Notes

Radical Annulation vs the 3-*Exo-Trig* Cyclization via Fine Tuning of the Substrate Structure[1]

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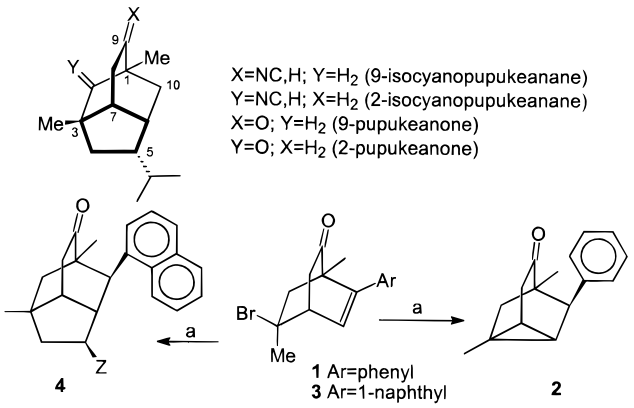
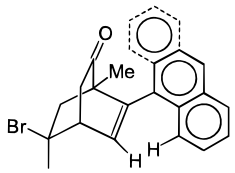
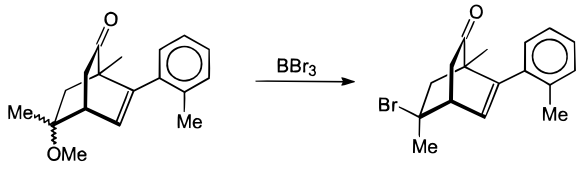
The marine sesquiterpenes 9- and 2-isocyanopupukeananes, containing the unique tricyclo[4.3.1.$0^{3,7}$]decane (isotwistane) carbon framework, were first isolated by Scheuer *et al.* from *Phyllidia varicosa* and also from its prey, a sponge *Hymeniacidon sp.* The structures of these metabolites, which protects the delicate shell-less, brightly colored opisthobranch mollusk from its predators, were established by a combination of degradative and single-crystal X-ray diffraction studies.[2] The presence of a novel isotwistane carbon framework and the thermodynamically unfavorable endo orientation of the isopropyl group made isocyanopupukeananes and the corresponding ketones 9- and 2-pupukeanones as challenging synthetic targets.[3] Earlier, we have developed a radical annulation-based methodology[4] for the construction of chiral isotwistane, in which the key concept was the intermolecular Michael addition of a bicyclo[2.2.2]oct-5-en-2-yl radical onto a radicophile followed by 5-*exo-trig* cyclization of the resulting radical to generate the tricyclo-[4.3.1.$0^{3,7}$]decane system. Interestingly, the phenyl derivative **1** resulted only in the formation of the cyclopropane compound **2** via a 3-*exo-trig* cyclization without incorporation of the radicophile, whereas the corresponding 1-naphthyl derivative **3** resulted in the formation of the isotwistane derivative **4** *via* radical annulation. The



difference in reactivity of the two substrates **1** and **3** can be visualized as follows: The phenyl substitution, due to the styrenic nature, made the olefin in **1** electrophilic enough to promote the 3-*exo-trig* radical cyclization. Whereas, in the compound **3**, due to the presence of steric



crowding between the *peri*-hydrogen of the naphthyl group with the olefinic proton on one side and with the bridgehead methyl group on the other side, the olefin and the naphthyl moieties lie orthogonal to each other, and hence the electrophilicity of the olefin in **3** will be much less than that of the phenyl derivative **1**. An analysis of these radical reactions revealed that only the *peri*-hydrogen present in the naphthyl group is responsible for the generation of the isotwistane from naphthyl derivative **3**. Hence, it could be reasoned that an *o*-methyl group on a phenyl ring in the place of the second ring of the naphthyl group is good enough to bring about the radical annulation reaction to generate the isotwistane. To substantiate our hypothesis, we have investigated the radical annulation reactions of the *o*-methylphenyl substituted derivative **5**, and herein we describe our results.



