

## Electrolytic Decarboxylation. 6. A Convenient Synthesis of 3-(*cis*-3-Hexenyl)-2-cyclopentenone, a Precursor of *cis*-Jasmone Synthesis

Sigeru TORII,\* Hideo TANAKA, Tsutomu INOKUCHI, and Kazuo TOMOZANE  
Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700  
(Received June 24, 1982)

**Synopsis.** A regioselective electro-acetoxylation of 1-(*cis*-3-hexenyl)-2-cyclopentene-1-carboxylic acid in a  $\text{Et}_3\text{N}$ -AcOH-AcOEt-*t*-BuOH-(Pt electrodes) system afforded 3-acetoxy-1-(*cis*-3-hexenyl)-1-cyclopentene (**7a**) (98%). Alkaline hydrolysis of **7a** followed by the oxidation with chromium trioxide gave the desired 3-(*cis*-3-hexenyl)-2-cyclopentenone smoothly.

The cyclization of 1,4-diketone (**2**) with base is a key strategy in *cis*-jasmone synthesis.<sup>1)</sup> As an extension of the investigation, a device has been made by McCurry and co-worker since 3-(*cis*-3-hexenyl)-2-cyclopentenone (**3**) can be smoothly converted into **1** via the intermediate **2** by a simple retro-aldol-aldol condensation reaction in an aqueous alkaline solution<sup>2)</sup> (Scheme 1).

In the course of our investigation on electrolytic decarboxylation of aliphatic carboxylic acids (non Kolbe type reactions), we have found that the electrolytic decarboxylation of  $\beta,\gamma$ -unsaturated carboxylic acids affords exclusively  $\gamma$ -acetoxy- $\alpha,\beta$ -unsaturated com-

pounds.<sup>3)</sup> The success prompted us to synthesize the important intermediate **3** by the electro-decarboxylative acetoxylation of 1-(*cis*-3-hexenyl)-2-cyclopentene-1-carboxylic acid (**6b**) (Scheme 2).

The  $\beta,\gamma$ -unsaturated carboxylic acid **6b** was obtained by the following manner: Treatment of methyl 2-oxocyclopentanecarboxylate (**4a**) with *cis*-3-hexenyl *p*-toluenesulfonate in acetone in the presence of KI and  $\text{K}_2\text{CO}_3$  gave **4b** (89%), which was subjected to reduction with  $\text{LiAl}(\text{t-BuO})_3\text{H}$  in tetrahydrofuran (THF) to give the alcohol **5a** (99%). Dehydration of **5a** was performed by heating the corresponding methanesulfonate **5b** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *N,N*-dimethylformamide (DMF), yielding **6a** (86%). Hydrolysis of **6a** in a methanolic alkaline solution afforded **6b** (98%).

