Novel Base-Induced [1,2]-Acyl Shift of Allylic Esters of Cyclopropanecarboxylic Acids

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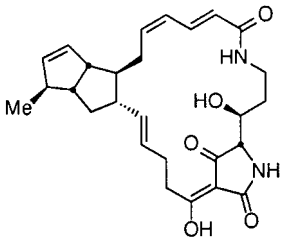
Introduction and Background

The cylindramides are marine natural products containing a tetramic acid lactam and an interesting bicyclo[3.3.0] ring system.[1] Cylindramide **1** has shown strong cytotoxicity against cancer cell lines (IC_{50} of 0.8 mg/mL against B16 melanoma cells) while several other natural products with structures similar to that of cylindramide have interesting biological properties.[2−5] Our synthetic studies on the cylindramides focused on the use of a novel, tandem radical rearrangement to synthesize the bicyclo[3.3.0]octane ring system of the natural product.

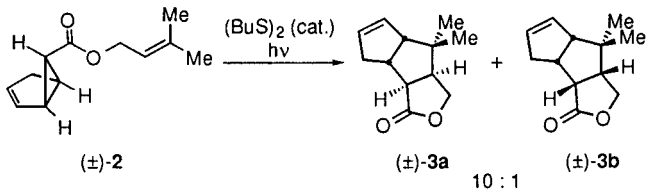


cylindramide (1)

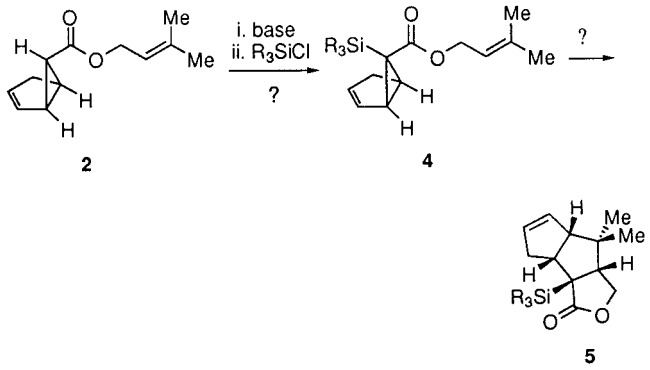
Previous work on a model system had validated the radical rearrangement that we planned to use in preparing the bicyclic core.[6,7] Thus, treatment of the ester (±)-**2** with the thiolate radical generated from dibutyl disulfide led to the tricyclic compounds (±)-**3a** and (±)-**3b** (Scheme 1). The major product of the cyclization, however, was compound (±)-**3a**, which contained the undesired cis-anti-cis ring geometry, rather than the compound (±)-**3b** with the desired cis-syn-cis ring geometry.

Nevertheless, we reasoned that a sterically large, removable substituent α to the ester carbonyl could conceivably direct the cyclization to give the cis-syn-cis ring geometry as in the tricyclic compound **5**. We therefore decided to prepare and study the model system **4**, in which a silyl group α to the ester carbonyl might encourage the formation of the desired ring geometry. We proposed that **4** could be easily prepared from **2** as shown in Scheme 2 by silylation of the ester enolate since

Scheme 1



Scheme 2



silylations of analogous cyclopropane carboxylates on carbon had been reported earlier by Larson.[8]

Results and Discussion

Treatment of the ester (±)-**2** with base followed by silylating agents (trimethylsilyl chloride, methyldiphenylsilyl chloride) led to complex mixtures of products. To determine whether we were, in fact, generating the enolate, we attempted to trap the enolate with more reactive electrophiles. Surprisingly, the only products cleanly isolated from these reactions were the rearranged products (±)-**6**, in which the ester moiety had rearranged into an α-hydroxyketone (Table 1). In all cases, the products **6** were obtained as a 1:1 mixture of diastereomers.

The structures of the products **6** suggested a [1,2]-shift of the acyl group (Scheme 3) which could occur from the allylic anion **A** by a normal [1,2]-Wittig rearrangement,[9] e.g., via the radical intermediate **B**, to give the alkoxide **C**. However, it is also possible that an intramolecular nucleophilic addition took place wherein the allylic anion **A** attacked the ester carbonyl to give the oxiranol anion **D**, which then underwent ring opening by breaking the C−O bond to give the alkoxide **C**. Deprotonation of the alkoxide **C** would then give the dianion **E**, an enediolate, which could react with electrophiles to give the observed products **6**.