For the preparation of the radical precursor **5**, the methoxy enone **6**, readily available[5] from (*R*)-carvone in four steps, was chosen as the starting material. The reaction of an epimeric mixture of the methoxy enone **6** with boron tribromide in methylene chloride at low temperature furnished the bromoenone **5**, mp 68 °C, in 68% yield, as a single diastereomer whose structure was delineated from its spectral data. Reaction of the bromo enone **5** with 1.1 equiv of tri-*n*-butyltin hydride in the presence of an excess of methyl acrylate (20 equiv) and a catalytic amount of AIBN in refluxing benzene furnished, as anticipated, the annulation product **7**, mp 118 °C, in 39% yield in a regio- and stereospecific manner.[6] The structure of the annulated product **7** was established

(1) Chiral synthons from carvone, Part 27. For part 26, see: Srikrishna, A.; Reddy, T. J.; Kumar, P. P. *Synlett* **1997**, 663.

(2) (a) Burreson, B. J.; Scheuer, P. J.; Finer, J.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 4763. (b) Hagadone, M. R.; Burreson, B. J.; Scheuer, P. J.; Finer, J. S.;Clardy, J. *Helv. Chim. Acta* **1979**, *62*, 2484.

(3) For 9-isocyanopupukeanane and 9-pupukeanone, see: Corey, E. J.; Behforouz, M.; Ishiguro, M. *J. Am. Chem. Soc.* **1979**, *101*, 1608. Yamamoto, H.; Sham, H. L. *J. Am. Chem. Soc.* **1979**, *101*, 1609. White, J. D.; Schiesher, G. A. *J. Org. Chem.* **1980**, *45*, 1864. Piers, E.; Winter, M. *Justus Liebigs Ann. Chem.* **1982**, 973. Hsieh, S.-L.; Chiu, C.-T.; Chang, N.-C. *J. Org. Chem.* **1989**, *54*, 3820. For 2-isocyanopupukeanane and 2-pupukeanone, see: Corey, E. J.; Ishiguro, M. *Tetrahedron Lett.* **1979**, 2745. Frater, G.; Wenger, J. *Helv. Chim. Acta* **1984**, *67*, 1702. Chang, N.-C.; Chang, C.-K. *J. Org. Chem.* **1996**, *61*, 4967. Srikrishna, A.; Vijaykumar, D.; Sharma, G. V. R. *Tetrahedron Lett.* **1997**, *38*, 2003. Subba Rao, G. S. R.; Kaliappan,K. *Tetrahedron Lett.* **1997**, *38*, 2185.

(4) Srikrishna, A.; Hemamalini, P.; Sharma, G. V. R., *J. Org. Chem.* **1993**, *58*, 2509.

(5) Srikrishna, A.; Sharma, G. V. R.; Danieldoss, S.; Hemamalini,P. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1305.

(6) In addition, as earlier,[5] varying amounts of minor products derived from simple Michael addition of the initial radical were also formed, but no attempt was made to either purify or characterize them.

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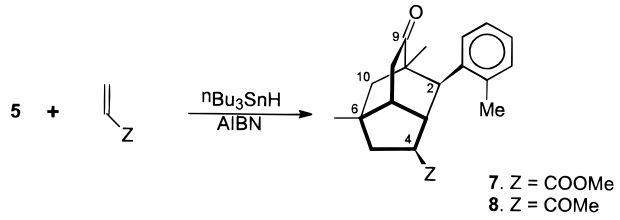
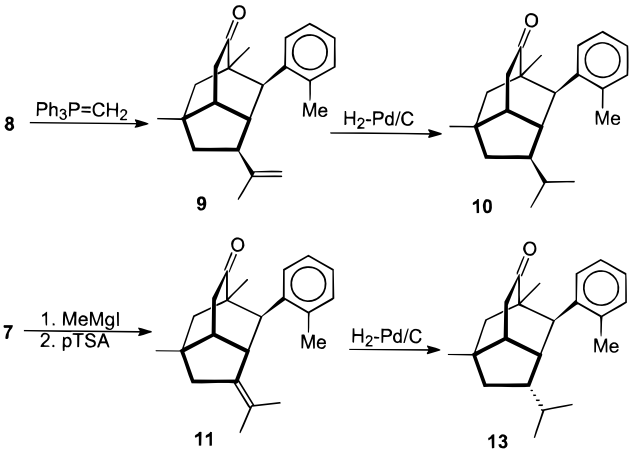
from its spectral data (see the Experimental Section). The exo,exo stereochemistry at the carbons C-4 and C-2 bearing the methoxycarbonyl and aryl groups was assigned on the basis of the weak coupling (2.6 and 0 Hz) of the C-2 and C-4 endo protons with the bridgehead proton at C-3.[7] The generation of the isotwistane **7** is totally in agreement with our reasoning that only an *o*-methyl group is enough (instead of the naphthyl group) to change the course of the reaction and to bring about the radical annulation reaction. To substantiate further, radical annulation reaction of the bromo enone **5** with methyl vinyl ketone as radicophile was also carried out. Thus, reaction of the bromo enone **5** with tri-*n*-butyltin hydride (1.1 equiv), excess of methyl vinyl ketone, and AIBN (catalytic) in refluxing benzene (0.01 M) furnished the diketone **8**, mp 125 °C, in 40% yield, whose structure was delineated from its spectral data in comparison with that of the keto ester **7**.