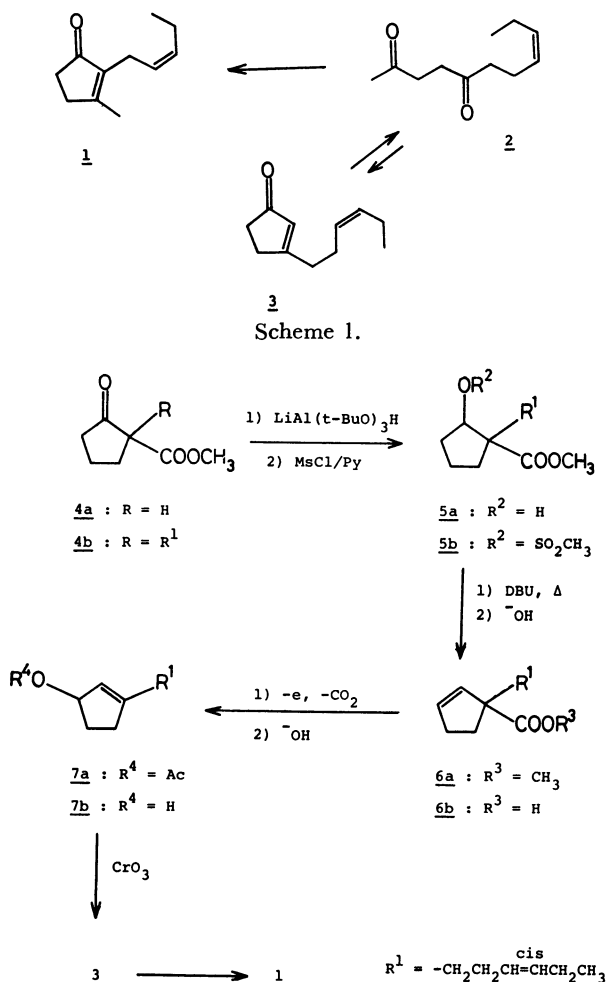
Electrolytic decarboxylation of **6b** was carried out in either a divided or an undivided cell using two Pt electrodes. A solution of **6a** in acetic acid, ethyl acetate, and *t*-butyl alcohol (2/5/0.3) containing triethylamine was charged into the anode compartment of the divided cell, and a regulated DC power (terminal voltage: 35 V) was supplied for 21 h. In the course of the electrolysis, the initial current of 6 mA/cm<sup>2</sup> dropped onto 1 mA/cm<sup>2</sup>. Workup of the anolyte gave the acetate **7a** (68%). On the other hand, the electrolysis of **6a** in the same medium was carried out in an undivided cell (without separation of the two electrode compartments), there was also obtained **7a** (98%) without detectable amounts of the hydrogenated products on the C-C double bond. This is in contrast to the results of the electrolytic decarboxylation of some carboxylic acids bearing isopropenyl moiety,<sup>4)</sup> in which, the hydrogenation of the C-C double bond proceeds competitively at the cathode.

The transformation of **7a** into 3-(*cis*-3-hexenyl)-2-cyclopentenone (**3**) was performed by the hydrolysis of **7a** followed by the oxidation with chromium trioxide.<sup>5)</sup> The spectral data and physical properties of **3** were fully identical with those of the reported one.<sup>2)</sup>

### Experimental

All boiling points are uncorrected. IR spectra were determined with a JASCO IRA-I infrared spectrometer. <sup>1</sup>H NMR spectra were obtained at 60 MHz with a Hitachi R-24 spectrometer.

**Methyl 1-(*cis*-3-Hexenyl)-2-oxocyclopentane-1-carboxylate (4b).** A mixture of **4a** (480 mg, 3.38 mmol), *cis*-3-hexenyl *p*-toluenesulfonate (1.05 g, 4.12 mmol), KI (1.03 g, 6.18 mmol), and  $\text{K}_2\text{CO}_3$  (4.73 g, 34.3 mmol) in acetone (40 ml) was heated to reflux for 2 d. After removal of the solids by filtration, the filtrate was concentrated and the residue was chromatographed ( $\text{SiO}_2$ , hexane-AcOEt: 35/1), giving **4b** (676 mg, 89%): bp 93–96 °C/2 Torr†; IR (neat) 3101 (HC=C), 1755 (C=O),



Scheme 2.

† 1 Torr = 133.322 Pa.

1723  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.96 (3H, t,  $J=7.4$  Hz,  $\text{CH}_3$ ), 1.36–2.67 (12H, m), 3.65 (3H, s,  $\text{CH}_3\text{O}$ ), 5.23–5.43 (2H, m,  $\text{HC=CH}$ ).

Found: C, 69.76; H, 9.11%. Calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_3$ : C, 69.91; H, 8.99%.

