Tetrahedron Vol. 49, No. 45, pp. 10263-10270, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Total Synthesis of (±)-Acoradiene via Radical Cyclization

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(*Received in Japan* 3 *August* 1993; *accepted* 13 *September* 1993)

Abstract : Acoradiene **7a**, isolated from vetiver oil, is one kind of spirocyclic sesquiterpenes containing the spiro[4 5]decane nucleus A new synthetic approach towards the total synthesis of (±)-acoradiene via free radical cyclization for the construction of the spiro[4.5]decane nucleus has been completed.

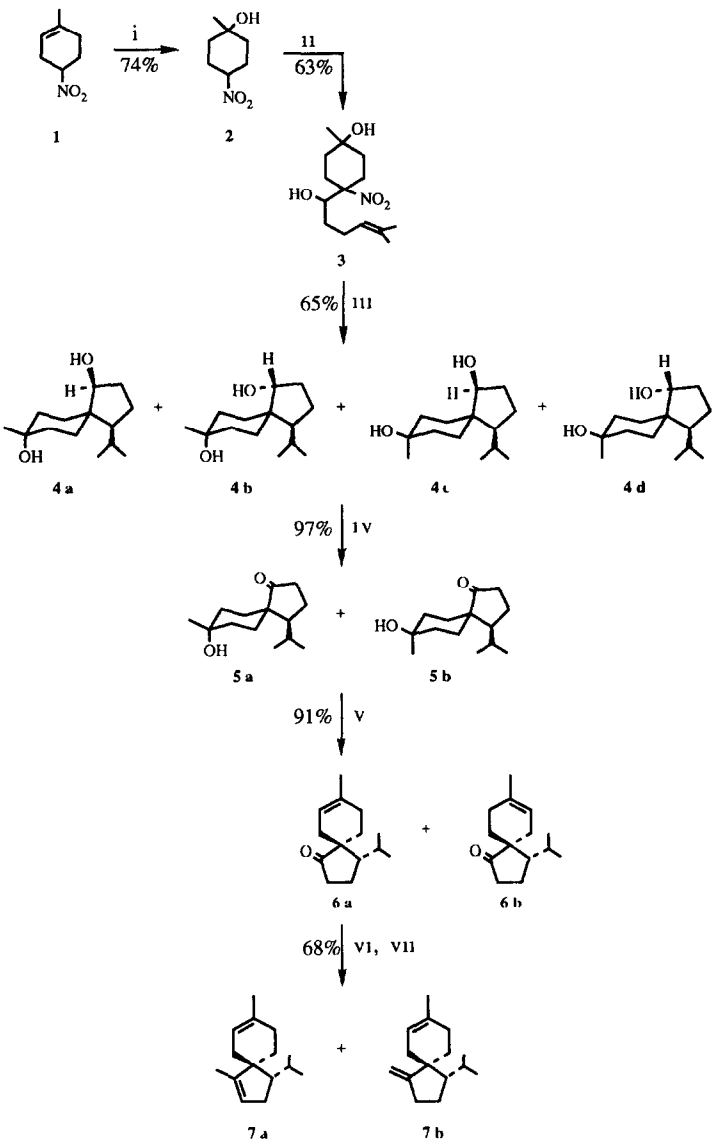
INTRODUCTION

Acoradiene **7a**, isolated from vetiver oil by Kaiser and Naegeli,[1] is one kind of spirocyclic sesquiterpenes containing the spiro[4 5]decane nucleus For the synthesis of acoradiene **7a**, the construction of the spiro[4.5]decane nucleus turns out to be a synthetic challenge. There are many methods recorded for the syntheses of acorane analogs through such as intramolecular Michael addition,[2] photochemical Wolff rearrangement,[3] Diels-Alder reaction,[4] intramolecular ene reaction,[5] aldolization,[6] electrophilic cleavage of the cyclopropane ring,[7] Robinson annulation,[8] photo[2+2]addition and reductive fragmentation,[9] and intramolecular Sakurai-Hosomi type condensation [10] However, only two methods reported for the synthesis of acoradiene **7a** are the cyclization[1] of allylic alcohol induced by stannic chloride and the acylation of ynamine by enol-lactone.[11] As parts of our studies in free radical cyclizations,[12] we report here a new synthetic approach towards the total synthesis of (±)-acoradiene via free radical cyclization for the construction of the spiro[4.5]decane nucleus The synthetic versatility of the nitro group in Diels-Alder reaction, ionic nitroaldol reaction (Henry reaction), and free radical cyclization will also be demonstrated.

