reaction was quenched by the addition of methanol followed by dilution with water. The product was isolated by extraction with chloroform. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the crude product was chromatographed on 6.0 g of silica gel. Elution with 2:1 hexane–ether gave 1.0 mg of recovered methyl ether and 14.5 mg (80% based on recovered starting material) of pure crystalline racemic estrone: R_f 0.31 (1:1 hexane–ether); mp 254.5–256.0 °C (acetone) [lit.[15] mp 252.8–254.7 °C (acetone)].

Acknowledgment. This investigation was supported by a Public Health Service research grant from the National Cancer Institute.

Registry No. **2**, 73178-94-6; **3**, 73178-95-7; **4**, 19973-76-3; **4** methyl ether, 1091-94-7; **16**, 73178-96-8; **17**, 60100-25-6; **18**, 73178-97-9; **19**, 73178-98-0; **24**, 73178-99-1; **24** hydroxy acid, 73179-00-7; **25**, 73179-01-8; **26**, 73179-02-9; **26** selenide, 73179-03-0; **27**, 3855-62-7; 7-[2-(3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)ethyl]spiro[bicyclo-[2.2.1]hept-5-ene-2,2′-[1,3]dioxolane]-7-methanol, 73193-02-9; 7-[2-(3-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)ethyl]spiro[bicyclo-[2.2.1]hept-5-ene-2,2′-[1,3]dioxolane]-7-methanol mesylate, 73179-04-1.

Notes

An Improved Route to a Key Hydroazulenone Intermediate for Helenanolide Synthesis

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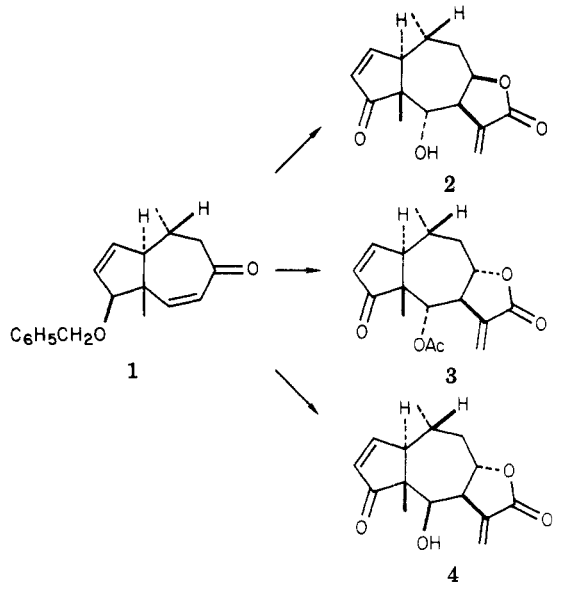
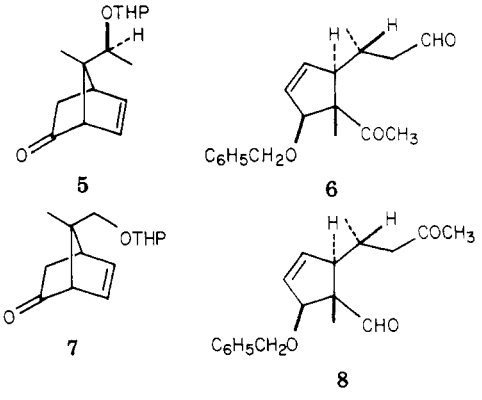
Received December 10, 1979

Considerable progress in the total synthesis of ambrosanolides (e.g., ambrosin,[2] confertin,[3] damsin,[2,3d,4] hymenin,[5] parthenin,[5] and stramonin-B[6]) has been recorded during the past 4 years. In contrast, progress in helenanolide total synthesis has been limited due to problems encountered in elaborating the six chiral centers located on the flexible seven-membered ring [cf. helenalin (**2**)].[7]

We have recently reported total syntheses of helenalin (**2**),[7a] bigelovin (**3**),[7b] and mexicanin I (**4**)[7c] which proceeded via the common intermediate hydroazulenone **1**. Enone **1** was synthesized previously from keto aldehyde **6**[7a] by employing a lengthy sequence of reactions starting from the bicyclo[2.2.1]heptenone derivative **5**.[2] We detail below a shorter, more efficient route to **1** which (a) utilizes as a starting material the known bicyclo[2.2.1]heptenone **7**[8] and (b) proceeds via the intermediacy of keto aldehyde **8**, a direct precursor to hydroazulenone **1**.





