**2a** is the kinetic product ratio.

It thus appears that the favored approach of diene and dienophile occurs with the trifluoromethyl group in an endo orientation. While those explanations which invoke $\pi$-orbital overlap do not apply,[1,3a,4,14] the results may be explained by steric interaction between the trifluoromethyl group and the methylene protons of cyclopentadiene in the exo transition state,[6,7,15] electrostatic effects,[9] or secondary orbital overlap effects.[3b,5,16]

## Experimental Section

**General Methods.** The NMR experiments were carried out in chloroform-*d*. The $^{19}$F spectra were obtained on a Varian T-60 spectrometer equipped with a wide-sweep accessory and operating at 56.4 MHz. Chemical shifts are reported in parts per million downfield (negative values upfield) from an external CFCl$_3$ standard; coupling constants are in hertz. The $^1$H NMR spectra were obtained on a Nicolet NIC-360-WB spectrometer operating at 360 MHz in a pulsed Fourier transform mode. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane standard; coupling constants are in hertz. Preparative and analytical gas chromatography were carried out on a Perkin-Elmer 3920B chromatograph utilizing a 2 m × 6 mm column packed with 3% OV-17 on 60/80-mesh Chromosorb W (helium carrier at 60 mL/min) and a thermal-conductivity detector. Cyclopentadiene was prepared by cracking[17] technical grade dicyclopentadiene from Eastman Organic Chemicals; 3,3,3-trifluoropropene was purchased from Fairfield Chemical Co.

***endo*- and *exo*-5-(Trifluoromethyl)bicyclo[2.2.1]hept-2-ene (2a and 3a).** A mixture of 3.3 g (0.05 mol) of freshly cracked, cold cyclopentadiene and 4.8 g (0.05 mol) of condensed 3,3,3-trifluoropropene were combined with 0.05 g of hydroquinone in a heavy-walled Pyrex tube at −78 °C. The tube was sealed and heated in a 135 °C oil bath behind a safety shield for 84 h. After being cooled to −78 °C, the tube was opened. A small amount of volatile material boiled away upon warming to room temperature, whereupon the cloudly liquid was transferred to a still equipped with a 10-cm Vigreux column. Distillation at 130 torr gave 5.66 g (70%) of a colorless liquid at 66 °C [lit.[9] bp 119 °C (760 torr)]: $^{19}$F NMR $\delta$ −66.2 (d, $J$ = 20.3, 79%), −68.1 (d, $J$ = 20.3, 21%); partial $^1$H NMR shown in figure 1, complete spectrum included as supplementary material. In a separate experiment three samples at 0.1 this scale were sealed in small tubes and heated at 135 °C for 5, 17, and 40 h. When the tubes were cooled and opened, $^{19}$F NMR analysis showed only the signals observed previously, and in each case the ratio was (80 ± 2):(20 ± 2). Separation of isomers was carried out by preparative gas chromatography at 80 °C. The minor isomer appeared at 5.4 min, and the major isomer appeared at 6.9 min; the minor isomer was collected from 4.7 to 5.7 min, and the major isomer was collected from 6.3 to 7.6 min. Analytical gas chromatography showed each isomer to be >95% pure. Small samples of each isomer were sealed in melting point tubes and heated in a 135 °C oil bath for 22 h. After the samples were cooled, gas chromatographic analysis showed each isomer to be unchanged.

**Registry No.** **1a**, 677-21-4; **2a**, 84029-15-2; **3a**, 84029-16-3; cyclopentadiene, 542-92-7.

**Supplementary Material Available:** Figure 2 containing a $^1$H NMR spectrum of a mixture of compounds **2a** and **3a** (1 page). Ordering information is given on any current masthead page.

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(14) Calculations on trifluoromethyl-substituted cations reveal little donation of electron density by the trifluoromethyl group into a vacant $\pi$ orbital. Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6563.