RESULTS AND DISCUSSION

As shown in Scheme 1, the synthesis of (±)-acoradiene **7a** from the readily accessible nitroolefin **1** is outlined A radical 5-*exo*-trigonal ring closure reaction was used as the key step to generate the spirocyclic center in the acorane skeleton. The nitrodiol **3** was chosen as a radical cyclization precursor, based on the synthetic versatility of the nitro group in Diels-Alder reaction, ionic nitroaldol reaction (Henry reaction), and free radical cyclization.

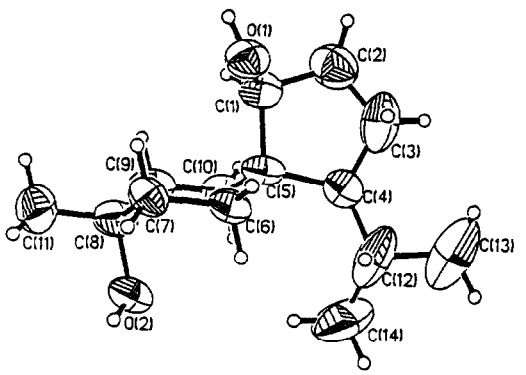
Nitroolefin **1** was easily prepared from isoprene and nitroethylene through Diels-Alder reaction [14] The nitro group not only activates the dienophile, but also controls regioselectivity. The



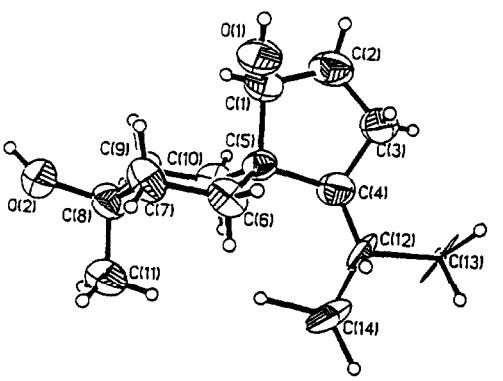
Scheme 1 i) H_2O, H^+, ii) Amberlyst A-21, $Me_2C{=}CHCH_2CH_2CHO$, iii) Bu_3SnH, AIBN, PhH, reflux, iv) CrO_3, v) $SOCl_2$, pyridine, vi) MeLi, $CeCl_3$, THF, vii) $SOCl_2$, pyridine

hydration of nitroolefin **1** with 58% aqueous sulfuric acid at 0 °C for 36 h afforded nitroalcohol **2** in 74% yield. An ionic nitroaldol reaction of **2** with 5-methyl-4-hexenal was catalyzed by Amberlyst at room temperature for 24 h to give nitrodiol **3** in 63% yield. Radical cyclization was carried out by treatment of **3** with tributyltin hydride in the presence of 10 mol% of azobisisobutyronitrile (AIBN) in benzene at 80 °C to afford a separable mixture of spirocyclic diols **4a**, **4b**, **4c**, and **4d** in 21%, 19%, 13%, and 12% yields, respectively As in the synthesis of the acorane skeleton **4** constructed in two steps from nitroalcohol **2**, the nitro group not only activates α-carbon to make a carbon-carbon bond, but also serves as a convenient radical precursor.

The structures of **4a**, **4b**, **4c**, and **4d** were assigned on the basis of the following considerations. The X-ray crystallographic analysis[13] of **4a** and **4c**, shown in Figure 1, confirmed their stereochemical assignments, respectively The stereochemistry of **4b** was verified by the fact that a same product **5a** was obtained from Jone's oxidation of **4a** and **4b**, respectively. By the same method, the stereochemistry of **4d** was also confirmed.



4 a



4 c

Figure 1 X-ray structures of **4a** and **4c**.