The C(3) endo-methylated bicyclo[2.2.1]heptenone **9** was readily prepared in 94% yield upon treatment of the lithium enolate of **7**[8] in tetrahydrofuran cooled to 0 °C with methyl iodide. As anticipated, the bulky C(7) *syn*-methyl group completely blocks exo approach to the enolate. During the course of the base-catalyzed Baeyer–Villiger oxidation (H_2O_2, OH^-, 1:1 HOH–MeOH)[9] and subsequent esterification,[10] which unravels the bicyclo[2.2.1]heptenone

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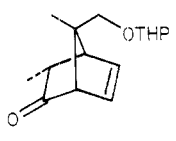
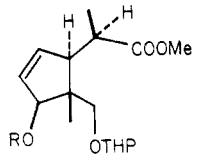
into cyclopentenol **10** possessing the proper stereochemical



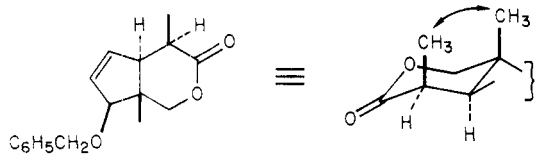
9



10, R = H
11, R = $CH_2C_6H_5$

configuration at C(1), C(5), and C(10) (pseudoguaianolide numbering) for elaboration into ambrosanolides, no epimerization occurred adjacent to the carbonyl function. Whereas cyclopentenol **10** constitutes a useful intermediate for transformation into ambrosin and related pseudoguaianolides, its use in helenanolide synthesis requires inversion of configuration at C(10).

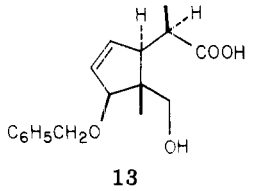
To accomplish the required inversion with complete stereochemical control, we set out to prepare lactone **12**.



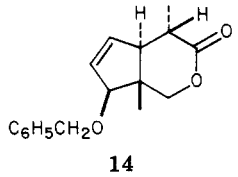
12

Close scrutiny of **12** reveals a severe 1,3-diaxial methyl–methyl interaction which suggests that treatment of **12** with base should alleviate this serious interaction and give way exclusively to the isomeric lactone **14**. Our assumption proved correct.

Benzylation of cyclopentenol **10** was carried out at reflux by employing sodium hydride in tetrahydrofuran containing benzyl bromide, hexamethylphosphoramide, and tetra-*n*-butylammonium iodide.[11] In the absence of tetra-*n*-butylammonium iodide there was no benzyl ether formation. Cleavage of the tetrahydropyranyl ether and hydrolysis of the methyl ester gave rise to hydroxy carboxylic acid **13** which resisted lactonization when treated



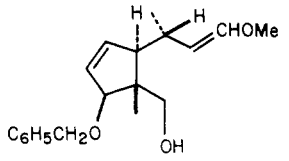
13



14

with *p*-toluenesulfonic acid in benzene. The reluctance of **13** to lactonize was overcome by preparing [TsCl, toluene, 0 °C] the mixed anhydride of **13** which spontaneously closed to lactone **12**. Without isolation, **12** was directly treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in order to effect the necessary inversion of configuration at C(10).

With the proper orientation of the C(10) methyl group, we concentrated on converting **14** into keto aldehyde **8** via enol ether **15**. Reduction of lactone **14** with diisobutylaluminum hydride generated the corresponding lactol which upon condensation with (methoxymethylene)triphenylphosphorane (generated in benzene with sodium *tert*-amylate) provided enol ether **15**. Hydrolysis of **15**



15

afforded the corresponding aldehyde which upon treatment with methyllithium and subsequent oxidation with pyridinium chlorochromate[12] yielded keto aldehyde **8**.