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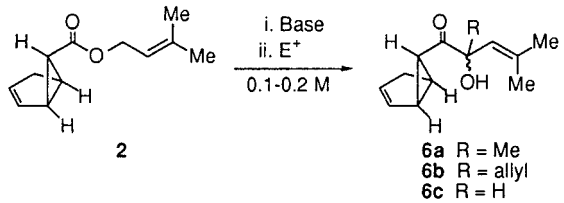
Table 1

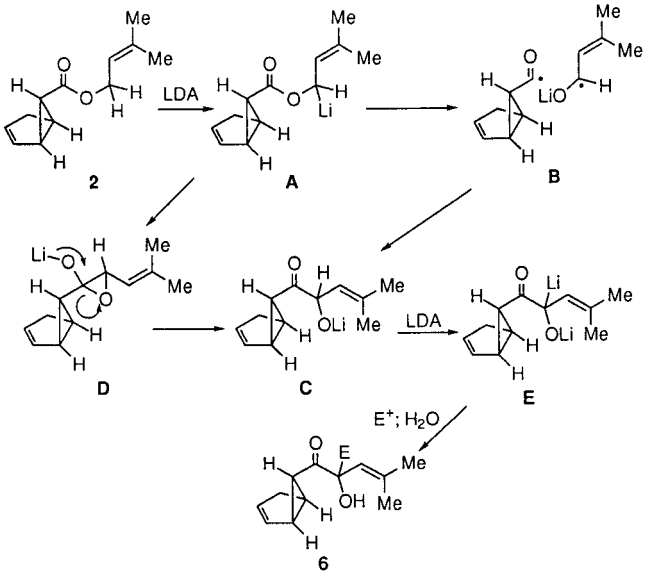


base	temp, °C	E^+	solvent	modifications	products
LDA	−78 to rt to −78	MeI	THF		**6a**, 25%
NaH		rt	MeI	DMF	recovered **2**
LDA	−78 to rt to −78	allyl bromide	THF		**6b**, 28%
KHMDS	−78 to rt to −78	allyl bromide	THF		recovered **2**
LDA	−78 to rt to −78	H_2O	THF		**6c**, 23%
LDA	−78 to rt to −78	H_2O	THF	*t*-BuLi	**6c**, 18%
LDA	0 °C	H_2O	THF	reverse addn	**6c**, 18%
LDA	−78 to rt to −78	H_2O	Et_2O		**6c**, 46%
LDA		rt	H_2O	THF	
LDA	0 °C		H_2O		THF/dioxane

Table 2

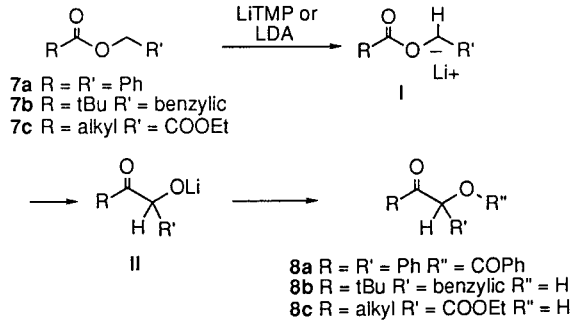
base	temperature, °C	modifications	products
LDA	−78 to 0 to −78		**12**, 22%
LDA	−78 to 0 to −78	LiCl (4 equiv)	**12**, 27%
NaH	−78 °C to rt	18-crown-6	recovered **11**
KH	−78 °C to rt	18-crown-6	decomposition
KHMDS	−78 to 0 to −78		recovered **11**
KHMDS	−78 to 0 to −78	18-crown-6	recovered **11**

