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Cyclopentenones. An Efficient Synthesis of *cis*-Jasmone

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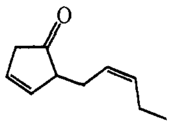
cis-Jasmone (**9**) is found in the flower oils of several varieties of Jasminum and is indispensable in the reproduction of jasmine fragrance from substances of synthetic origin. Total syntheses of *cis*-jasmone have been reported;[1] however, the routes employed are lengthy and suffer from low over-all yields. Jasmone has received considerable attention as a result of new methods of synthesizing 1,4 diketones which have been key intermediates leading to the cyclopentenone system.

We have developed a synthesis which allows the production of *cis*-jasmone in $\sim$40% over-all yield from the readily available cyclopentadiene. In addition, cyclopentadiene is easily transformed into Δ^3-cyclopentenones with substitution adjacent to the carbonyl function (*e.g.*, **6**). Δ^3-Cyclopentenones of type **6** are potentially versatile intermediates and, moreover, they can be expected to equilibrate to the more stable α,β-unsaturated ketone (*e.g.*, **7**).



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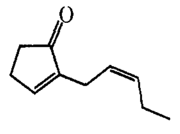

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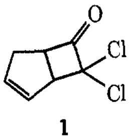
The starting point for the present synthetic scheme was the position-specific addition of dichloroketene to cyclopentadiene.[2] Treatment of a solution of cyclopentadiene and dichloroacetyl chloride in hexane at 0° with an excess of dry triethylamine in hexane resulted in an 85% yield of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (**1**). Dechlorination was effected with excess zinc dust in glacial acetic acid at $\sim$60° for approximately 1 hr to afford the bicyclic ketone **2** in >90% yield. Treatment of a solution of **2** in glacial acetic acid with 30% aqueous hydrogen peroxide at 0° for 24 hr produced in 90% yield the bicyclic lactone **3**.[3] The lactone **3** was reduced quantitatively to the hemiacetal **4** employing diisobutylaluminum hydride in toluene at −78°. The cis double bond present in jasmone was introduced in 70% yield by treatment of the hemiacetal **4** with the ylide derived from propyltriphenylphosphonium bromide in dimethyl sulfoxide.[4] The resulting alcohol could be oxidized with Jones reagent at 0° in acetone to afford a quantitative yield of the Δ^3-2-(*cis*-2-pentenyl)cyclopentenone (**6**).



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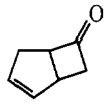

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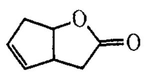

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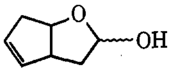

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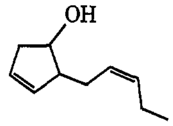

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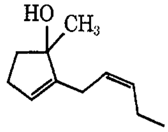

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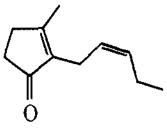
Initial attempts to isomerize the Δ^3-cyclopentenone **6** to the more stable α,β-unsaturated ketone **7** employing aqueous sodium hydroxide–ethanol proved disappointing. The predominant product was the desired dienone **7**; however, the yields ranged from 50 to 60%. Isomerization of the double bond was successfully accomplished in 90% yield with 2% aqueous sodium hydroxide at $\sim$70°. The dienone **7** was transformed into *cis*-jasmone (**9**) by addition of methyllithium followed by oxidation of the resulting carbinol **8** with chromium trioxide.[1j] *cis*-Jasmone (**9**), $\nu_{max}^{CHCl_3}$ 1685 and 1640 cm^{-1}, was characterized by its 2,4-dinitrophenylhydrazone.[5] Ir and nmr spectra of synthetic *cis*-jasmone were identical with those of an authentic sample.[6]



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The present synthesis allows the conversion of cyclopentadiene to *cis*-jasmone (**9**) in seven steps with an over-all yield of $\sim$40%.

