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

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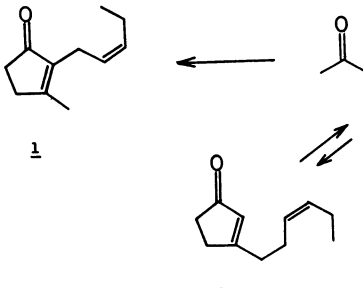
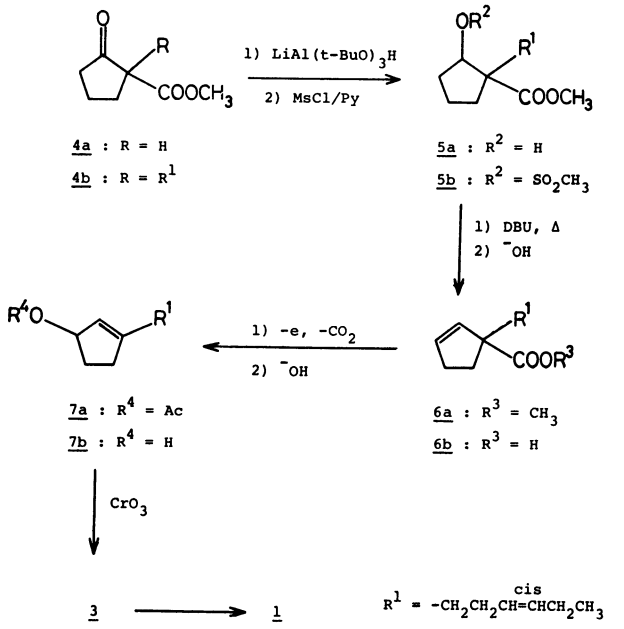
Synopsis. A regioselective electro-acetoxylation of 1-(*cis*-3-hexenyl)-2-cyclopentene-1-carboxylic acid in a Et_3N–AcOH–AcOEt–*t*-BuOH–(Pt electrodes) system afforded 3-acetoxy-1-(*cis*-3-hexenyl)-1-cyclopentene (**7a**) (98%). Alkaline hydrolysis of **7a** followed by the oxidation with chromium trioxide gave the desired 3-(*cis*-3-hexenyl)-2-cyclopenone smoothly.

The cyclization of 1,4-diketone (**2**) with base is a key strategy in *cis*-jasmone synthesis.[1] 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[2] (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 β,γ-unsaturated carboxylic acids affords exclusively γ-acetoxy-α,β-unsaturated compounds.[3] 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).



Scheme 1.



Scheme 2.

The β,γ-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 K_2CO_3 gave **4b** (89%), which was subjected to reduction with $LiAl(t\text{-}BuO)_3H$ 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^2 dropped onto 1 mA/cm^2. 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,[4] 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.[5] The spectral data and physical properties of **3** were fully identical with those of the reported one.[2]

Experimental

All boiling points are uncorrected. IR spectra were determine with a JASCO IRA-I infrared spectrometer. ^1H 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 K_2CO_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 (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),

† 1 Torr=133.322 Pa.

1723 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.96 (3H, t, J=7.4 Hz, CH_3), 1.36—2.67 (12H, m), 3.65 (3H, s, CH_3O), 5.23—5.43 (2H, m, HC=CH).

Found: C, 69.76; H, 9.11%. Calcd for $C_{13}H_{20}O_3$: 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 $LiAl(t\text{-}BuO)_3H$ (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 (HC=C), 1731 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.94 (3H, t, J=7.2 Hz, CH_3), 1.20—2.32 (12H, m), 2.62 (1H, br s, OH), 3.62 (3H, s, CH_3O), 4.15 (1H, m, CH–O), 5.12—5.45 (2H, m, HC=CH).

Found: C, 68.85; H, 9.74%. Calcd for $C_{13}H_{22}O_3$: 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 (HC=C), 1729 (C=O), 1356, 1177 cm^{-1} (CH_3SO_3); ^1H NMR (CCl_4) δ 0.96 (3H, t, J=7.2 Hz, CH_3), 1.21—2.40 (12H, m), 2.91 (3H, s, CH_3SO_3), 3.67 (3H, s, CH_3O), 5.07—5.38 (3H, m, HC–O, 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 (SiO_2, hexane–AcOEt: 12/1) gave **6a** (141 mg, 86%): bp 82—83 °C/10 Torr; IR (neat) 3050, 3005 (HC=C), 1733 (C=O), 1650 cm^{-1} (C=C); ^1H NMR CCl_4) δ 0.95 (3H, t, J=7.4 Hz, CH_3), 1.21—2.61 (10H, m), 3.61 (3H, s, CH_3O), 5.12—5.44 (2H, m, HC=CH), 5.49—5.81 (2H, m, 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 (SiO_2, hexane–AcOEt: 4/1): IR (neat) 3690—2230 (OH), 1697 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.94 (3H, t, J=7.4 Hz, CH_3), 1.38—2.75 (10H, m), 5.07—5.46 (2H, m, HC=CH), 5.50—5.92 (2H, m, HC=CH), 12.15 (1H, s, COOH).

Found: C, 74.38; H, 9.45%. Calcd for $C_{12}H_{18}O_2$: 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 (2×3 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*-BuOH (0.27 ml) containing Et_3N (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/cm^2 dropped onto 20 mA/cm^2 durring the electrolysis. The mixture was concentrated to *ca.* 2 ml and the residue was taken up with ether, washed with brine, and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2, hexane–ether: 2/1) gave **7a** (125 mg, 98%): bp 64—66 °C/2 Torr; IR (neat) 3054, 3005 (HC=C), 1728 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.93 (3H, t, J=7.4 Hz, CH_3), 1.48—2.73 (10H, m), 1.91 (3H, s, CH_3CO), 5.11—5.56 (4H, m, HC=CH, HC=C, CH–O).

Found: C, 74.77; H, 9.86%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

Procedure B: Electrolysis was carried out in a divided cell, separated with glass-frit, using two Pt electrodes (2×3 cm^2). A mixture of AcOH (8 ml), AcOEt (20 ml), *t*-BuOH (1.2 ml), and Et_3N (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/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 (SiO_2, hexane–ether: 1/1) gave **7b** (57 mg, 95%): bp 62—64 °C/2 Torr: IR (neat) 3330 (OH), 3305 (HC=C), 1650 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 0.96 (3H, t, J=7.4 Hz, CH_3), 1.47—2.80 (10H, m), 4.67 (1H, m, HC–O), 4.50—4.84 (3H, m, HC=CH, HC=C), which was treated with aqueous chromium trioxide (1.3 M, 0.5 ml) in CH_2Cl_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.[2]

References

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