Scheme 3

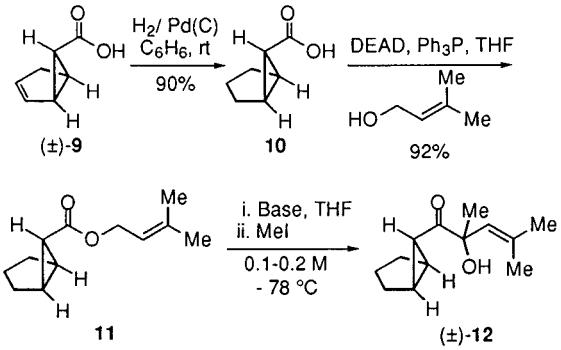


Similar rearrangements have been reported in the literature.[10] For example, benzyl benzoate **7a** on treatment with LiTMP afforded benzoin benzoate **8a**; benzylic pivalate **7b** when treated with LDA furnished the α-hydroxyketone **8b**; and alkyl α-acyloxyacetates **7c** gave the α-hydroxy-*β*-keto esters **8c** on treatment with LDA (Scheme 4). In the first two cases, there is no possibility of forming the normal anion α to the ester since there are no α-protons present, while in the last case the difference in acidity greatly favors the anion α to both the ester and the acyloxy group. In our case destabilization of the anion of the cyclopropanecarboxylate, due to I strain, presumably causes the reaction to occur via the 1,2-shift pathway rather than via simple deprotonation of the ester. We have no evidence to support either of the two mechanistic possibilities although the oxiranol anion intermediate has been suggested to be involved in similar rearrangements[10c] and thus may be the most likely intermediate in the present case.

Scheme 4



Scheme 5

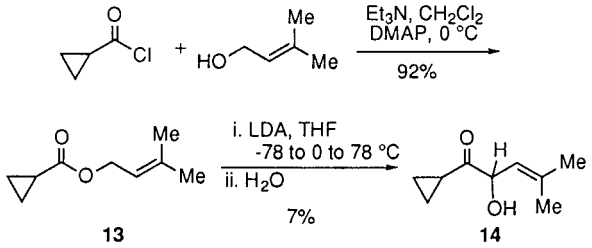


Since the compounds **6** were isolated from complex product mixtures, we reasoned that we could better study the reaction mechanism by removing the cyclopentene olefin, thus reducing the number of diastereomerically different products and facilitating their identification (Scheme 5). We therefore prepared the saturated acid **10** by reduction of the unsaturated acid **9** followed by a Mitsunobu reaction[11] to give ester **11** and examined its reactions with base and methyl iodide. Unfortunately,

(10) a) Upton, C. J.; Beak, P. *J. Org. Chem.* **1975**, *40*, 1094. (b) Zajc, B.; Lakshman, M. K. *J. Org. Chem.* **1995**, *60*, 4936. (c) Lee, S. D.; Chan, T. H.; Kwon, K. S. *Tetrahedron Lett.* **1984**, *25*, 3399. (d) Rubin, M. B.; Inbar, S. *J. Org. Chem.* **1988**, *53*, 3355. (e) Eichinger, P. C. H.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 1949.

(11) Mitsunobu, O. *Synthesis* **1981**, 1.

Scheme 6



the reactions of the ester **11** gave product mixtures that were similar in complexity to those obtained from the ester **2**. The reactions of the esters **2** and **11** do, however, reveal the important role of the base. Sodium hydride did not effect the expected rearrangement of **11**, even in the presence of 18-crown-6. Similarly, potassium hexamethyldisilazane did not cause the rearrangement. These studies suggest that the strength of the base may be important in determining whether the reaction does indeed occur.

To ascertain whether the bicyclic[3.1.0] cores of the esters **2** and **11** played a role in the rearrangement, we next prepared the less elaborate ester **13** (Scheme 6). As anticipated, the ester **13** also participated in this novel [1,2] shift, although the rearranged product **14** was isolated only in low yield.

In conclusion, we have discovered a novel base-induced rearrangement of allylic esters of cyclopropane carboxylates. Treatment of these esters with bases of sufficient strength causes the formation of the allylic anion (homoenolate) which undergoes a [1,2]-acyl shift, leading to the formation of the enolate of the corresponding α-hydroxyketones, which on addition of electrophiles affords the trapped products in fair yield.