Intramolecular aldol condensation with methanol–potassium hydroxide gave the intermediate aldol which was smoothly dehydrated with *p*-toluenesulfonic acid in benzene to the crystalline hydroazulenone **1**, mp 79–80 °C, which was shown to be identical in all respects (NMR, IR, TLC, mp, mmp) with a sample of **1** prepared in our laboratory previously.[7a]

Experimental Section

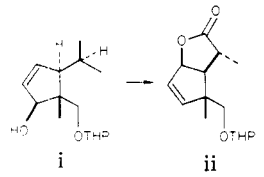
Melting points were determined on a Fisher-Johns hot-stage melting point apparatus. All melting points and boiling points are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 247 grating infrared spectrometer, and nuclear magnetic resonance (NMR) spectra were recorded either at 60 MHz (T-60 spectrometer) or at 250 MHz as indicated. Chemical shifts are reported in parts per million (δ) relative to Me_4Si (δ_{Me_4Si} 0.0) as an internal standard. Low-resolution mass spectra were recorded on an LKB-9000 spectrometer. High-resolution spectra were recorded on a Varian MAT CH-5DF instrument. Microanalyses were performed by Galbraith Laboratories, Inc.

Reactions were run under an atmosphere of nitrogen. "Dry" solvents were dried immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride; dimethylformamide (DMF), hexamethylphosphoramide (HMPA), dimethyl sulfoxide (Me_2SO), and pyridine were distilled from calcium hydride. Diethyl ether was distilled from sodium. Methylene chloride was passed through a column of alumina prior to use.

***endo*-3,*syn*-7-Dimethyl-7-[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]bicyclo[2.2.1]hept-5-en-2-one (9).** To a solution of lithium diisopropylamide, prepared from 9.06 g (89.7 mmol) of diisopropylamine in 75 mL of freshly distilled tetrahydrofuran and 51.1 mL (81.8 mmol) of *n*-butyllithium (1.50 M in hexane) at 0 °C, was added a solution of 10.59 g (44.9 mmol) of tetrahydropyranyl ether **7**[8] in 50 mL of tetrahydrofuran over 1 h. After an additional 1 h at 0 °C, 68.3 g (0.481 mol) of methyl iodide was added. The reaction mixture was warmed to room temperature. After 2 h at room temperature, the reaction was quenched with 10 mL of saturated ammonium chloride solution, and the solvent was removed under reduced pressure. The oily residue was taken up in 50 mL of water and was extracted with three 200-mL portions of ether. The combined ether extracts were washed with 30 mL of brine and dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent in vacuo afforded 11.6 g of crude **9**. Purification on 300 g of silica gel (2:1 hexanes–ether) afforded 10.59 g (94%) of desired methylated bicyclo[2.2.1]heptenone **9** which was homogeneous on TLC analysis (1:1 hexanes–ether): R_f 0.57; IR ($CHCl_3$) 3000, 2950, 2880, 2850, 1735, 1610, 1470, 1455, 1445, 1400, 1385, 1358, 1325, 1310, 1300, 1265, 1220, 1190, 1160, 1140, 1120, 1080, 1060, 1030, 990, 910, 890, 870, 815 cm^{-1}; NMR (CCl_4) δ 1.00 (d, 1.5 H, J = 7 Hz), 1.20 (d, 1.5 H, J = 7 Hz), 1.20 (s, 3 H), 1.8–2.3 (m, 1 H), 2.65 (br s, 2 H), 3.1–4.0 (m, 4 H), 4.40 (br s, 1 H), 5.8–6.1 (m, 1 H), 6.3–6.6 (m, 1 H). An analytical sample was prepared by distillation [54–61 °C (bath temperature) (0.21 mmHg)].

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.70; H, 9.09.