Experimental Section

Microanalyses were performed by the Spang Microanalytical Laboratories, Ann Arbor, Mich. Melting and boiling points are uncorrected. The following spectrometers were used: nuclear magnetic resonance (nmr), Varian T-60 and A-60D (in δ units, with TMS as internal reference in CCl_4 unless stated otherwise); infrared (ir), Perkin-Elmer Model 247 and Beckman IR-8; mass spectrometer (mass spectrum) LKB-9. Vapor phase chromatography (vpc) analyses were performed on a Varian Aerograph Model 90-P instrument using silicone rubber SE-30 and Carbowax 20 M columns. Pre-coated PLC silica gel F-254 Merck plates were used for preparative tlc.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (1).—To a vigorously stirred solution of 27.2 g of freshly distilled cyclopentadiene, 30.5 g of dichloroacetyl chloride, and 200 ml of hexane (dried over molecular sieves) was added 21.7 g of dry triethylamine in 200 ml of hexane over a period of 1.5 hr. After stirring for 15 hr under an atmosphere of nitrogen, the reaction mixture was filtered and

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[1] (a) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952); (b) S. H. Harper and R. J. D. Smith, *ibid.*, 1512 (1955); (c) J. H. Amin, R. K. Razden, and S. C. Bhattacharyya, *Perfum. Essent. Oil Rec.*, **49**, 502 (1958); (d) G. Stork and R. Borch, *J. Amer. Chem. Soc.*, **86**, 936 (1964); (e) K. S. Sido, Y. Kawasima, and T. Isida, *Perfum. Essent. Oil Rec.*, **57**, 364 (1966); (f) G. Büchi and R. Wuest, *J. Org. Chem.*, **31**, 977 (1966); (g) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc. C*, 1024 (1969); (h) J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971); (i) G. Stork, F. Rouessac, and O. Gringore, *J. Amer. Chem. Soc.*, **93**, 3091 (1971); (j) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971); (k) J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).

[2] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *ibid.*, **87**, 5257 (1965); L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Lett.*, 135 (1966).

[3] E. J. Corey, Z. Arnold, and J. Hutton, *ibid.*, 307 (1970).

[4] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963); E. Hamanaka, Ph.D. Thesis, Harvard University, Cambridge, 1967. The cis geometry for the double bond in **5** is identicated by the absence of the absorption characteristic of trans CH=CH– at 10.3–10.4 μ. The subsequent synthetic transformations also allow the cis assignment.

[5] Y. R. Naves and A. V. Grampoloff, *Helv. Chim. Acta*, **25**, 1500 (1942).

[6] Kindly supplied by International Flavors and Fragrances, Union Beach, N. J.

the filter cake was washed with hexane. The solvent was removed *in vacuo*, yielding a liquid weighing 35.2 g. Vacuum distillation afforded 30.0 g of product ($\sim$85%): bp 49–50° (0.3 mm); ir ($CHCl_3$) 1805 (C=O) and 1608 cm^{-1} (C=C); nmr (CCl_4) δ 2.70 (m, 2 H, $-CH_2-$), 4.10 (m, 2 H, bridgehead), 5.90 (m, 2 H, CH=CH).

Anal. Calcd for $C_7H_6Cl_2O$: C, 47.47; H, 3.42; Cl, 40.06. Found: C, 47.33; H, 3.48; Cl, 40.16.

Bicyclo[3.2.0]hept-2-en-6-one (2).—To a vigorously stirred suspension of 11.0 g (0.169 g-atom) of zinc dust in 15 ml of glacial acetic acid at room temperature was added dropwise 5.00 g (0.028 mol) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one in 5 ml of glacial acetic acid. After addition was complete, the temperature was raised to and maintained at 70° for 40 min. Tlc analysis (pentane–I_2) after 40 min indicated no starting material remaining. The reaction mixture was cooled and treated with ether, and the zinc residue was filtered. The ethereal layer was washed with a saturated solution of Na_2CO_3 to remove the acetic acid and dried ($MgSO_4$). The solvent was removed on a rotary evaporator at *ca.* 10° and the product (2.89 g, 95%, homogeneous by tlc) was isolated by distillation: bp 60° ($\sim$15 mm); ir ($CHCl_3$) 1778 (C=O) and 1605 cm^{-1} (C=C); nmr (CCl_4) δ 2.4–2.9 (3 H, m), 3.0–3.6 (2 H, m), 3.6–4.0 (1 H, m), 5.80 (2 H, broad singlet).