Experimental Section

General. ^{1}H NMR spectra were recorded at 360.134 MHz, 400.130 MHz, or 500.130 MHz and are so indicated. ^{13}C NMR were recorded at 90.556, 100.613, or 125.773 MHz and are so indicated. ^{1}H NMR and ^{13}C NMR data are reported in parts per million (δ) downfield from tetramethylsilane. Infrared spectra were recorded on an FTIR as a film. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} 0.2 mm plates. Flash chromatography was carried out using ICN Biomedicals silica gel 60 (230−400 mesh). Solvent systems are reported as volume percent mixtures. All inorganic solutions are aqueous, and concentrations are indicated in percent weight, except for saturated sodium chloride and saturated sodium bicarbonate. The following solvents and reagents were distilled from the indicated agent under argon: tetrahydrofuran (THF) and diethyl ether from sodium benzophenone ketyl; dichloromethane and triethylamine from calcium hydride. All reactions were performed under argon unless otherwise noted.

(±)-(3-Methyl-2-butenyl) 1α,5α,6α-bicyclo[3.1.0]hex-2-ene-6-carboxylate, 2. The 1α,5α,6α-bicyclo[3.1.0]hex-2-ene-5-carboxylic acid (**9**)[12] (0.25 g, 2.0 mmol) was weighed into an air-dry 25 mL flask. The sample was put under argon, and THF (7 mL) and triethylamine (0.28 mL, 2.0 mmol) were added. 2,4,6-Trichlorobenzoyl chloride[13] (0.32 mL, 2.0 mmol) was added, causing a white precipitate to form. 4-(*N*,*N*-Dimethylamino)-pyridine (DMAP, 0.27 g, 2.2 mmol) was added, followed by 3-methyl-2-buten-1-ol (0.21 mL, 2.0 mmol). After the reaction had stirred for 16 h at room temperature, the reaction was diluted with water and ether. The aqueous layer was removed, and the organic layer was washed with 10% potassium dihydrogen-phosphate solution, saturated sodium bicarbonate solution, and brine. The organic solution was dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel (6% ethyl acetate in hexanes) provided the desired ester **2** as a colorless oil (0.335 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.91 (1H, m), 5.53 (1H, m), 5.34 (t, J = 7.2 Hz, 1H), 4.55 (d, J = 7.2 Hz, 2H), 2.71−2.18 (m, 4H), 1.75 (s, 3H), 1.70 (s, 3H), 0.98 (dd, J = 2.7, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 138.9, 132.0, 130.3, 118.6, 61.2, 36.1, 34.4, 30.3, 26.1, 25.7, 17.9. IR (neat): 3063, 2973, 2911, 1723, 1445 cm^{-1}.

(±)-6-(2-Hydroxy-2,4-dimethyl-1-oxo-3-pentenyl)-1α,5α,6α-bicyclo[3.1.0]hex-2-ene, 6a. The following is a representative procedure for the formation of the compound **6a** from **2**. The ester **2** (150 mg, 0.79 mmol) was weighed into an oven-dried 10 mL flask. The flask was flushed with argon, and THF (2 mL) was added. The solution was stirred and cooled to −78 °C, at which point 3.3 mL (1.7 mmol) of a freshly prepared 2.6 M solution of lithium diisopropylamide (LDA; 0.50 mL diisopropylamine + 1.2 mL (2.6 M) *n*-butyllithium + 4.3 mL THF, mix at 0 °C) was added. The cold bath was removed, and the reaction was allowed to warm to room temperature over 15 min. The reaction was cooled to − 78 °C, and methyl iodide (0.2 mL, 3.2 mmol) was added. The reaction was allowed to warm to room temperature, diluted with ether, then washed with 10% potassium dihydrogenphosphate solution. The organic layer was removed, washed with brine, dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel (10% ethyl acetate/hexanes) provided the hydroxy ketone **6a**, as a colorless oil (39.6 mg, 25%). The hydroxy ketone **6a** occurred as an inseparable 1:1 mixture of diastereomers. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 5.95 (m, 2H), 5.60 (m, 2H), 5.40 (m, 2H), 4.15 (s, 1H), 4.14 (s, 1H), 2.75−2.65 (m, 2H), 2.65−2.45 (m, 2H), 2.42 (m, 1H), 2.40−2.20 (m, 2H), 1.74 (m, 6H), 1.68 (br s, 1H), 1.58 (br s, 6H), 1.44 (s, 3H), 1.42 (s, 3H), 1.36 (m, 2H). ^{13}C NMR (CD_2Cl_2, 125 MHz) δ: 212.21, 212.19, 140.15, 140.08, 132.61, 132.58, 131.46, 131.38, 126.2, 126.1, 77.4, 77.3, 38.7, 38.3, 36.9, 36.8, 35.5, 35.3, 30.7, 30.3, 28.5, 28.2, 26.72, 26.68, 18.77, 18.75. IR (neat) 3462, 3063, 2975, 2911, 1682, 1449 cm^{-1}.