As in the examples above, the radical cyclization could not undergo stereoselectively very well probably because no groups existed in the molecule were large enough for differentiating these ring closure reactions. However, all of four diastereoisomers **4a**, **4b**, **4c**, and **4d** would be transformed their functionalities from alcohols to enones **6** , which would lost their stereochemistry at C1 and C8 due to sp^2 carbons. Thus, the direct oxidation of a mixture of **4a**, **4b**, **4c**, and **4d** was carried out with Jones reagent in acetone at 0~5 °C for 30 min to form a mixture of **5a** and **5b** in 97% yield. Dehydration of **5a** and **5b** with thionyl chloride in pyridine at 0 °C for 10 min gave a mixture of two enones **6a** and **6b** in 91% yield The ratio of **6a** to **6b** was determined to be 1:1 based upon integration of the vinyl protons of 5 33 ppm and 5 41 ppm, respectively For the assignment of the stereochemistry for isopropyl group at C4 in **6a** and **6b**, respectively, two enones were separated by MPLC. The enone **6a** was then treated with methyllithium and cerium chloride in THF at -78 °C to afford a mixture of tertiary alcohol (IR· v ~ 3492 cm^{-1}). Without further purification, dehydration of the crude alcohols with thionyl chloride in pyridine gave a mixture of two dienes **7a** and **7b** as a ratio of 68·32, respectively, in 68% yield for two steps. These were separated by chromatography on a column of 15% $AgNO_3$-silica gel and elution with hexane, and then ethyl acetate. The major product had spectral properties consistent with the endocyclic isomer, which was assigned as the natural (±)-acoradiene **7a** by comparision with the reported data.[1, 11] Hence, the minor product containing two vinyl protons of methylene group at 4 70~4.74 and 4.74~4 78 ppm, respectively, was assigned as the exocyclic isomer **7b** with the same stereochemistry of isopropyl group at C4 as **7a**. According to the above functionality transformations, the stereochemistry of isopropyl group at C4 in **6a** was assigned as *anti* to the double bond at C7 Therefore, the isopropyl group at C4 of the other stereoisomer **6b** was assigned as *syn* to the double bond at C7

In conclusion, a new synthetic approach towards the total synthesis of (±)-acoradiene via free radical cyclization for the construction of the spiro[4 5]decane nucleus has been completed. The synthetic versatility of the nitro group in Diels-Alder reaction, ionic nitroaldol reaction (Henry reaction), and free radical cyclization also have been demonstrated.

EXPERIMENTAL SECTION

Melting points (Buchi 535 capillary melting point apparatus) are uncorrected Infrared spectra were recorded on a Hitachi 270-30 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian VXR-300S or a Varian VXR-200S spectrometer. NMR data are reported as follows· chemical shift [multiplicity (*s*=singlet, *d*=doublet, *t*=triplet, *q*=quartet, *m*=multiplet), coupling constant, integration] in units of ppm Mass spectra were recorded on JOEL JMS-HX 110 and JEOL NMS-SX/SX 102A mass spectrometers Silica-gel plates (Merck 60 F-254) were used for analytical thin-layer chromatography Column chromatography was performed on SiO_2 (70-230 mesh) with elution of gradients of EtOAc and hexane. CH_2Cl_2 was distilled over P_2O_5 under nitrogen. THF and benzene were distilled over sodium under nitrogen.

1-Methyl-4-nitrocyclohexanol (2). 1-Methyl-4-nitrocyclohexene **1** (1.021 g, 7.24 mmol), readily prepared from nitroethylene and isoprene,[14] was mixed with a solution of H_2SO_4 (150 mL) and H_2O (210 mL) at 0 °C. The reaction mixture was stirred for 36 h, and then diluted with water (1 L) and extracted with ethyl acetate (200 mL x 3). The organic layer was dried over $MgSO_4$ and evaporated to give a pale yellow solid After chromatography by using hexane/ethyl acetate (8:1) as eluent, two stereoisomers of tertiary alcohol **2** were obtained as colorless solids in 74% total yield. One isomer : mp 70~71 °C; IR (CCl_4) 3616, 1548, 1448, 1380 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.28(*s*, 3H, CH_3), 1 33(*bs*, 1H, OH), 1 48(*dt*, J = 3 9, 13.8 Hz, 2H), 1 72~1 88(*m*, 2H), 2 04~2 38(*m*, 4H), 4 34(*tt*, J = 3.9, 11.7 Hz, 1H, $CHNO_2$), ^{13}C NMR ($CDCl_3$) δ 26 3(*t*), 30 6(*q*), 36.6(*t*), 67 8(*s*), 84.0(*d*), Anal. Calcd for $C_7H_{13}NO_3$; C, 52.80, H, 8.20; N, 8.80, Found: C, 52.88, H, 8 19, N, 8 69. The other one : mp 53 5~55.5 °C; IR (CCl_4) 3404, 1544, 1444, 1380 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1 29(*s*, 3H, CH_3), 1.43(*bs*, 1H, OH), 1.57(*dt*, J = 6.0, 13.5 Hz, 2H), 1.72(*tt*, J = 6 9, 13 8 Hz, 2H), 2.10~2.25(*m*, 4H), 4.50(*tt*, J = 5.4, 10.2 Hz, 1H, $CHNO_2$); ^{13}C NMR ($CDCl_3$) δ 25.9(*t*), 29.2(*q*), 35.2(*t*), 68.8(*s*), 81.9(*d*); Anal. Calcd for $C_7H_{13}NO_3$; C, 52.80; H, 8 20; N, 8 80, Found. C, 52.80; H, 8 19; N, 8.74.