**Methyl 1-(cis-3-Hexenyl)-2-hydroxycyclopentane-1-carboxylate (5a).** A mixture of **4b** (200 mg, 0.89 mmol) and  $\text{LiAl}(t\text{-BuO})_3\text{H}$  (453 mg, 1.25 mmol) in THF (10 ml) was stirred at 0–5 °C for 3 h. The usual workup gave **5a** (200 mg, 99%): bp 130–132 °C/7 Torr; IR (neat) 3439 (OH), 3000 ( $\text{HC=C}$ ), 1731  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.94 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.20–2.32 (12H, m), 2.62 (1H, br s, OH), 3.62 (3H, s,  $\text{CH}_3\text{O}$ ), 4.15 (1H, m,  $\text{CH-O}$ ), 5.12–5.45 (2H, m,  $\text{HC=CH}$ ).

Found: C, 68.85; H, 9.74%. Calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_3$ : C, 68.99; H, 9.80%.

**1-(cis-3-Hexenyl)-2-cyclopentene-1-carboxylic Acid (6b).** To a solution of **5a** (178 mg, 0.79 mmol) in pyridine (3 ml) was added methanesulfonyl chloride (270 mg, 2.36 mmol) at 0 °C. After being stirred for 3 h at this temperature, the usual workup gave methanesulfonate **5b** (239 mg, 100%): IR (neat) 3012 ( $\text{HC=C}$ ), 1729 (C=O), 1356, 1177  $\text{cm}^{-1}$  ( $\text{CH}_3\text{SO}_3$ );  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.96 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.21–2.40 (12H, m), 2.91 (3H, s,  $\text{CH}_3\text{SO}_3$ ), 3.67 (3H, s,  $\text{CH}_3\text{O}$ ), 5.07–5.38 (3H, m,  $\text{HC-O}$ ,  $\text{HC=CH}$ ). The product **5b** was heated in DMF (1 ml) containing DBU (122 mg, 0.8 mmol) at 140 °C for 8 h. The mixture was diluted with water and the extractive workup with benzene–ether (1/1) followed by column chromatography ( $\text{SiO}_2$ , hexane–AcOEt: 12/1) gave **6a** (141 mg, 86%): bp 82–83 °C/10 Torr; IR (neat) 3050, 3005 ( $\text{HC=C}$ ), 1733 (C=O), 1650  $\text{cm}^{-1}$  (C=C);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.95 (3H, t,  $J=7.4$  Hz,  $\text{CH}_3$ ), 1.21–2.61 (10H, m), 3.61 (3H, s,  $\text{CH}_3\text{O}$ ), 5.12–5.44 (2H, m,  $\text{HC=CH}$ ), 5.49–5.81 (2H, m,  $\text{HC=CH}$ ).

Hydrolysis of **6a** (585 mg, 2.81 mmol) in aqueous 80% MeOH (10 ml) containing KOH (1.26 g, 22.5 mmol) at 65 °C for 6 h gave **6b** (534 mg, 98%) after column chromatography ( $\text{SiO}_2$ , hexane–AcOEt: 4/1): IR (neat) 3690–2230 (OH), 1697  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.94 (3H, t,  $J=7.4$  Hz,  $\text{CH}_3$ ), 1.38–2.75 (10H, m), 5.07–5.46 (2H, m,  $\text{HC=CH}$ ), 5.50–5.92 (2H, m,  $\text{HC=CH}$ ), 12.15 (1H, s, COOH).

Found: C, 74.38; H, 9.45%. Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_2$ : C, 74.19; H, 9.34.

**Electrolysis of 1-(cis-3-Hexenyl)-2-cyclopentene-1-carboxylic Acid (6b).** Procedure A: Electrolysis was carried out in an undivided cell fitted with two Pt electrodes ( $2 \times 3 \text{ cm}^2$ ), a thermometer, and a gas lead pipe. A solution of **6b** (120 mg, 0.61 mmol) in AcOH (2 ml), AcOEt (5 ml), and  $t\text{-BuOH}$  (0.27 ml) containing  $\text{Et}_3\text{N}$  (0.85 ml) was charged in the cell and electrolysed at 20–22 °C under a constant applied voltage (30 V) for 7 h. The initial current of 30 mA/ $\text{cm}^2$

