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A Novel Approach to *cis*-Jasmone and Dihydrojasmone from 2-(2-Benzothiazolylthio)-2-(3-oxobutyl)oct-5-en(or -an)oic Acid by Electrolytic Procedure

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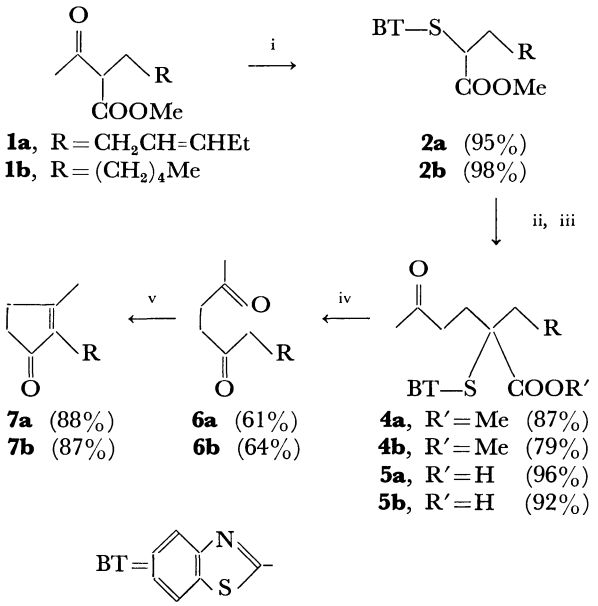
Synopsis. *cis*-Jasmone (**7a**) and dihydrojasmone (**7b**) have been synthesized by facile five-step processes starting from methyl acetoacetate involving electrolysis procedure. Methyl 2-(2-benzothiazolylthio)oct-5-en(or -an)oate, prepared from methyl 2-acetyloct-5-en(or -an)oate (**1**) by the reaction with the *N*-(2-benzothiazolylthio)morpholine, were allowed to react with methyl vinyl ketone, leading to the Michael adducts **4**. After hydrolysis of **4**, the corresponding acids **5** were electrolyzed to afford the desired 1,4-diketone **6** in 45—48% overall yields (based on **1**), whose base-catalyzed cyclization gave **7** smoothly.

As part of our program to investigate the electrochemical functionalization of carboxylates, we examined the conversion of the carboxylates bearing 2-benzothiazolylthio group in the α-position into the corresponding oxo compounds by electrolysis. Our efforts to utilize 2-(2-benzothiazolylthio)-2-(3-oxobutyl)oct-5-en(or -an)oic acid (**4**) in such a reaction led successfully to the expected 1,4-diketone **6**,[1] important precursors of *cis*-jasmone (**7a**) and dihydrojasmone (**7b**).

Methyl 2-(2-benzothiazolylthio)oct-5-en(or -an)oate (**2**) was smoothly prepared by treatment of methyl 2-acetyloct-5-en(or -an)oate (**1**) with *N*-(2-benzothiazolylthio)morpholine (**3**)[2] in methanol under refluxing for *ca.* 16 h.[3] The reaction of **2** with methyl vinyl ketone was carried out successfully in refluxing acetone using excess amounts of potassium carbonate for 12 h in the presence of a trace of 2,5-di-*t*-butylhydroquinone as a polymerisation inhibitor. This afforded **4a** in 87% yield and **4b** in 79% yield. Hydrolysis of Michael adducts **4** in aqueous methanol in the presence of potassium carbonate at 45—55 °C for 14 h afforded the corresponding acids **5** in 92—96% yields.

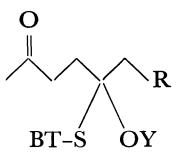
The electrolysis of **5a** using carbon rod electrodes in acetic acid–*t*-butyl alcohol–triethylamine (6/3/0.2, v/v) at a current of 20 mA/cm² (applied voltage 18—25 V) at 45—55 °C for 2.5 h gave **6a** in 61% yield. Similarly, the electrolysis of **5a** could be carried out using platinum electrodes in methanol–triethylamine (10/0.2, v/v) at a current of 30 mA/cm² (applied voltage 18—22 V) at 45—50 °C for 2.5 h, giving **6a** in 54% yield. On the other hand, the acid **5b** favored the electrolysis in the two-phase system, consisting of water and hexane (extracting solvent) layers as described in the preceeding paper.[4] Thus, an aqueous solution of **5b** and sodium hydroxide was electrolyzed using an undivided cell fitted with two platinum electrodes under a current of 30 mA/cm² (applied voltage 7—9 V) at 46—50 °C for 4 h, giving the desired **6b** in 64% after evaporation of the organic layer.



i) BT-S-N⟨ ⟩O (**3**)-MeOH; ii) $MeCOCH{=}CH_2$-K_2CO_3-Aceton; iiii) K_2CO_3-aqueous MeOH; iv) $-e$, $-CO_2$; v) aqueous KOH.