4-(1'-Hydroxy-5'-methyl-4'-hexenyl)-1-methyl-4-nitrocyclohexanol (3). A solution of **2** (700 mg, 4 4 mmol) and 5-methyl-4-hexenal (1 20 g, 10 7 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 10 min Amberlyst A-21 (10 g) was then added, and the reaction mixture was stirred for 1 h. After standing for 24 h, the mixture was extracted by ether (50 ml x 2) and the solvent was evaporated to give a pale yellow liquid. The crude product was purified by chromatography using hexane/ethyl acetate (4·1) as eluent to give **3** (752 mg, 63%): IR (neat) 3420, 1636, 1538, 1444 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1 22(*s*, 3H, CH_3), 1.22~1 65(*m*, 7H), 1 61(*s*, 3H, CH_3), 1.69(*s*, 3H, CH_3), 1.90~2.47(*m*, 7H), 3 65~3.75(*m*, 1H, HOC<u>H</u>), 5 03~5.13(*m*, 1H, =CH), MS m/z, 271(M^+), 207, 141, 95(base); HRMS Calcd for $C_{14}H_{25}O_4N$ (M^+) 271.1784, Found 271.1779

8-Hydroxy-4-isopropyl-8-methylspiro[4.5]decan-1-ol (4). To a solution of **3** (137 mg, 0.50 mmol) in dry benzene (25 mL) at 80 °C was added by syringe pump a solution of Bu_3SnH (0.17 mL, 0 63 mmol) and AIBN (10 mg, 0.06 mmol) in dry benzene (31.5 mL). After the addition completed in 3 h, the reaction mixture was refluxed for additional 12 h and then cooled and evaporated to give a pale yellow liquid The crude product was purified by chromatograpgy using hexane (500 mL) and then changed to hexane/ethyl acetate (2:1) as eluent to remove the by-product of tin compounds. After the further purification by MPLC method using hexane/ethyl acetate (5.1) as eluent, four diastereoisomers of **4a** (24 mg, 21%), **4b** (21 mg, 19%), **4c** (15 mg, 13%), and **4d** (13 mg, 12%) were obtained as colorless solids, respectively, in 65% total yield Compound **4a**. mp 122 5~123.5 °C; IR (CCl_4) 3400 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0 84(*d*, J = 6 9 Hz, 3H, CH_3), 0.95(*d*, J = 6 3 Hz, 3H, CH_3), 1 19(*s*, 3H, CH_3), 1 08~1 25(*m*, 2H), 1 42~1 80(*m*, 14H), 3 98~4 02(*m*, 1H, HOC<u>H</u>); ^{13}C NMR ($CDCl_3$) δ 21 0(*q*), 22.0(*t*), 24.4(*q*), 25 4(*t*), 27 8(*d*), 31 4(*q*), 33.4(*t*), 34.8(*t*), 36 5(*t*), 36.7(*t*), 46.3(*s*), 56 5(*d*), 69 1(*s*), 78 1(*d*); MS m/z, 208(base), 190, 165, 147, 138; HRMS Calcd for $C_{14}H_{26}O_2$ (M^+) 226 1933, Found 226 1930 Compound **4b**. mp 89 5~90.5 °C; IR (CCl_4) 3376 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0 89(*d*, J = 6 9 Hz, 3H, CH_3), 1 02(*d*, J = 6.3 Hz, 3H, CH_3), 1 23(*s*, 3H, CH_3), 1 22~2.04(*m*, 16H), 4 17(*m*, 1H, HOC<u>H</u>), ^{13}C NMR ($CDCl_3$) δ 22 5(*q*), 23.7(*t*), 23.9(*q*), 25 7(*t*), 26.0(*t*), 28.4(*d*), 31.3(*q*), 31 5(*t*), 34 9(*t*), 36 5(*t*), 48 1(*s*), 51 3(*d*). 69 3(*s*), 76 1(*d*), MS m/z 226(M^+), 208(base), 190, 165, 147,