Lactone of *cis*-2-Hydroxycyclopent-4-ene-1-acetic Acid (3).—To a solution of 3.24 g (30 mmol) of bicyclo[3.2.0]hept-2-en-6-one in 85 ml of 90% aqueous acetic acid cooled to 0° was added 8.15 g of 30% hydrogen peroxide in 70 ml of 90% aqueous acetic acid. The reaction was stirred at 0° for 24 hr (overnight). The product was extracted with ether and washed with 10% aqueous sodium sulfite and saturated sodium bicarbonate. The ether layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Distillation afforded 3.35 g (90%) of lactone **3**: bp 70–71° (0.2 mm); ir ($CHCl_3$) 1760 (C=O) and 1605 cm^{-1} (C=C); nmr (CCl_4) δ 2.0–3.0 (4 H, m), 3.45 (1 H, m), 5.05 (1 H, m), 5.65 (2 H, m); mass spectrum *m/e* 124.

Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.49. Found: C, 67.83; H, 6.40.

Reduction of 3 to Hemiacetal 4.—Diisobutylaluminum hydride (6.39 g, 45 mmol) was added dropwise with stirring to a solution of pure lactone **3** (3.72 g, 30 mmol) in 200 ml of dry toluene cooled to −78°. The reaction mixture was stirred under nitrogen at −78° for 2 hr. The reaction was quenched by the addition of methanol (1.0 ml until gas evolution ceased) and was warmed to room temperature. After it was stirred for an additional 15 min, the reaction mixture was diluted with 100 ml of ether and 100 ml of 50% brine solution. The resulting emulsion was destroyed by the addition of 100 ml of an aqueous solution containing 5 ml of concentrated hydrochloric acid. An additional 150 ml of ether were added and the organic layer was separated. The aqueous layer was extracted with ether (2 × 50 ml). The combined organic extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent *in vacuo* afforded 3.68 g (99%) of a clear liquid, bp 44–45° (0.01 mm), which was homogeneous by tlc (methylene chloride–methanol, 19:1, R_f 0.58): ir ($CHCl_3$) 3598, 3395 (OH), and 1605 cm^{-1} (C=C); nmr (CCl_4) δ 1.50–2.20 (2 H, m), 2.40–2.70 (2 H, m), 3.30 (1 H, m), 4.50–4.95 (2 H, m), 5.25–5.65 (3 H, m); mass spectrum *m/e* 108 (M − 18).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.75; H, 7.86.

2-(*cis*-2-Pentenyl)cyclopent-3-en-1-ol (5).—*n*-Propyltriphenylphosphonium bromide (17.71 g, 46 mmol), dried for 1 hr at 75° (0.2 mm), was dissolved in 90 ml of freshly distilled dimethyl sulfoxide (DMSO, distilled from CaH_2). To this solution at room temperature under nitrogen was added sodium methylsulfinylmethide, which yielded a red-orange solution. The anion of DMSO was prepared as follows: 2.90 g (69 mmol) of 57% sodium hydride dispersion was washed with dry pentane to remove the mineral oil. Dry DMSO (50 ml) was added and the mixture was stirred at 75° for *ca.* 1.5 hr.

Pure hemiacetal **4** (2.90 g, 23 mmol) in dry DMSO (10 ml) was added after 5 min. The reaction was stirred at room temperature for 2.5 hr, at which time tlc analysis (CH_2Cl_2–MeOH, 99:1) indicated no starting material remaining. The reaction was quenched by the addition of ice water and the mixture was extracted with hexane. The organic layer was washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to afford 3.35 g of crude product. Distillation of the product afforded 2.45 g (70%) of pure product, bp 48° (0.01 mm), homogeneous by tlc (CH_2Cl_2–MeOH, 99:1, R_f 0.60): ir ($CHCl_3$) 3600, 3460 (OH), and 1605 cm^{-1} (C=C); nmr (CCl_4) δ 1.00 (3 H, t), 1.80–2.80 (8 H, m), 4.30 (1H, m), 5.30–5.70 (4 H, m); mass spectrum *m/e* 152, 135 (M − 18).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 79.02; H, 10.64.