The carbonyl group of **6** seems to be formed by electrolytic decarboxylation of **5** followed by hydroxylation (methoxylation, acetoxylation), leading to intermediate (A), and subsequent elimination of 2-benzothiazolylthio group.[5]

The base-catalyzed cyclization of the 1,4-diketones **6** afforded *cis*-jasmone (**7a**) and dihydrojasmone (**7b**), respectively.[1]



(A)

Y=H, Me, or Ac

Experimental

All boiling points were uncorrected, the boiling points indicated being air-bath temperatures. IR spectra were determined with a JASCO Model IRA-1 spectrophotometer

with a grating. ^{1}H NMR spectra were obtained with Hitachi R-24 and/or JEOL MH-100 spectrometers. Elemental analyses were carried out in this laboratory.

*Methyl (Z)-2-Acetyl-5-octenoate (**1a**).* A suspension of methyl acetoacetate (540 mg, 4.65 mmol), (*Z*)-3-hexenyl bromide (836 mg, 5.13 mmol), K_2CO_3 (2.57 g, 18.6 mmol), and KI (1.07 g, 6.45 mmol) in acetone (20 ml) was heated to reflux for 6 h. Insoluble materials were filtered off and the filtrate was concentrated. The residue was chromatographed (SiO_2, benzene/AcOEt, 30/1) to give **1a** (840 mg, 91%): bp 94—98 °C/9 Torr; IR (neat) 1745 (ester C=O), 1717 (C=O), 1649 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.98 (t, 3, J=7 Hz, CH_3), 1.55—2.34 (m, 9), 3.34 (t, 1, J=7 Hz, CH), 3.70 (s, 3, CH_3O), 4.89—5.66 (m, 2, HC=CH). Found: C, 66.56; H, 9.14%. Calcd for $C_{11}H_{18}O_3$: C, 66.44; H, 9.15%.

*Methyl (Z)-2-(2-Benzothiazolylthio)-5-octenoate (**2a**).* A solution of **1a** (619 mg, 3.12 mmol) and *N*-(2-benzothiazolylthio)morpholine[2] (**3**, 886 mg, 3.51 mmol) in MeOH (7 ml) was heated to reflux for 15 h. After evaporation of the solvent, the residue was chromatographed (SiO_2, benzene/hexane/AcOEt, 20/10/1) to give **2a** (955 mg, 95%): bp 120—124 °C/0.01 Torr; IR (neat) 3056 (HC=C), 1734 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.93 (t, 3, J=7 Hz, CH_3), 1.72—2.30 (m, 6, CH_2), 3.70 (s, 3, CH_3O), 4.68 (t, 1, J=7 Hz, CH), 5.22—5.57 (m, 2, HC=CH), 7.02—7.92 (m, 4, HC=C). Found: C, 59.61; H, 6.11%. Calcd for $C_{16}H_{19}NO_2S_2$: C, 59.78; H, 5.96%.

Similarly, *methyl 2-(2-benzothiazolylthio)octanoate (**2b**)* was obtained in 98% yield, bp 120—123 °C/0.004 Torr (lit,[3] bp 123—126 °C/0.005 Torr).

*Methyl (Z)-2-(2-Benzothiazolylthio)-2-(3-oxobutyl)-5-octenoate (**4a**).* A mixture of **2a** (515 mg, 1.60 mmol), methyl vinyl ketone (562 mg, 8.01 mmol), K_2CO_3 (443 mg, 3.21 mmol), and 2,5-di-*t*-butylhydroquinone (7 mg) in acetone (7 ml) was heated to reflux for 12 h. The insoluble materials were filtered off and the filtrate was concentrated. The residue was chromatographed (SiO_2, benzene/AcOEt, 15/1) to give **4a** (547 mg, 87%): bp 150—154 °C/0.005 Torr; IR (neat) 3061 (HC=C), 1729 (ester C=O), 1717 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.92 (t, 3, J=7 Hz, CH_3), 1.68—2.85 (m, 13), 3.69 (s, 3, CH_3O), 5.12—5.50 (m, 2, HC=CH), 7.10—8.00 (m, 4, HC=C). Found: C, 61.43; H, 6.69%. Calcd for $C_{20}H_{25}NO_3S_2$: C, 61.35; H, 6.44%.

Similarly, *methyl 2-(2-benzothiazolylthio)-2-(3-oxobutyl)-octanoate (**4b**)* was obtained in 79% yield, bp 152—155 °C/0.01 Torr; IR (neat) 3058 (HC=C), 1731 (ester C=O), 1716 cm^{-1} (C=O); ^{1}H NMR (CCl_4) δ 0.62—1.04 (m, 3, CH_3), 1.04—2.81 (m, 17), 3.71 (s, 3, CH_3O), 7.08—8.02 (m, 4, HC=C). Found: C, 60.95; H, 7.04%. Calcd for $C_{20}H_{27}NO_3S_2$: C, 61.04; H, 6.92%.