138; HRMS Calcd for $C_{14}H_{26}O_2$ (M^+) 226.1933, Found 226.1933 Compound **4c**: mp 134.5~135.5 °C; IR (CCl_4) 3388 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.89(*d*, J = 6.9 Hz, 3H, CH_3), 0.95(*d*, J = 6.3 Hz, 3H, CH_3), 1 27(*s*, 3H, CH_3), 1 27~1 80(*m*, 16H), 3 99~4.04(*m*, 1H, HOCH); ^{13}C NMR ($CDCl_3$) δ 20.6(*q*), 23.9(*t*), 24.5(*q*), 25.1(*t*), 26 8(*q*), 27 8(*d*), 33 0(*t*), 36 4(*t*), 37.7(*t*), 38.0(*t*), 46.7(*s*), 54.9(*d*), 70.3(*s*), 79.0(*d*), MS m/z 226(M^+), 208, 190, 165(base), 147, 138, HRMS Calcd for $C_{14}H_{26}O_2$ (M^+) 226 1933, Found 226 1935. Anal Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.05; H, 11.52. Compound **4d**: mp 118 5~119.5 °C; IR (CCl_4) 3396 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.87(*d*, J = 6.0 Hz, 3H, CH_3), 0.95(*d*, J = 6.3 Hz, 3H, CH_3), 1.19~2.05(*m*, 16H), 1.27(*s*, 3H, CH_3), 4.16~4.21(*m*, 1H, HOCH); ^{13}C NMR ($CDCl_3$) δ 21.7(*q*), 23.9(*q*), 24.4(*t*), 25.5(*t*), 27.1(*d*), 28.2(*q*), 29.7(*t*), 31.2(*t*), 36.4(*t*), 37 3(*t*), 48.0(*s*), 49 9(*d*), 70 6(*s*), 76 6(*d*); MS m/z 208, 190, 165(base), 147, 138; HRMS Calcd for $C_{14}H_{26}O_2$ (M^+) 226 1933, Found 226.1932

8-Hydroxy-4-isopropyl-8-methylspiro[4.5]decan-1-one (5). A solution of **4** (196 mg, 0.86 mmol) in acetone (20 mL) at 0~5 °C was stirred for 5 min and then to this was added dropwise 0.48 mL of Jones reagent (2 67 g of CrO_3 and 2 3 mL of H_2SO_4 were diluted by water up to 10 mL) within 10 min. After stirring for 20 min, to the reaction mixture was added ethyl acetate (20 mL) and water (20 mL) and the layer was separated The aqueous layer was extracted by ethyl acetate (20 mL x 2). The combined organic layer was dried over $MgSO_4$ and evaporated to give a pale yellow solid. After chromatography by using hexane/ethyl acetate (5 1) as eluent, two diastreoisomers of **5a** and **5b** were obtained as colorless solids in 97% total yield Compound **5a**: mp 51~52 °C, IR (CCl_4) 3448, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81(*d*, J = 6 9 Hz, 3H, CH_3), 1.01(*d*, J = 6.9 Hz, 3H, CH_3), 1.26(*s*, 3H, CH_3), 1.30~2 10(*m*, 13H), 2.15~2 30(*m*, 2H, $C(O)CH_2$), ^{13}C NMR ($CDCl_3$) δ 19.6(*q*), 20.3(*t*), 22.4(*t*), 22.8(*q*), 27 8(*d*), 29.8(*t*), 30 2(*q*), 34.5(*t*), 34.9(*t*), 36.4(*t*), 50.0(*s*), 51.9(*d*), 69.4(*s*), 223.3(*s*); MS m/z 224(M^+), 206, 163(base), HRMS Calcd for $C_{14}H_{24}O_2$ (M^+) 224.1776, Found 224.1773. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74 96; H, 10.78 Found· C, 75 16, H, 10.76. Compound **5b**: mp 100~101 °C; IR (CCl_4) 3300, 1728 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.71(*d*, J = 6.9 Hz, 3H, CH_3), 0.99(*d*, J = 6.9 Hz, 3H, CH_3), 1 24(*s*, 3H, CH_3), 1 30~2 00(*m*, 13H), 2 02~2 40(*m*, 2H, $C(O)CH_2$); ^{13}C NMR ($CDCl_3$) δ 18 1(*q*), 18 3(*t*), 22 5(*q*), 22 6(*t*), 27 5(*d*), 29 4(*q*), 29 7(*t*), 35 1(*t*), 35.6(*t*), 35.7(*t*), 47.0(*d*), 51.4(*s*), 68.8(*s*), 223 2(*s*), MS m/z 224(M^+), 206, 188, 163(base), HRMS Calcd for $C_{14}H_{24}O_2$ (M^+) 224 1777, Found 224.1770 Anal Calcd for $C_{14}H_{24}O_2$ C, 74 96; H, 10 78 Found· C, 74 44; H, 10.66