(±)-6-(2-Hydroxy-4-methyl-1-oxo-2-(2-propenyl)-3-pentenyl)-1α,5α,6α-bicyclo[3.1.0]hex-2-ene, 6b. The following is a representative procedure for the formation of **6b** from **2**. The ester **2** (106 mg, 0.56 mmol) was weighed into an oven-dried 10 mL flask. The flask was flushed with argon, and THF (2 mL) was added. The solution was stirred and cooled to −78 °C, at which point a freshly prepared 0.5 M LDA solution (2.4 mL, 1.2 mmol) was added. The reaction was warmed to room temperature over 20 min and then cooled to −78 °C. Allyl bromide (100 μL, 1.1 mmol) was added, and the reaction was allowed to warm to room temperature. The reaction was diluted with ether and then washed with 10% potassium dihydrogenphosphate solution until the pH of the aqueous phase was <6. The organic solution was dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel (3% ethyl acetate in hexanes) provided the hydroxy ketone **6b** as an inseparable 1:1 mixture of diastereomers (35.8 mg, 28%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 5.95 (m, 2H), 5.70 (m, 2H), 5.62 (m, 2H), 5.38 (m, 2H), 5.11 (m, 2H), 5.09 (br s, 2H), 4.02 (s, 1H), 4.00 (s, 1H), 2.7 (m, 2H), 2.6−2.0 (m, 10H), 1.75 (m, 6H), 1.57 (m, 6H), 1.38 (m, 2H). ^{13}C NMR (CD_2Cl_2, 125 MHz) δ: 211.1, 210.9, 140.7, 140.6, 132.95, 132.91, 132.62, 132.61, 131.5, 131.4, 124.9, 124.8, 118.82, 118.78, 80.2, 80.1, 45.5, 45.3, 38.9, 38.3, 37.0, 36.9, 35.9, 35.7, 30.8, 30.2, 26.81, 26.76, 18.94, 18.92. IR (neat) 3457, 3065, 2977, 1682, 1435 cm^{-1}.

(±)-6α-(2-hydroxy-1-oxo-3-pentenyl)-1α,5α-bicyclo[3.1.0]-hex-2-ene, 6c. The following is a representative procedure for the formation of **6c** from **2**. The ester **2** (104 mg, 0.545 mmol) was weighed into an oven-dried 10 mL flask. The flask was flushed with argon, and THF (2 mL) was added. The solution was stirred and cooled to −78 °C, at which point 2.4 mL (1.2 mmol) of a freshly prepared 2.6 M solution of lithium diisopropylamide (LDA; 0.50 mL diisopropylamine + 1.2 mL of 2.6 M *n*-butyllithium + 4.3 mL THF, mix at 0 °C) was added. The cold bath was removed, and the reaction was allowed to warm to room temperature over 15 min. The reaction was then quenched with 10% potassium dihydrogenphosphate solution. The reaction was diluted with ether and washed with 10% potassium dihydrogenphosphate solution. The organic layer was removed,

(12) Meinwald, J.; Labana, S. S.; Chadha, S. *J. Am. Chem. Soc.* **1963**, *85*, 582.