(10) The intermediate hydroxy carboxylic acid i, which is obtained from Baeyer–Villiger reaction on ketone **9**, is extremely sensitive and will rearrange on standing to bicyclic lactone ii.



i ii

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Methyl α,5-Dimethyl-4-hydroxy-5-[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]-2-cyclopenteneacetate (10). A solution of 10.48 g (41.9 mmol) of ketone **9** in methanol (160 mL) containing water (63 mL) was cooled to 0 °C and treated dropwise with a solution of 13.41 g (0.335 mol) of sodium hydroxide in 50 mL of water followed by 66.5 mL of 30% hydrogen peroxide (0.586 mol). After ca. 48 h at 0–5 °C the reaction was extracted twice with 200-mL portions of ether. The excess hydrogen peroxide was destroyed by the addition of solid sodium thiosulfate (135 g, 0.54 mol). The aqueous portion was then acidified to pH 4.5 and extracted with 500 mL of ethyl acetate. After the pH was readjusted to pH 4.5, the aqueous portion was extracted with 10 × 100 mL of ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to afford 11.69 g (93%) of the desired hydroxy acid which was directly esterified with an ether solution of diazomethane. Chromatography of the condensed residue on 400 g of silica gel (elution with 1:2 hexanes–ether) provided 10.78 g (86%, overall) of desired cyclopentenol methyl ester **10**: IR (CCl_4) 3650–3400, 3060, 2975, 2950, 2925, 2875, 2850, 1740, 1465, 1455, 1440, 1385, 1350, 1320, 1260, 1200, 1175, 1135, 1120, 1108, 1080, 1060, 1035, 1000, 980, 905, 870 cm^{-1}; NMR (CCl_4) δ 0.99 (s, 3 H), 1.21 (d, 3 H, J = 7 Hz), 3.60 (s, 3 H), 4.0–4.4 (m, 1 H), 4.5 (br s, 1 H), 5.5–5.9 (m, 2 H). An analytical sample was prepared by distillation [100–107 °C (bath temperature) (0.175 mmHg)].

Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78. Found: C, 64.11; H, 8.82.

Methyl α,5-Dimethyl-4-(phenylmethoxy)-5-[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]-2-cyclopenteneacetate (11). To a stirred suspension of 480 mg (10.0 mmol) of 50% sodium hydride dispersion (washed with dry hexanes prior to use) in 15 mL of dry tetrahydrofuran cooled at 0 °C was added dropwise a solution of cyclopentenol **10** (2.20 g, 7.43 mmol) and 1.4 mL of HMPA in 6.0 mL of tetrahydrofuran. After the reaction mixture was stirred at 0 °C for 15 min, it was warmed to room temperature where stirring was continued for an additional 1 h. Freshly distilled α-bromotoluene (1.91 g, 10.0 mmol) was added, followed by the addition of 1.1 g (3.0 mmol) of tetra-*n*-butylammonium iodide. The reaction was heated at 50 °C for 3 h followed by cooling to room temperature. The reaction was quenched with a saturated aqueous ammonium chloride solution. The product was isolated by extraction with ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude material was chromatographed on 130 g of silica gel. Elution with 2:1 hexanes–ether provided 1.7 g (60%) of pure benzyl ether **11**: R_f 0.71 (1:1 hexanes–ether); IR (CCl_4) 3090, 3065, 3030, 2980, 2950, 2925, 2900, 2875, 1738, 1495, 1465, 1455, 1441, 1432, 1420, 1385, 1360, 1350, 1340, 1320, 1300, 1282, 1260, 1240, 1200, 1192, 1168, 1138, 1120, 1075, 1068, 1011, 975, 890, 880, 871, 855, 840, 721, 695 cm^{-1}; NMR (CCl_4) δ 7.20 (s, 3 H), 4.52 (s, 2 H, $CH_2C_6H_5$), 3.60 (s, 3 H, CO_2CH_3). An analytical sample was prepared by distillation [87–95 °C (bath temperature) (0.04 mmHg)].

Anal. Calcd for $C_{23}H_{32}O_5$: C, 71.11; H, 8.30. Found: C, 71.25; H, 8.26.

(4α,4aα,7β,7aβ)-4,4a,7,7a-Tetrahydro-4,7a-dimethyl-7-(phenylmethoxy)cyclopenta[*c*]pyran-3(1*H*)-one (14). A solution of 1.60 g (4.15 mmol) of tetrahydropyranyl ether **11** in 25 mL of absolute methanol was treated at 0 °C for 1 h with 30 mg of *p*-toluenesulfonic acid. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched by the addition of 200 mg of sodium bicarbonate. Removal of the solvent under reduced pressure gave an oil which was directly chromatographed on silica gel. Elution with 2:1 hexanes–ether, gave 1.21 g (96%) of the desired hydroxy ester [R_f 0.44 (2:1 hexanes–ether); IR (CCl_4) 3640, 3400–3200, 1735 cm^{-1}] which was used directly in the next reaction.