With the ready availability of the annulated products **7** and **8**, attention was turned to their elaboration into pupukeanones exploiting the steric crowding of the C-9 keto group. Thus, reaction of the tricyclic diketone **8** with methylenetriphenylphosphorane furnished the keto olefin **9**, mp 117 °C, in 56% yield in a highly regioselective manner. Catalytic hydrogenation of the keto olefin **9** using 10% Pd−C in ethyl acetate at one atmosphere pressure of hydrogen (balloon) furnished 10-(2-methylphenyl)-5-epipupukean-9-one (**10**), mp 84 °C, in 90% yield. Whereas treatment of the ester **7** with an excess of methylmagnesium iodide furnished the tertiary alcohol **12**, which on dehydration with *p*-toluenesulfonic acid in refluxing benzene using a Dean−Stark apparatus furnished the olefin **11**. Finally, stereoselective hydrogenation of the olefin **11** using 10% Pd−C in ethanol at 40 psi of hydrogen pressure furnished 10-(*exo*-2-methylphenyl)pupukean-9-one **13**, mp 86 °C, containing traces of the epimer **10**, in 92% yield.



In conclusion, the radical annulation mediated formation of the isotwistanes **7** and **8** from the bromo enone **5**, in contrast to the corresponding phenyl derivative **1**, demonstrated the possibility of fine tuning, by slight variation in substrate structure, to alter the course of an organic reaction and to bring about a reaction of choice.

(7) Greuter, H.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 2382.

Experimental Section

Melting points were recorded in capillaries and not corrected. In ^{1}H and ^{13}C NMR spectra, chemical shifts (δ) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^{1}H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). In ^{13}C NMR spectra, the nature of the individual carbons were identified by either off-resonance decoupling or SEFT experiments and are given in parentheses. Dry benzene was obtained by distillation over sodium. Dry ether was obtained by washing with ferrous sulfate followed by distillation over sodium. BBr_3, $^nBu_3SnH$, 10% Pd/C, and *p*-TSA were obtained from Fluka and were used without further purification. AIBN was recrystallized from methanol and stored in dark.

(−)-(1*R*,4*R*,8*S*)-8-Bromo-1,8-dimethyl-6-(2-methylphenyl)bicyclo[2.2.2]oct-5-en-2-one (5). To a cold (−78 °C), magnetically stirred, methylene chloride solution of an epimeric mixture of the enone **6**[5] (3.0 g, 11.1 mmol) was added boron tribromide (1.4 mL, 3.71 g, 14.8 mmol). The reaction mixture was stirred at −30 °C for 1.5 h and then quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The organic layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 10 mL). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the product on a silica gel (25 g) column using ethyl acetate−hexane (1:4) as eluent furnished the bromo enone **5** (2.4 g, 67.7%) which was recrystallized from hexanes: mp 68 °C; $[\alpha]^{25}_D$ −164.2 (*c* 0.14; $CHCl_3$); IR (neat) 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20−7.0 (3 H, m), 6.8 (1 H, br s), 6.31 (1 H, d, J = 6.7 Hz), 3.28 (1 H, m), 3.14 (1 H, d of $^1/_2$ AB q, J = 18.7 and 2 Hz), 2.62 (1 H, $^1/_2$ AB q, J = 15.2 Hz), 2.39 (1 H, d of $^1/_2$ AB q, J = 18.7 and 3.3 Hz), 2.3−2.0 (7 H, m), 0.85 (3 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 209.9 (s), 144.5 (s), 137.3 (s), 135.4 (s), 131.5 (d), 129.8 (d), 128.6 (d), 127.7 (d), 125.4 (d), 67.6 (s), 53.4 (s), 50.7 (t), 47.2 (d), 38.9 (t), 36.7 (q), 20.4 (q), 15.2 (q); mass, *m*/*z* 320 (M^+ for $C_{17}H_{19}{}^{81}BrO$, 20), 318 (M^+ for $C_{17}H_{19}{}^{79}BrO$ 20); HRMS *m*/*z* calcd for $C_{17}H_{19}BrO$ 318.0619, found 318.0625. Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.96; H, 6.00. Found: C, 64.16; H, 5.95.