(15) A comparison with the reaction of propene with cyclopentadiene is of interest since this reaction is reported to give an endo/exo ratio of 3.1:1. It should be noted that the exact numerical value of this ratio is in some doubt and that no effort was made to determine if this represents a kinetic or a thermodynamic ratio. Belikova, N. A.; Berezkin, V. G.; Platé, A. F. *Zh. Obshch. Khim.* **1962**, *32*, 1942.

(16) Stephenson, L. M.; Grdina, M. J.; Organopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419.

(17) Korach, M.; Nielson, D. R.; Rideout, W. H. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 414.

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# Efficient Synthesis of Methyl 3-Oxo-2,6,6-trimethylcyclohex-1-ene-1-carboxylate, an A-Ring Intermediate for (±)-Strigol

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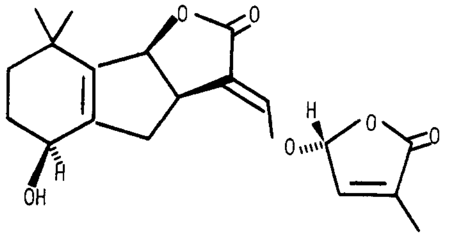
Strigol (**1**) is a highly potent seed germination stimulant for witchweed, a harmful parasitic plant that attacks numerous gramineous crops including corn, sorghum, sugar cane, and rice.[1] Natural strigol is available only in small quantities by tedious isolation from root exudates of cotton, and therefore, efficient chemical synthesis of **1** is prompted. Several partial[2] and two total syntheses[3,4] of (±)-strigol have been reported. The elegant synthesis of **1** by Sih and co-workers has provided gram quantities for biological evaluation. However, there is need to further improve the synthesis to a multigram scale to provide sufficient material for testing strigol as a control agent in witchweed infested fields.



strigol (**1**)

We describe a simple, efficient preparation of methyl 3-oxo-2,6,6-trimethylcyclo-1-ene-1-carboxylate **7** (see Scheme I), a key A-ring intermediate used in the Sih synthesis of **1**. Regioselective epoxidation[5] of commercially available $\alpha$-ionone **2** with *m*-chloroperoxybenzoic acid gave a mixture of isomeric epoxides **3a** and **3b** in 98% yield. Oxidation[6] of the isomeric mixture **3a,b** with sodium metaperiodate and a catalytic amount of potassium permanganate in aqueous 2-methyl-2-propanol resulted in cleavage of the enone functionality to provide the epoxycarboxylic acid **4**. Direct esterification of crude **4** with iodomethane in acetone containing excess potassium carbonate gave epoxy ester **5** in 60% overall yield from **2**. Treatment of **5** with sodium methoxide in methanol resulted in epoxide opening to the allylic alcohol **6** in 96% yield. Oxidation of **6** with pyridinium chlorochromate gave the desired enone **7** in 85% yield.

The synthesis of **7** is accomplished in five steps from readily available and relatively inexpensive $\alpha$-ionone with a 48% overall yield. The synthesis utilizes operationally simple procedures, involves no chromatography, and is

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(1) (a) Cook, C. E.; Whichard, L. P.; Turner, B.; Wall, M. E.; Egley, G. E. *Science (Washington, D.C.)* **1966**, *154*, 1189. (b) Cook, C. E.; Whichard, L. P.; Wall, M. E.; Egley, G. E.; Croggon, P.; Luhan, P. A.; McPhail, A. T. *J. Am. Chem. Soc.* **1972**, *94*, 6198.

(2) (a) Dolby, L. J.; Hanson, G. *J. Org. Chem.* **1976**, *41*, 563. (b) Cooper, G. K.; Dolby, L. J. *Ibid.* **1979**, *44*, 3414. (c) Pepperman, A. B. *Ibid.* **1981**, *46*, 5039.

(3) (a) Heather, J. B.; Mittal, R. S. D.; Sih, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 1976; (b) **1976**, *98*, 3661.