A solution of 1.20 g (4.0 mmol) of the above ester was treated at reflux with 450 mg (8.0 mmol) of potassium hydroxide in 30% aqueous ethanol (15 mL). After 18 h, the reaction mixture was cooled and the solvent was removed under reduced pressure. The aqueous residue was extracted with ether. The aqueous layer was acidified with 10% hydrochloric acid to pH 3. The product was isolated by extraction (3 × 20 mL) with ethyl acetate. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. There was obtained 1.20 g (100%) of crude hydroxy acid **13** [R_f 0.65 (99:1 ether–acetic acid); IR ($CHCl_3$) 3600–2500, 1705 cm^{-1}] which was used directly in the next reaction.

To a solution of 789 mg (3.17 mmol) of *p*-toluenesulfonyl chloride and 920 mg (3.17 mmol) of hydroxy acid **13** in 12 mL of dry toluene at 0 °C was added dropwise over 40 min a solution of 1.52 g (10 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene in 5 mL of toluene. The reaction mixture was stirred at 0 °C for 15 min and then allowed to reflux for 3 h. The reaction mixture was cooled to room temperature, quenched by the addition of cold 10% aqueous hydrochloric acid, and diluted with ether. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude lactone was purified on silica gel with 3:1 hexanes–ether. There was obtained 590 mg (70%) of pure crystalline lactone: mp 97–98 °C; IR (CCl_4) 3060, 3030, 2970, 2935, 2880, 2850, 2800, 1735, 1495, 1475, 1455, 1390, 1375, 1355, 1340, 1300, 1270, 1250, 1195, 1180, 1158, 1148, 1118, 1085, 1055, 1025, 1015 cm^{-1}; NMR (250 MHz) (CCl_4) δ 1.10 (s, 3 H), 1.30 (d, 3 H, J = 7 Hz), 2.44 (m, 2 H, C(1) and C(10) protons), 4.18 (br s, 1 H, C(4) H), 4.26 (AB q, 2 H, J = 8 Hz, $\Delta\nu_{AB}$ = 14 Hz, CH_2OCO), 4.46 (s, 2 H, $CH_2C_6H_5$), 5.76 (m, 1 H, C(3) olefinic proton), 5.84 (m, 1 H, C(2) olefinic proton), 7.24 (m, 5 H, C_6H_5).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.75; H, 7.39.

2-(3-Methoxy-1-methyl-2-propenyl)-1-methyl-5-(phenylmethoxy)-3-cyclopentenemethanol (15). To a solution of 129 mg (0.47 mmol) of lactone **14** in 4.0 mL of dry toluene cooled to −78 °C was added dropwise 1.08 mL of a 0.9 M solution of diisobutylaluminum hydride in toluene. After 15 min, the reaction was quenched at −78 °C with 0.3 mL of a saturated aqueous ammonium chloride solution. The reaction was diluted with 12 mL of ethyl acetate and warmed to room temperature. Anhydrous magnesium sulfate (2.0 g) was added directly and stirring was continued for 15 min. Filtration and evaporation of the solvent afforded 130 mg of lactol which was used directly in the next reaction.

A solution of 130 mg (0.47 mmol) of the above lactol in 2.0 mL of anhydrous benzene was added at room temperature to a benzene solution of (methoxymethylene)triphenylphosphorane (prepared from 923 mg (3.8 mmol) of (methoxymethyl)triphenylphosphonium chloride and 418 mg (3.8 mmol) of sodium *tert*-amylate in 12 mL of dry benzene). After 1 h at room temperature, the reaction was quenched by the addition of a saturated ammonium chloride solution. The aqueous layer was extracted with ether, and the combined organic extracts were dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo provided after chromatography on silica gel (elution with 2:1 hexanes–ether) 124 mg (87%) of pure enol ether **15** as an oil: IR (CCl_4) 3650, 3600–3200, 1650 cm^{-1}.