(+)-Methyl (1*R*,2*R*,3*R*,4*S*,6*R*,7*R*)-1,6-Dimethyl-2-(2-methylphenyl)-9-oxotricyclo[4.3.1.0^{3,7}]decane-4-carboxylate (7). A solution of the bicyclic bromo enone **5** (354 mg, 1.11 mmol), $^nBu_3SnH$ (0.35 mL, 1.21 mmol), freshly distilled methyl acrylate (2.0 mL, 20 mmol), and AIBN (∼10 mg) in dry benzene (55 mL) was refluxed for 1 h. The reaction mixture was cooled, washed with 1% aqueous NH_4OH solution and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (15 g) column using ethyl acetate−hexane (1:9) as eluent furnished the annulated product **7** (140 mg, 38%), which was recrystallized from hexanes: mp 118 °C; $[\alpha]^{24}_D$ +22.2 (*c* 0.045, $CHCl_3$); IR (neat) 1722, 1700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15−7.0 (3 H, m), 6.83−6.79 (1 H, m), 3.63 (3 H, s), 2.94 (1 H, d, J = 2.6 Hz), 2.89 (1 H, dd, J = 9.2 and 5.3 Hz), 2.6 (2 H, d of AB q, J = 16.0 and 2.0 Hz), 2.6 (1 H, m), 2.35 (3 H, s), 2.16 (1 H, d of $^1/_2$ AB q, J = 14 and 9.2 Hz), 2.04 (1 H, d of $^1/_2$ AB q, J = 14 and 5.3 Hz), 1.95−2.25 (1 H, m), 1.66 (2 H, AB q, J = 15.2 Hz), 1.17 (3 H, s), 0.75 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.9 (C), 176.2 (C), 141.8 (C), 136.0 (C), 130.5 (CH), 126.6 (CH), 126.3 (2 C, CH), 52.9 (CH_3), 51.8 (CH), 50.9 (CH_2), 50.5 (CH), 49.5 (CH), 48.1 (C), 45.4 (CH_2), 43.3 (CH), 39.5 (C), 35.5 (CH_2), 26.0 (CH_3), 20.8 (CH_3), 17.9 (CH_3); mass, *m*/*z* 326 (M^+, 45); HRMS *m*/*z* calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1871. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.04; H, 8.11.

(+)-(1*R*,2*R*,3*R*,4*S*,6*R*,7*R*)-1,6-Dimethyl-4-acetyl-2-(2-methylphenyl)tricyclo[4.3.1.0^{3,7}]decan-9-one (8). A solution of the bicyclic bromo enone **5** (432 mg, 1.34 mmol), $^nBu_3SnH$ (0.4 mL, 1.47 mmol), freshly distilled methyl vinyl ketone (2.2 mL, 26 mmol) and AIBN (∼10 mg) in dry benzene (73 mL) was refluxed for 1 h. The reaction mixture was cooled to room temperature, washed with 1% aqueous NH_4OH solution and

brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (15 g) column using ethyl acetate−hexane (1:9) as eluent furnished the annulated product **8** (166 mg, 40%), which was recrystallized from hexanes: mp 125 °C; $[\alpha]^{24}_D$ +90 (*c* 0.1, $CHCl_3$); IR (neat) 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2−7.0 (3 H, m), 6.85−6.75 (1 H, m), 2.99 (1 H, dd, *J* = 9.5 and 5.3 Hz), 2.97 (1 H, d, *J* = 3.0 Hz), 2.66 and 2.49 (2 H, d of AB q, *J* = 20.1 and 3.1 Hz), 2.58 (1 H, m), 2.34 (3 H, s), 2.13 (3 H, s), 2.1 (1 H, d of $^1/_2$ AB q, *J* = 13.5 and 9.5 Hz), 1.90 (1 H, m), 1.92 (1 H, d of $^1/_2$ AB q, *J* = 13.5 and 5.3 Hz), 1.71 and 1.62 (2 H, AB q, *J* = 14.5 Hz), 1.14 (3 H, s), 0.75 (3 H, s); ^{13}C NMR (100 MHz, SEFT, $CDCl_3$) δ 215.8 (C), 209.1 (C), 141.9 (C), 135.8 (C), 130.5 (CH), 126.7 (CH), 126.4 (CH), 126.3 (CH), 58.9 (CH), 53.0 (CH), 50.8 (CH_2), 48.3 (C), 47.6 (CH), 44.1 (CH_2), 43.0 (CH), 39.9 (C), 35.6 (CH_2), 28.7 (CH_3), 26.0 (CH_3), 20.9 (CH_3), 17.9 (CH_3); mass, *m*/*z* 310 (M^+, 100); HRMS *m*/*z* calcd for $C_{21}H_{26}O_2$ 310.1933, found 310.1944.

(+)-(1*R*,2*R*,3*S*,4*S*,6*R*,7*R*)-1,6-Dimethyl-4-isopropenyl-2-(2-methylphenyl)tricyclo[4.3.1.0^{3,7}]decan-9-one (9). To a magnetically stirred suspension of methyltriphenylphosphonium bromide (85 mg, 0.24 mmol) in dry benzene (1 mL) was added a 1 M solution of potassium *tert*-amyloxide in dry *tert*-amyl alcohol (0.16 mL, 0.16 mmol), and the resultant yellow solution was stirred at room temperature for 30 min. The Wittig reagent was cooled to 0 °C, a benzene (0.5 mL) solution of the tricyclic ketone **8** (25 mg, 0.08 mmol) was added, and the mixture stirred at room temperature for 5 h. The reaction mixture was diluted with ether (5 mL), washed with aqueous 0.5 N HCl and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (5 g) column using ethyl acetate−hexane (1:9) as eluent furnished the tricyclic olefin **9** (14 mg, 56%) which was recrystallized from hexanes: mp 117 °C; $[\alpha]^{24}_D$ +13.33 (*c* 0.15, $CHCl_3$); IR (neat) 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2−7.0 (3 H, m), 6.82 (1 H, dd, *J* = 7.1 and 2.3 Hz), 4.68 (2 H, s), 2.98 (1 H, d, *J* = 2.4 Hz), 2.64 (1 H, dd, *J* = 9 and 5.6 Hz), 2.57 (2 H, t, *J* = 3.4 Hz), 2.35 (3 H, s), 2.24 (1 H, m), 2.09 (1 H, d of $^1/_2$ AB q, *J* = 13.0 and 9.2 Hz), 2.0 (1 H, m), 1.77 (3 H, s), 1.73 and 1.60 (2 H, AB q, *J* = 18.2 Hz), 1.73−1.60 (1 H, m), 1.13 (3 H, s), 0.81 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, SEFT) δ 217.3 (C), 148.9 (C), 142.6 (C), 136,.2 (C), 130.5 (CH), 126.4 (CH), 126.0 (2 C, CH), 108.2 (CH_2), 54.4 (CH), 53.9 (CH), 51.3 (CH_2), 50.0 (CH), 48.1 (C), 47.6 (CH_2), 43.2 (CH), 39.8 (C), 35.9 (CH_2), 26.2 (CH_3), 22.0 (CH_3), 20.9 (CH_3), 18.2 (CH_3); mass, *m*/*z* 308 (M^+, 93); HRMS *m*/*z* calcd for $C_{22}H_{28}O$ 308.2140, found 308.2149.