(4) (a) MacAlpine, G. A.; Raphael, R. A.; Shaw, A.; Taylor, A. W.; Wild, H. J. *J. Chem. Soc., Chem. Commun.* **1974**, 834; (b) *J. Chem. Soc., Perkins Trans.* **1976**, *1*, 410.

(5) Modified epoxidation procedure of the following: von P. Karren; Sturzinger, H. *Helv. Chim. Acta* **1946**, *29*, 1829.

(6) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701.

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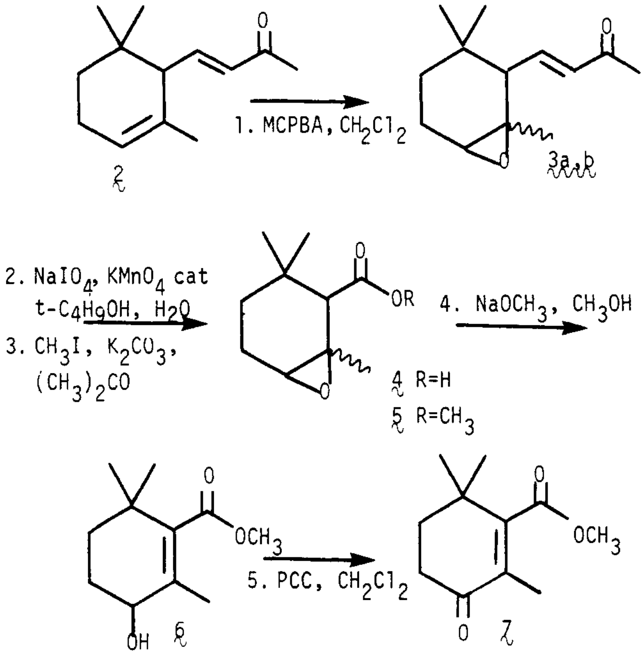
Scheme I



suitable for large-scale preparation.

## Experimental Section[7]

**4-(2,6,6-Trimethyl-2,3-epoxycyclohexan-1-yl)-3-buten-2-one (3a,b).**[5] To a rapidly stirred solution of 100 g (0.52 mol) of $\alpha$-ionone in dichloromethane (1.35 L) was added 108 g (0.62 mol) of *m*-chloroperoxybenzoic acid, at 0 °C. The solution was kept between 0 and 5 °C for 3 h. The solids were removed by suction filtration and washed with dichloromethane (2 × 50 mL). The filtrate was washed with aqueous 5% $Na_2CO_3$ (500 mL) and aqueous saturated NaCl (200 mL), dried over $MgSO_4$, filtered, and evaporated to give 108 g (98%) of a mixture of isomers **3a** and **3b** (6:1 ratio). Major isomer **3a**: IR (neat) 2960 (s), 1675 (s), 1620 (m), 1360 (s), 1250 (s), 985 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.74 (3 H, s), 0.90 (3 H, s), 1.20 (3 H, s), 1.3–2.1 (5 H, m), 2.24 (3 H, s), 3.03 (1 H, 5, $J$ = 2 Hz), 6.10 (1 H, d, $J$ = 18 Hz), 6.70 (1 H, dd, $J$ = 10 Hz, $J$ = 18 Hz).

**2,3-Epoxy-2,6,6-trimethylcyclohexane-1-carboxylic Acid (4).** To a solution of 232 g (1.08 mol) of sodium metaperiodate in water (5 L) was added 3.42 g (0.022 mol) of potassium permanganate. The solution was stirred at room temperature for 30 min, and then 17 g (0.123 mol) of potassium carbonate, 2-methyl-2-propanol (2.5 L), and 25 g (0.12 mol) of **3a,b**, obtained from the previous reaction, were added in succession. The reaction mixture was stirred for 48 h at room temperature. Then ethylene glycol (25 mL) was added to quench any excess periodate, and the solution was allowed to stir for 3 h. The solids were removed by suction filtration and washed with water (2 × 50 mL). The filtrate was concentrated on a rotary evaporator to 2.5 L and extracted with ether (2 × 300 mL). The aqueous layer was acidified to pH 2 with 1 N HCl and extracted with ethyl acetate (4 × 500 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give **4** as a yellow oil: 16.3 g (75%); IR (neat) 3450 (br), 2960 (s), 1725 (s), 1370 (m), 1250 (br), 1040 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.0 (3 H, s), 1.50 (3 H, s), 1.7–2.1 (4 H, m), 2.55 (1 H, s), 3.15 (1 H, t, $J$ = 2 Hz), 9.40 (1 H, br s).