*(Z)-2-(2-Benzothiazolylthio)-2-(3-oxobutyl)-5-octenoic Acid (**5a**).* A solution of **4a** (950 mg, 2.43 mmol) and K_2CO_3 (1.01 g, 7.31 mmol) in MeOH (20 ml) containing water (5 ml) was stirred at 45—55 °C for 14 h. The solution was concentrated to *ca.* 5 ml of total volume, diluted with brine, acidified with aqueous 10% HCl, and extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4) and concentrated. The residue was chromatographed (SiO_2, benzene/AcOEt/MeOH, 30/3/1) to give **5a** (882 mg, 96%): IR (neat) 3650—2200 (COOH), 1713 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3, J=7 Hz, CH_3), 1.69—2.95 (m, 15), 5.14—5.54 (m, 2, HC=CH), 7.20—8.08 (m, 4, HC=C), 10.41 (s, 1, COOH). Found: C, 60.40; H, 6.13%. Calcd for $C_{19}H_{23}NO_3S_2$: C, 60.45; H, 6.14%.

Similarly, hydrolysis of **4b** afforded **5b** in 92% yield, IR (Nujol) 2996 (COOH), 1713 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3, J=6 Hz, CH_3), 1.02—2.96 (m, 17), 7.22—8.07 (m, 4, HC=C), 12.10 (s, 1, COOH). Found: C, 60.34; H, 6.64%. Calcd for $C_{19}H_{25}NO_3S_2$: C, 60.13; H, 6.64%.

*Electrolytic Decarboxylation of **5**.* *Method A*: A solution of **5a** (51 mg, 0.14 mmol) in AcOH (6 ml), *t*-BuOH (3 ml), and Et_3N (0.2 ml) was electrolyzed under a constant current of 20 mA/cm^2 (applied voltage 18—25 V) at 42 °C using two carbon electrodes (1.5×2 cm^2) for 2.5 h. Evaporation of the solvents followed by column chromatography (SiO_2, benzene/AcOEt, 10/1) gave **6a** (15 mg, 61%), whose IR and NMR spectra were identical with those of reported one.[1]

Method B: The electrolysis of **5a** (48 mg, 0.13 mmol) in MeOH (10 ml) and Et_3N (0.2 ml) at 30 mA/cm^2, 18—22 V, at 45—55 °C using platinum electrodes (1.5×2 cm^2) for 2.5 h gave **6a** (12.5 mg, 54%). Similarly, the electrolysis of **5b** gave **6b** in 54% yield.

Method C: The electrolysis of **5b** (101 mg, 0.27 mmol) in aqueous 0.025 M NaOH (20 ml) covered with hexane (10 ml) using platinum electrodes (1.5×2 cm^2) at 30 mA/cm^2, 7—9 V, at 46—50 °C for 4 h gave **6b** (31 mg, 64%) after evaporation of the organic layer (upper layer). Extractive workup of the aqueous alkaline solution gave **5b** (7 mg, 5%).

*cis-Jasmone (**7a**) and Dihydrojasmone (**7b**).* According to the reported procedure,[1a] a solution of **6a** (15 mg, 0.08 mmol) in aqueous 2% KOH was heated to reflux for 3 h. Extractive workup of the solution gave **7a** (12 mg, 89%). Similarly, **7b** was obtained in 87% yield. Their spectral data were identical with those of reported ones.[1]

References

1) (a) S. Torii, H. Tanaka, and Y. Tomotaki, *Bull. Chem. Soc. Jpn.*, **50**, 537 (1977); (b) S. Torii and H. Tanaka, *Koryo*, **114**, 41, (1976); (c) T.-L. Ho, *Synth. Commun.*, **4**, 256 (1974); (d) R. A. Ellison, *Synthesis*, **1973**, 397, and references cited therein.

2) *N*-(2-Benzothiazolylthio)morpholine (**3**) has been electrosynthesized: S. Torii, H. Tanaka, and M. Ukida, *J. Org. Chem.*, **43**, 3223 (1978).

3) S. Torii, H. Tanaka, and H. Okumoto, *Bull. Chem. Soc. Jpn.*, **52**, 267 (1979).

4) S. Torii, T. Okamoto, and T. Oida, *J. Org. Chem.*, **43**, 2294 (1978).

5) Bis(2-benzothiazolyl) disulfide was isolated in 20—45% yields. The details of the reaction mechanism will be discussed elsewhere.