(+)-(1*R*,2*R*,3*R*,4*S*,6*R*,7*R*)-1,6-Dimethyl-4-(propan-2-yl)-2-(2-methylphenyl)tricyclo[4.3.1.0^{3,7}]decan-9-one (10) [10-(2-Methylphenyl)-5-epipupukean-9-one]. A suspension of the tricyclic olefin **9** (5 mg, 0.02 mmol) and 10% Pd−C (catalytic) in ethyl acetate (5 mL) was magnetically stirred under a H_2 atmosphere (balloon) for 4 h. The reaction mixture was filtered through a silica gel (2 g) column using ethyl acetate−hexane (1:9) as eluent to furnish the hydrogenated product **10** (4 mg, 80%), which was recrystallized from hexanes: mp 84 °C; $[\alpha]^{24}_D$ +84.6 (*c* 0.13, $CHCl_3$); IR (neat) 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.1−6.95 (3 H, m), 6.73 (1 H, d, *J* = 7.04 Hz), 2.9 (1 H, d, *J* = 2.2 Hz), 2.55 and 2.45 (2 H, d of AB q, *J* = 19.9 and 3.0 Hz), 2.28 (3 H, s), 2.08 (1 H, br s), 1.86 (1 H, d of $^1/_2$ AB q, *J* = 13.3 and 8.7 Hz), 1.74 (1 H, m), 1.65−1.50 (3 H, m), 1.36 (1 H, m), 1.34 (1 H, d of $^1/_2$ AB q, *J* = 13.0 and 4.6 Hz), 1.04 (3 H, s), 0.77 (3 H, d, *J* = 6.5 Hz), 0.74 (3 H, d, *J* = 6.5 Hz), 0.66 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, SEFT) δ 217.3 (C), 142.6 (C), 136.0 (C), 130.3 (CH), 126.5 (CH), 126.3 (CH), 125.9 (CH), 55.5 (CH), 54.8 (CH), 50.7 (CH_2), 49.1 (CH), 48.4 (C), 46.5 (CH_2), 42.7 (CH), 39.7 (C), 36.0 (CH_2), 33.0 (CH), 26.6 (CH_3), 21.7 (CH_3), 20.9 (CH_3), 20.2 (CH_3), 18.1 (CH_3); mass, *m*/*z* 310 (M^+, 100); HRMS *m*/*z* calcd for $C_{22}H_{30}O$ 310.2296, found 310.2301.

(+)-(1*R*,2*R*,3*R*,6*R*,7*R*)-1,6-Dimethyl-4-isopropylidene-2-(2-methylphenyl)tricyclo[4.3.1.0^{3,7}]decan-9-one (11): Grignard Reaction. To a freshly prepared, magnetically stirred, ice-cold suspension of methylmagnesium iodide [prepared from methyl iodide (0.56 mL, 8 mmol) and magnesium (190 mg, 8 mmol) in 5 mL of dry ether] was added a solution of the tricyclic ester **7** (50 mg, 0.16 mmol) in dry benzene (5 mL). The reaction mixture was refluxed for 4 h, cooled, and quenched with aqueous NH_4Cl solution (5 mL). The organic phase was separated, and the aqueous phase was extracted with ether (3 × 10 mL). The combined ether extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified on a silica gel (5 g) column using ethyl acetate−hexane (1:9) as eluent to furnish the tertiary alcohol **12** (30 mg, 60%) which was recrystallized from hexanes: mp 121 °C; $[\alpha]^{24}_D$ −28 (*c* 0.25, $CHCl_3$); IR (neat) 3450, 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.2−7.0 (3 H, m), 6.86−6.81 (1 H, m), 3.03 (1 H, d, *J* = 2.4 Hz), 2.7 and 2.51 (2 H, d of AB q, *J* = 20.1 and 3.0 Hz), 2.36 (3 H, s), 2.28 (1 H, m), 2.10 (1 H, d of $^1/_2$ AB q, *J* = 13.4 and 8 Hz, H-5a), 1.95 (1 H, m), 1.84 (1 H, d, *J* = 13.4 Hz), 1.71 and 1.59 (2 H, AB q, *J* = 14.2 Hz), 1.54 (1 H, m), 1.16 (9 H, s), 0.73 (3 H, s); mass, *m*/*z* 326 (M^+, 4); HRMS *m*/*z* calcd for $C_{22}H_{30}O_2$ 326.2246, found 326.2222.