Keto Aldehyde 8. A solution of 118 mg (0.39 mmol) of enol ether **15** in 4.0 mL of tetrahydrofuran was treated with 0.15 mL of 1 N hydrochloric acid. After 1 h at room temperature, the reaction mixture was neutralized at 0 °C with powdered sodium bicarbonate and dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo afforded 100 mg of crude product which was chromatographed on silica gel. Elution with 1:1 ether–hexane gave 86 mg of pure aldehyde as a colorless oil [IR (CCl_4) 3650, 3600–3150, 2715, 1725 cm^{-1}] which was used directly in the next reaction.

To a solution of the above aldehyde (83 mg, 0.29 mmol) in 3.0 mL of dry ether cooled to −20 °C was added 1.0 mL of methyllithium (1 M in ether). After addition was complete the reaction mixture was warmed to 0 °C where stirring was continued for 30 min. The reaction was quenched by the addition of ice followed by a solution of saturated ammonium chloride. Isolation of the product by extraction with ether gave, after drying ($MgSO_4$) and evaporation of the solvent under reduced pressure, 75 mg of crude diol. Chromatography on silica gel employing ether yielded 50 mg (62%) of pure diol as a colorless oil [IR (CCl_4) 3640, 3550–3150 cm^{-1}] which was used directly in the next reaction.

To a suspension of 215 mg (1.0 mmol) of pyridinium chlorochromate and 165 mg (2.0 mmol) of sodium acetate in 10 mL of dry methylene chloride at room temperature was added a solution of 50 mg (0.16 mmol) of the above diol in 5.0 mL of methylene

chloride. After 30 min the reaction was quenched with ether (50 mL). Magnesium sulfate (5.0 g) was added to the reaction mixture. Filtration and evaporation of the solvent in vacuo gave 45 mg (90%) of crude keto aldehyde 8 which was homogeneous by TLC analysis [IR (CCl_4) 2700, 1720 cm^{-1}; NMR (CCl_4) δ 9.40 (s, 1 H, CHO), 7.21 (s, 5 H, C_6H_5), 5.80 (s, 2 H, CH = CH), 4.45 (br s, 3 H, C(5) H, CH_2O), 2.63 (m, 2 H, CH_2CO), 2.25 (m, 2 H, C(1) and C(10) protons), 2.03 (s, 3 H, $COCH_3$), 1.18 (s, 3 H, C(5) methyl), 0.91 (d, 3 H, J = 7 Hz, C(10) methyl)].

(1α,3aβ,4β,8aα)-3a,4,5,8a-Tetrahydro-4,8a-dimethyl-1-(phenylmethoxy)-6(1*H*)-azulenone (1). A solution of 44 mg (0.15 mmol) of keto aldehyde 8 in 3.0 mL of 5% potassium hydroxide–methanol solution was stirred at room temperature for 30 min. The reaction was quenched with an aqueous ammonium chloride solution. The product was extracted with ether. The combined ether layers were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded 40 mg of the intermediate aldol [R_f 0.15 (1:1 ether–hexane)], which was dissolved in 4 mL of benzene containing 1.0 mg of *p*-toluenesulfonic acid. After refluxing for 45 min, the reaction was quenched with powdered sodium bicarbonate, and the solvent was removed in vacuo. The crude hydroazulenone 1 (35 mg) was chromatographed on silica gel. Elution with 1:4 ether–hexane gave 30 mg (72% overall) of pure 1 as a crystalline substance: mp 77–78 °C; IR (CCl_4) 3070, 3025, 2970, 2940, 2900, 2870, 2825, 1670, 1605, 1458, 1385, 1368, 1348, 1305, 1260, 1230, 1215, 1168, 1140, 1085 1055, 1030 cm^{-1}; NMR (250 MHz) (CCl_4) δ 7.28 (br s, 5 H), 6.17 (AB q, 2 H, J = 11.5 Hz, $\Delta\nu_{AB}$ = 185.6 Hz, C(6) and C(7) olefinic protons), 5.77 (s, 2 H, C(2) and C(3), olefinic protons), 4.60 (AB q, 2 H, J = 12.1 Hz, $\Delta\nu_{AB}$ = 33.0 Hz, CH_2O), 4.52 (s, 1 H), 2.97 (dd, 1 H, J = 8.2 and 12.1 Hz), 2.30–2.15 (m, 2 H), 2.01 (heptet, 1 H), 1.16 (s, 3 H), 1.13 (d, 3 H, J = 6.6 Hz); high-resolution mass spectrum, m/e 282.16089 (calcd 282.16198). An analytical sample was prepared by recrystallization from hexanes–ether, mp 79–80 °C.