4-Isopropyl-8-methylspiro[4.5]dec-7-en-1-one (6). To a solution of **5** (131 mg, 0.58 mmol) in pyridine (10 mL) at 0 °C was added thionyl chloride (0 06 mL, 0.87 mmol) After stirring for 10 min, the reaction mixture was quenched by 5% HCl aqueous solution (20 mL) and then extracted by ethyl acetate The organic layer was dried over $MgSO_4$ and evaporated to give a pale yellow liquid. After chromatography by using hexane/ethyl acetate (10 1) as eluent, a 1·1 mixture (by NMR) of two diastreoisomers of **6a** and **6b** was obtained as colorless liquid (110 mg, 91%). This mixture was chromatographed using MPLC (Lobar size C, hexane/ethyl acetate = 1000:1) to give pure **6a** and **6b**. Compound **6a** . IR (neat) 1732 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.83(*d*, J = 6.3 Hz, 3H, CH_3), 0.98(*d*, J = 6.9 Hz, 3H, CH_3), 1.68(*s*, 3H, CH_3), 1 54~2 32(*m*, 12H), 5 33(*bs*, 1H, C=CH); ^{13}C NMR ($CDCl_3$) δ 19.7(*q*), 20.6(*t*), 22 6(*q*), 22 8(*t*), 23 5(*q*), 27.0(*t*), 28.1(*d*), 32.9(*t*), 35 7(*t*), 50 0(*s*), 50.3(*d*), 118.3(*d*), 133.9(*s*), 223.0(*s*), MS m/z, 206(M^+), 188, 173, 163(base), 145, 136, 121,105, HRMS Calcd for

$C_{14}H_{22}O$ (M^+) 206 1670, Found 206 1667. Compound **6b** IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0 69(*d*, J = 6 6 Hz, 3H, CH_3), 0 94(*d*, J = 6 9 Hz, 3H, CH_3), 1 65(*s*, 3H, CH_3), 1.40~2.44(*m*, 12H), 5 41(*bs*, 1H, C=CH), ^{13}C NMR ($CDCl_3$) δ 17 9(*t*), 18.1(*q*), 22 5(*q*), 23.2(*q*), 26.5(*t*), 27.2(*t*), 27 9(*d*), 30 4(*t*), 35 5(*t*), 47 7(*d*), 50.8(*s*), 119 3(*d*), 132.8(*s*), 223 3(*s*); MS m/z, 206(M^+), 188, 173, 163(base), 145, 136, 121,105, HRMS Calcd for $C_{14}H_{22}O$ (M^+) 206.1670, Found 206.1664

