925 (s), 2860 (s), 2730 (w), 1670 (w), 1650 (w), 1450 (m), and 1380 (m) cm^{-1}; NMR ($CDCl_3$) δ=5.56 (1H, b, $W_{1/2}$=9.0 Hz), 5.12 (1H, triplets of septet, J=7.0 and 1.4 Hz), 2.14—1.48 (6H, m), 1.68 (6H, bs), 1.62 (3H, bs), 1.39—1.05 (2H, m), 1.01—0.76 (2H, m), and 0.83 (3H, s); MS, m/z (rel intensity) 204 (M^+, 100), 161 (45), 135 (42), 134 (55), 133 (40), 122 (28) and 105 (38). Found: m/z 204.1855. Calcd for $C_{15}H_{24}$: 204.3546.

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