2-(*cis*-2-Pentenyl)-2-cyclopentenone (7).—A solution of 200 mg (1.32 mmol) of alcohol **5** in 10 ml of acetone was cooled to 0° and was treated dropwise with 1 equiv of standard Jones reagent ($\sim$0.4 ml). After 5 min, 0.2 ml of isopropyl alcohol was added and the mixture was extracted with pentane. The organic layer was subsequently washed with 10% $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated *in vacuo* to afford 190 mg of crude Δ^3-cyclopentenone **6**, homogeneous by tlc (methylene chloride, R_f 0.75): ir ($CHCl_3$) 1749 cm^{-1} (C=O); nmr (CCl_4) δ 0.98 (3 H, t), 1.70–2.60 (5 H, m), 2.60–3.00 (2 H, m), 5.35 (2 H, m), 6.05 (2 H, broad singlet).

The crude ketone **6** was treated with 8.0 ml of aqueous 2% NaOH solution under nitrogen at $\sim$70°. Isomerization to the more stable α,β-unsaturated ketone **7** was essentially complete after *ca.* 1 hr. The mixture was cooled, extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated, affording 166 mg of dienone **7**, bp 67–68° (0.05 mm), which was homogeneous by tlc (methylene chloride, R_f 0.53): ir ($CHCl_3$) 1690 (C=O) and 1630 cm^{-1} (C=C); nmr (CCl_4) δ 0.98 (3 H, t), 1.80–3.00 (8 H, m), 5.40 (2 H, m), 7.18 (1 H, broad singlet).

***cis*-Jasmone (9).**—To a solution of 140 mg (0.93 mmol) of ketone **7** in 3 ml of anhydrous ether cooled to 0° was added 1.2 ml (2.0 mmol) of 1.66 *M* methyllithium in ether. After 15 min at room temperature the mixture was quenched with cold water. The product was extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to afford 149 mg of alcohol **8**, ir ($CHCl_3$) 3610, 3430 cm^{-1}.

The crude carbinol was dissolved in 3 ml of ether, cooled to 0°, and treated dropwise with a solution of 100 mg of CrO_3 in 1.0 ml of aqueous 5% H_2SO_4. Stirring was continued for an additional 15 min at 0°. The reaction was quenched by the addition of water and the mixture was extracted with pentane. The organic layer was washed with 10% $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to give 138 mg (84% yield) of crude *cis*-jasmone (**9**). A pure sample was obtained by preparative tlc on silica gel plates using methylene chloride–methanol (99:1): ir ($CHCl_3$) 1685 (C=O) and 1640 cm^{-1} (C=C); nmr (CCl_4) δ 1.00 (3 H, t), 2.0 (3 H, s), 2.1–2.6 (6 H, m), 2.85 (2 H, d), 5.25 (2 H, m). Ir and nmr spectra and retention time on vpc were identical with those of an authentic[6] sample of *cis*-jasmone.

Registry No.—**1**, 5307-99-3; **2**, 13173-09-6; **3**, 34638-25-0; **4**, 34638-26-1; **5**, 34638-27-2; **6**, 34638-28-3; **7**, 34638-28-3; **9**, 4907-07-7.

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Ketenimines. II.[1] Lone-Pair Effects on Nuclear Magnetic Resonance Properties of the Cumulenic π System

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Allene (**1**) can be considered the parent molecule for a number of heterocumulene analogs of which the nitro-

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[1] See G. Krow, *Angew. Chem.*, **83**, 455 (1971); *Angew. Chem., Int. Ed. Engl.*, **7**, 435 (1971), for a review of ketenimine chemistry.