(13) Inanaga, J.; Hirata, K.; Saeki, H.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1989.

washed with brine, dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel (15% ethyl acetate/hexanes) provided the hydroxy ketone, **6c**, as a colorless oil (23.5 mg, 23%) and as an inseparable 1:1 mixture of diastereomers. ^{1}H NMR (360 MHz, $CDCl_3$) δ: 5.96 (m, 2H), 5.62 (m, 2H), 5.02 (m, 2H), 4.95 (m, 2H), 3.78 (s, 1H), 3.77 (s, 1H), 2.71 (m, 2H), 2.55 (m, 2H), 2.50−2.25 (m, 4H), 1.84 (s, 6H), 1.81 (s, 6H), 1.23 (s, 1H), 1.22 (s, 1H). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 209.0, 208.8, 139.9, 139.8, 132.3, 132.2, 131.2, 131.1, 121.4, 121.1, 74.4 (2 C's), 38.5, 38.2, 36.6, 36.5, 35.5, 35.2, 30.2, 29.9, 25.9 (2 C's), 18.6, 18.5. IR (neat) 3459, 3063, 2973, 2913, 1690, 1618, 1445 cm^{-1}.

(±)-1α,5α,6α-Bicyclo[3.1.0]hexane-6-carboxylic acid, 10. The carboxylic acid **9** (2.95 g, 24 mmol) was weighed into a 50 mL flask. The flask was flushed with argon, and benzene (25 mL) was added. Palladium on carbon (5%, 0.5 g) was added to the reaction, and the flask was flushed with hydrogen from a balloon. The balloon was replaced as it lost pressure, and the reaction was stirred at room temperature until ^{1}H NMR of aliquots taken from the reaction showed that the reaction was complete. The reaction was filtered through Celite, and then 100 mL of a saturated sodium bicarbonate solution was added. The mixture was shaken in a separatory funnel, and the organic layer was discarded. The aqueous phase was acidified to pH 1 using 3 M hydrochloric acid and then extracted with ether. The organic solution was dried ($MgSO_4$), filtered, and concentrated to give the acid **10** as a waxy solid (2.68 g, 90%). ^{1}H NMR (360 MHz, $CDCl_3$) δ: 12.0−10.0 (br s, 1H), 1.93 (br s, 2H), 1.85 (dd, J = 12.6, 8.1 Hz, 2H), 1.77 (dd, J = 20.9, 11.2 Hz, 2H), 1.61 (dt, J = 13.4, 8.1 Hz, 1H), 1.39 (t, J = 2.8 Hz, 1H), 1.08 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 181.0, 29.6, 27.2, 21.2, 20.0. IR (neat) 3050, 2955, 2867, 2760, 1690, 1445 cm^{-1}.

(±)-(3-Methyl-2-butenyl) 1α,5α,6α-bicyclo[3.1.0]hexane-6-carboxylate, 11. Triphenylphosphine (2.1 g, 7.9 mmol) and the carboxylic acid **10** (0.50 g, 4.0 mmol) were weighed into an oven-dried 25 mL flask. The flask was flushed with argon, and THF (8 mL) was added, followed by 3-methyl-2-buten-1-ol (0.45 mL, 4.4 mmol). The reaction was stirred and kept at room temperature using a water bath. Diethyl azodicarboxylate (DEAD, 1.25 mL, 7.9 mmol) was added dropwise, causing the solution to turn orange. After 1 h, the solution was concentrated onto silica gel and subjected to flash chromatography over silica gel (20% ethyl acetate/hexanes). The resulting solution was concentrated briefly by rotary evaporation, followed by Kugelrohr distillation (1 mmHg, collect at 0 °C), providing the ester **11** as a colorless oil (0.71 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.33 (br t, J = 7.2 Hz, 1H), 4.53 (d, J = 7.2 Hz, 2H), 1.85 (br s, 2H), 1.85−1.65 (m, 4H), 1.75 (s, 3H), 1.69 (s, 3H), 1.58 (dt, J = 13.4, 8.0 Hz, 1H), 1.39 (t, J = 2.9 Hz, 1H), 1.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 174.2, 138.8, 118.8, 61.1, 28.7, 27.2, 25.7, 21.3, 20.1, 18.0. IR (neat) 2938, 2865, 1725, 1447, 1412 cm^{-1}.