**Methyl 2,3-Epoxy-2,6,6-trimethylcyclohexane-1-carboxylate (5).** To a stirred solution of 12 g (0.09 mol) of anhydrous potassium carbonate in dry acetone (50 mL) was added 16 g of crude **4** from the previous reaction and 30 g (0.21 mol) of iodomethane. The mixture was stirred at 25 °C for 22 h. The excess iodomethane and acetone were removed on a rotary evaporator. The solid residue was suspended in aqueous 10% $NaHCO_3$ (60 mL) and extracted with ether (4 × 50 mL). The combined organic layers were washed with water (50 mL) and aqueous saturated NaCl (20 mL), dried over $Na_2SO_4$, and evaporated to give 9.3 g (60%) of **5** as a pale yellow oil: IR (neat) 2960 (s), 1740 (s), 1430 (m), 1240 (m), 1150 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (3 H, s), 0.95 (3 H, s), 1.39 (3 H, s), 1.7–2.0 (4 H, m), 2.45 (1 H, s), 3.0 (1 H, t, $J$ = 2 Hz), 3.72 (3 H, s).

**Methyl 3-Hydroxy-2,6,6-trimethylcyclohex-1-ene-1-carboxylate (6).**[3b] To a stirred solution of 1.0 g (0.043 mol) of sodium metal dissolved in methanol (100 mL) was added dropwise 9.0 g of **5** in 5 mL of methanol under a $N_2$ atmosphere. The solution was refluxed for 5 h, cooled to room temperature, and neutralized with 1 N HCl. The excess methanol was removed on a rotary evaporator, and the aqueous residue was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with aqueous saturated NaCl solution (20 mL), dried over $Na_2SO_4$, filtered, and evaporated to give 8.7 g (96%) of **6**: IR (neat) 3420 (br), 2960 (s), 1720 (s), 1430 (m), 1290 (m), 1230 (br), 1060 (m), 1020 (br), 900 (m), 725 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.05 (3 H, s), 1.10 (3 H, s), 1.2–2.1 (4 H, m), 1.78 (3 H, s), 2.2 (1 H, br s), 3.75 (3 H, s), 4.2 (1 H, m).

**Methyl 3-Oxo-2,6,6-trimethylcyclohex-1-ene-1-carboxylate (7).**[3b] To a stirred solution of 13 g (0.065 mol) of pyridinium chlorochromate in dry dichloromethane (25 mL) was added 8 g of **6**. After 4 h at room temperature, ether (200 mL) was added, and the solvent was decanted. The residue was triturated with ether (3 × 20 mL), and the solids were removed by filtration. The organic extracts were combined and evaporated at reduced pressure. The residue was then distilled at reduced pressure to give 6.9 g (85%) of pure **7**: bp 75 °C (0.02 mmHg). The IR and $^1H$ NMR spectral data of **7** were in accord with those previously reported.[3b] Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.41; H, 8.01.

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(7) Infrared spectra were obtained on a Perkin-Elmer Model 267 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Perkin-Elmer Model R 32 at 90 MHz, with $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Chemical shifts are given in parts per million ($\delta$) downfield from tetramethylsilane, and relative areas, multiplicities, and coupling constants in Hz are reported in parentheses. Microanalysis was performed by the Microanalytical Laboratory in the Department of Chemistry, Purdue University. All compounds prepared showed satisfactory low-resolution mass spectra.