4-Isopropyl-1,8-methylspiro[4.5]dec-1,7-diene (7a) and 4-isopropyl-8-methyl-1-methylenespiro[4.5]dec-7-ene (7b). Cerium chloride[15] ($CeCl_3$ $7H_2O$) (309 mg, 0.83 mmol) was placed in a 25 mL two-necked flask and was heated with stirring at 140 °C in vacuo for 2 h and cooled Dry THF (5 mL) was added and stirring was continued for 2 h. The resulted suspension was then cooled to -78 °C, and a 1 5 M solution of MeLi in hexane (0.5 mL, 0.77 mmol) was added, whereupon the color of suspension turned from white to dark orange After being kept at the same temperature for 0 5 h, a solution of **6a** (134 mg, 0 64 mmol) in THF (4 mL) was added. The reaction mixture was stirred for 3 h and then treated with sat NH_4Cl solution (50 mL) and extracted with ethyl acetate (30 mL x 2) The organic layer was dried over $MgSO_4$ and evaporated to give a mixture of tertiary alcohols (IR: ν ~ 3492 cm^{-1}) Without further purifications, the crude alcohols (141 mg) were mixed with pyridine (20 mL) and the mixture was cooled to 0 °C. After thionyl chloride (0.06 mL, 0.87 mmol) was added, the reaction mixture was stirred for 10 min and then treated with 5% HCl solution (40 mL) and extracted with hexane (40 mL x 2) The organic layer was dried over $MgSO_4$ and evaporated to give a pale yellow liquid After chromatography by using hexane as eluent, a 68 32 mixture (by NMR) of two dienes was obtained as colorless liquid (88 mg, 68%). For the further separation, two dienes were chromatographed on a column of 15% $AgNO_3$-silica gel with hexane and then ethyl acetate as eluent to give the endocyclic diene **7a** and the exocyclic diene **7b**, respectively Acoradiene **7a**.[1, 11] IR (neat) 3044, 1466, 1380, 1198, 1160, 1066, 1028, 1014, 956, 786 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0 81(*d*, J = 6 6 Hz, 3H, CH_3), 0.92(*d*, J = 6 6 Hz, 3H, CH_3), 1 50~2 20(*m*, 16H), 5 28(*bs*, 1H, C=CH), 5 38(*bs*, 1H, C=CH), ^{13}C NMR ($CDCl_3$) δ 14.8(*q*), 21.0(*q*), 22.8(*q*), 23 5(*q*), 26 3(*t*), 28 0(*d*), 28 7(*t*), 32 2(*t*), 34 3(*t*), 47 8(*s*), 55.0(*d*), 121 2(*d*), 123.6(*d*), 133.7(*s*), 148 7(*s*), MS m/z, 204(M^+), 189, 175, 161, 145, 136, 121, 105, 94(base), 79, 77, HRMS Calcd for $C_{15}H_{24}$ (M^+) 204 1878, Found 204 1874 Compound **7b** IR (neat) 3076, 1644, 1434, 1368, 1008, 886 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0 85(*d*, J = 6 6 Hz, 3H, CH_3), 0 94(*d*, J = 6 6 Hz, 3H, CH_3), 1 38~1 56(*m*, 4H), 1 64(*bs*, 3H), 1 67~2 00(*m*, 5H), 2.24~2 46(m, 3H), 4 70~4.74(*m*, 1H, $C=CH_2$), 4 74~4.78(*m*, 1H, $C=CH_2$), 5 36(*bs*, 1H, C=CH); ^{13}C NMR ($CDCl_3$) δ 20 7(*q*), 23 4(*q*), 23.8(*q*), 23.9(*t*), 24.8(*t*), 27 4(*t*), 27 7(*d*), 30 3(*t*), 36.6(*t*), 46 3(*s*), 53 9(*d*), 103.5(*t*), 120 5(*d*), 133.8(*s*), 160.6(*s*); MS m/z, 204(M^+), 189, 176, 161(base), 133. 119, 105, 84, 79, 77, HRMS Calcd for $C_{15}H_{24}$ (M^+) 204 1878, Found 204 1875

Acknowledgement. We thank the National Science Council of the Republic of China for financial support, and to professor T T. Jong for X-ray crystallography.

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13. Compound **4a** crystalizes in the rhombohedral $R\bar{3}$ space group with a=33.271(4), c=13.840(3) Å, V=13268(5) $Å^3$, and Z=21. The asymmetric unit contains two independent molecules. The final coordinates were solved by direct methods and refined by full matrix least square methods with R=6.06%, Rw=7.46%, and GOF=2.10 for 285 variables. Compound **4c** crystalizes in the monoclinic C2/c space group with a=29.154(8), b=7.258(3), c=14.312(4) Å, β=112.010(0)°, V=2807 7(16) $Å^3$, and Z=8 The final coordinates were solved by direct methods and refined by full matrix least square methods with R=6 30%, Rw=8 08%, and GOF=2 71 for 145 variables The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication.
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