Dehydration. A solution of the tertiary alcohol **12** (30 mg, 0.09 mmol) and *p*-toluenesulfonic acid (catalytic) in dry benzene (5 mL) was refluxed using a Dean−Stark apparatus for 30 min. The reaction mixture was cooled, washed with aqueous saturated $NaHCO_3$ solution and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified on a silica gel (5 g) column using ethyl acetate−hexane (1:9) as eluent to furnish the tricyclic olefin **11** (24 mg, 85%) as an oil: $[\alpha]^{26}_D$ +76 (*c* 0.72, $CHCl_3$); IR (neat) 1715 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.2−7.0 (3 H, m), 6.86 (1 H, d, *J* = 7.5 Hz), 3.06 (1 H, d, *J* = 1.9 Hz), 2.94 (1 H, br s), 2.73 (1 H, d of $^1/_2$ AB q, *J* = 20.3 and 3.2 Hz), 2.59 (1 H, d of $^1/_2$ AB q, *J* = 20.3 and 2.5 Hz), 2.38 and 2.25 (2 H, AB q, *J* = 15.6 Hz), 2.28 (3 H, s), 1.90 (1 H, br s), 1.71 and 1.62 (2 H, AB q, *J* = 14.3 Hz), 1.61 (3 H, s), 1.45 (3 H, s), 1.19 (3 H, s), 0.68 (3 H, s); ^{13}C NMR (100 MHz, SEFT, $CDCl_3$) δ 215.7 (C), 142.2 (C), 139.6 (C), 136.0 (C), 130.1 (CH), 126.7 (CH), 126.5 (CH), 126.0 (CH), 120.9 (C), 52.9 (CH), 49.6 (CH_2), 49.2 (C), 48.6 (CH), 47.5 (CH_2), 44.4 (CH), 39.1 (C), 36.3 (CH_2), 26.2 (CH_3), 21.0 (CH_3), 20.7 (CH_3), 20.5 (CH_3), 17.8 (CH_3); mass, *m*/*z* 308 (M^+, 60); HRMS *m*/*z* calcd for $C_{22}H_{28}O$ 308.2140, found 308.2134.

(+)-(1*R*,2*R*,3*R*,4*R*,6*R*,7*R*)-1,6-Dimethyl-4-*endo*-isopropyl-2-(2-methylphenyl)tricyclo[4.3.1.0^{3,7}]decan-9-one (13). A suspension of the tricyclic olefin **11** (70 mg, 0.22 mmol) and 10% Pd−C (70 mg, 0.06 mmol) in dry ethanol (2 mL) was placed in a 250 mL pressure bottle and hydrogenated at 40 psi for 5 h in a Parr type hydrogenation apparatus for 20 h. The catalyst was filtered off using a Buchner funnel. Evaporation of the solvent furnished the pupukean-9-one **13** (65 mg, 92%) which was recrystallized from hexanes: mp 86 °C; $[\alpha]^{25}_D$ +73.3 (*c* 0.6, $CHCl_3$); IR (Nujol) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.2−7.0 (3 H, m), 6.78 (1 H, d, *J* = 7.5 Hz), 3.17 (1 H, d, *J* = 3.1 Hz), 2.67 (1 H, d of $^1/_2$ AB q, *J* = 20 and 3.5 Hz), 2.51 (1 H, d of $^1/_2$ AB q, *J* = 20 and 2.5 Hz), 2.39 (1 H, q, *J* = 3.6 Hz), 2.33 (3 H, s), 2.07 (1 H, d of d, *J* = 13.5 and 9.8 Hz), 1.89 (1 H, q, *J* = 3.2 Hz), 1.75−1.5 (2 H, m), 1.43 (1 H, dd, *J* = 13.5 and 8.1 Hz), 1.12 (3 H, s), 0.91 (3 H, d, *J* = 6.2 Hz), 0.56 (3 H, d, *J* = 6.2 Hz), 0.66 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2 (C), 142.6 (C), 136.0 (C), 130.0 (CH), 127.4 (CH), 126.4 (CH), 125.9 (CH), 52.2 (CH_2), 50.7 (CH), 48.6 (C), 48.5 (CH), 48.3 (CH_2), 45.9 (CH), 43.0 (CH), 39.2 (C), 36.4 (CH_2), 31.1 (CH), 27.0 (CH_3), 21.7 (CH_3), 21.6 (CH_3), 20.4 (CH_3), 17.6 (CH_3); mass *m*/*z* 310 (M^+, 100); HRMS *m*/*z* calcd for $C_{22}H_{30}O$ 310.2296, found, 310.2293.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **8, 9, 10, 11,** and **13** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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