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.88; H, 7.74.

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Registry No. 1, 68241-54-3; 7, 63598-48-1; 8, 73198-39-7; 9, 73198-40-0; 10, 73198-41-1; 10, free acid, 73210-16-9; 11, 73198-42-2; 13 methyl ester, 73198-43-3; 13, 73198-44-4; 14, 73245-79-1; 14, lactol derivative, 73245-80-4; 15, 73198-45-5; 15, aldehyde derivative, 73198-46-6.

Synthesis of Tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene through Acid-Catalyzed Dehydration–Rearrangement of *exo*-Norbornane-2-spiro-1′-cyclopentan-2′-ol

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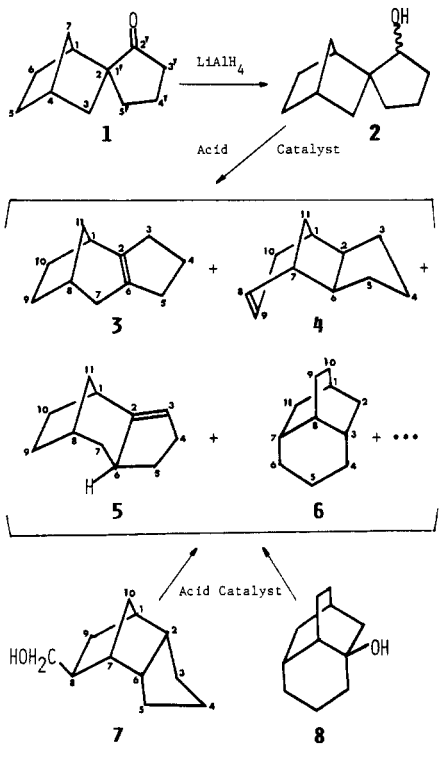
Tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene (3) contains the skeleton of β-patchoulene (1,*exo*-5,11,11-tetramethyl-3),[1] a naturally occurring sesquiterpene. This sesquiterpene is one of the constituents of patchouli oil, an essential oil which is indispensable to the perfume industry because of its characteristic wood-green odor. The structural similarity of 3 to β-patchoulene suggested to us the possibility that some appropriate reactions of 3 would lead to derivatives with desirable fragrance properties. The study[2] of the reactivity of 3 is also of interest[3] from an academic viewpoint, since the compound has a skeleton that has been found only rarely among natural as well as synthetic substances.[3,4]

Scheme I



The tricycloundecene 3 was prepared for the first time by us through phosphoric acid catalyzed dehydration–rearrangement of some tricycloundecanols and tricyclodecylcarbinols.[5] Products of these reactions, however, were distributed among a variety of isomeric tricyclic olefins and alkanes, of which the desired olefin 3 amounted to less than 70%. Herein we report a better synthetic route to the olefin 3 by the dehydration–rearrangement of *exo*-norbornane-2-spiro-1′-cyclopentan-2′-ol (2) (Scheme I). A number of reviews of the dehydration–rearrangement of bicyclic spiro alcohols to internal olefins have been compiled,[6] but no precedent seems to exist for tricyclic spiro alcohols. Formation of 3 from 2 is thus regarded as the first example of a tricyclic analogue of the rearrangement of cyclopentane-1-spiro-1′-cyclopentan-2′-ol to 2,3,4,5,6,7-hexahydroindene.

The starting tricyclic spiro alcohol 2 was prepared by lithium aluminum hydride reduction of the corresponding spiro ketone 1, which was synthesized as described by

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