(±)-6-(1-Oxo-4-methyl-3-pentenyl)-1α,5α,6α-bicyclo[3.1.0]-hexane, 12. The following is a representative procedure for the formation of **12** from **11**. Into a 10 mL flask under argon were added THF (3.5 mL) and diisopropylamine (220 μL, 1.5 mmol). The solution was stirred and cooled to −78 °C, at which point the ester **11** was added as a solution in THF, using a total of 1.5 mL of THF for the transfer. The reaction was warmed to 0 °C for 15 min and then cooled to −78 °C. Methyl iodide (130 μL, 2.1 mmol) was added, and the reaction was allowed to warm to room temperature. The solution was diluted with ether and then washed with 10% potassium dihydrogenphosphate solution. The organic solution was dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel provided the hydroxy ketone **12** as a colorless oil (23 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.42 (s, 1H), 4.19 (s, 1H), 2.0−1.85 (m, 3H), 1.85−1.5 (m, 5H), 1.75 (s, 3H), 1.55 (s, 3H), 1.42 (s, 3H), 1.3−1.0 (m, 1H). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 212.3, 140.1, 125.9, 76.9, 33.2, 32.9, 28.3, 27.39, 27.4, 26.6, 26.2, 20.2, 18.6. IR (neat) 3457, 3040, 2965, 2934, 1686, 1449, 1399 cm^{-1}.

3-Methyl-2-buten-1-yl Cyclopropanecarboxylate, 13. Into a 50 mL flask under argon was added dichloromethane (25 mL). The flask was cooled to 0 °C, and 3-methyl-2-buten-1-ol (1.75 mL, 17.4 mmol) was added, followed by triethylamine (5 mL, 35 mmol). Cyclopropanecarbonyl chloride (1.6 mL, 17.4 mmol) was added dropwise, followed by DMAP (0.1 g, 0.82 mmol). The reaction was warmed to room temperature, giving a solution thick with white precipitate. The solution was washed with 10% potassium dihydrogen phosphate solution, until the pH of the aqueous layer was below 5. The organic solution was washed with saturated sodium bicarbonate solution, dried ($MgSO_4$), filtered, and concentrated briefly by rotary evaporation. Kugelrohr distillation of the resulting oil provided the desired ester **13** as a colorless oil (2.47 g, 92%). ^{1}H NMR (360 MHz, $CDCl_3$) δ: 5.35 (br t, J = 7.2 Hz, 1H), 4.56 (d, J = 7.2 Hz, 2H), 1.75 (s, 3H), 1.70 (s, 3H), 1.60 (tt, J = 11.5, 7.9 Hz, 1H), 0.99 (dt, J = 7.9, 3.7 Hz, 2H), 0.83 (dt, J = 11.5, 3.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 174.9, 138.8, 118.7, 61.4, 25.7, 17.9, 12.8, 8.3. IR (neat): 3017, 2975, 2936, 1727, 1449, 1399 cm^{-1}.

1-Cyclopropyl-2-hydroxy-4-methyl-3-penten-1-one, 14. The allylic ester **13** (101 mg, 0.65 mmol) was weighed into an oven-dried 10 mL flask. The flask was flushed with argon, and THF (4 mL) was added. The flask was cooled to −78 °C, and a 3.8 mL of a freshly prepared 0.5 M LDA solution was added (0.98 mL diisopropylamine + 8.6 mL THF + 2.6 mL of 2.4 M *n*-butyllithium, mixed at 0 °C). The flask was warmed to room temperature and quenched with 10% potassium dihydrogenphosphate solution. The organic layer was removed, dried ($MgSO_4$), filtered, and concentrated to an oil. Flash chromatography over silica gel provided the hydroxy ketone **14** as a colorless oil (7.2 mg, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.06 (d septet, J = 9.6, 1.4 Hz, 1H), 4.98 (dd, J = 9.6, 4.1 Hz, 1H), 4.2 (d, J = 4.2 Hz, 1H), 1.95−1.85 (m, 1H), 1.90 (d, J = 1.3 Hz, 3H), 1.82 (d, J = 1.2 Hz, 3H), 1.2−0.9 (m, 4H). ^{13}C NMR ($CDCl_3$, 90 MHz) δ: 210.7, 139.9, 121.4, 74.7, 26.0, 18.6, 17.0, 12.3, 11.7. IR (neat): 3459, 3011, 2975, 2917, 1700, 1615, 1447 cm^{-1}.

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Supporting Information Available: Proton NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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