dropped onto 20 mA/ $\text{cm}^2$  during the electrolysis. The mixture was concentrated to ca. 2 ml and the residue was taken up with ether, washed with brine, and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvents followed by column chromatography ( $\text{SiO}_2$ , hexane–ether: 2/1) gave **7a** (125 mg, 98%): bp 64–66 °C/2 Torr; IR (neat) 3054, 3005 ( $\text{HC=C}$ ), 1728  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.93 (3H, t,  $J=7.4$  Hz,  $\text{CH}_3$ ), 1.48–2.73 (10H, m), 1.91 (3H, s,  $\text{CH}_3\text{CO}$ ), 5.11–5.56 (4H, m,  $\text{HC=CH}$ ,  $\text{HC=C}$ ,  $\text{CH-O}$ ).

Found: C, 74.77; H, 9.86%. Calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_2$ : C, 74.96; H, 9.68%.

**Procedure B:** Electrolysis was carried out in a divided cell, separated with glass-frit, using two Pt electrodes ( $2 \times 3 \text{ cm}^2$ ). A mixture of AcOH (8 ml), AcOEt (20 ml),  $t\text{-BuOH}$  (1.2 ml), and  $\text{Et}_3\text{N}$  (3 ml) was charged into both anode and cathode compartments, and **6b** (80 mg, 0.41 mmol) was added to the anode compartment. DC powder (35 V) was supplied for 21 h (6–1 mA/ $\text{cm}^2$ ) and workup of the anolyte in the same manner as described above gave **7a** (58 mg, 68%).

**3-(cis-3-Hexenyl)-2-cyclopentenone (3).** A mixture of **7a** (75 mg, 0.36 mmol) and KOH (80 mg) in aqueous 90% MeOH (5 ml) was stirred at room temperature for 2 h and the extractive work-up with ether followed by column chromatography ( $\text{SiO}_2$ , hexane–ether: 1/1) gave **7b** (57 mg, 95%): bp 62–64 °C/2 Torr; IR (neat) 3330 (OH), 3305 ( $\text{HC=C}$ ), 1650  $\text{cm}^{-1}$  (C=C);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.96 (3H, t,  $J=7.4$  Hz,  $\text{CH}_3$ ), 1.47–2.80 (10H, m), 4.67 (1H, m,  $\text{HC-O}$ ), 4.50–4.84 (3H, m,  $\text{HC=CH}$ ,  $\text{HC=C}$ ), which was treated with aqueous chromium trioxide (1.3 M, 0.5 ml) in  $\text{CH}_2\text{Cl}_2$  (2 ml) at 0 °C for 4 h. The organic layer was worked up in the usual manner to give **3** (40 mg, 71%), whose spectral data were identical with those of the reported one.<sup>21</sup>

## References

- 1) S. Torii and H. Tanaka, *Kogyo*, **114**, 41 (1976); T.-L. Ho, *Synth. Commun.*, **4**, 256 (1974); R. A. Ellison, *Synthesis*, **1973**, 397.
- 2) P. M. McCurry, Jr., and R. K. Singh, *J. Org. Chem.*, **39**, 2317 (1974). Recently, an improved synthesis of **1** via **3** has been reported: T. Yoshida, T. Miyakoshi, H. Ohmichi, and S. Saitoh, 25th Symposium on Chemistry of Terpenes, Essential Oils, and Aromatics, Yamaguchi, October 1981, Abstr. p. 234.
- 3) S. Torii, T. Inokuchi, M. Mizuguchi, and M. Yamazaki, *J. Org. Chem.*, **44**, 2203 (1979) and references cited therein.
- 4) S. Torii and T. Okamoto, *Bull. Chem. Soc. Jpn.*, **49**, 771 (1976).
- 5) H. C. Brown, C. P. Gang, and K.-T. Liu, *J. Org. Chem.*, **36**, 387 (1971).