A New Synthesis of (E,E)-8,10-Dodecadien-1-ol, Sex Pheromone of Codling Moth*

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* Selective Alkylation of Ethyl 3-Oxoglutarate. Part IV. For part III, see ref. 3.

EXPERIMENTAL PROCEDURES

All boiling points and melting points were uncorrected. IR spectra were determined with a Hitachi 260-10 spectrometer. NMR spectra were recorded with a Hitachi R-24B instrument at 60 MHz using TMS as an internal standard. GC-MS was performed with a JEOL JMS-D300 spectrometer at 22 eV.

(E,E)-2,4-Hexadienyl bromide (sorbyl bromide). The compound was prepared by treating sorbyl alcohol with triphenylphosphine dibromide in methylene chloride.

Ethyl 2-(E,E)-2,4-Hexadienyl-3-oxoglutarate (2). To a solution of magnesium ethoxide prepared freshly from magnesium turnings (7.2 g, 0.3 mol) and iodine in absolute alcohol (270 ml), ethyl 3-oxoglutarate (1, 40.4 g, 0.2 mol) was added dropwise over a period of 0.5 hr with stirring and the solution was refluxed for 1 hr. The solution was then allowed to cool to room temperature, sorbyl bromide (35.4 g, 0.22 mol) was added over 1 hr at a constant rate and the mixture was refluxed for 18 hr with stirring. After the solvent in the reaction mixture was distilled off in vacuo, the residue was acidified with 10% HCl and extracted with ether. The ether solution was washed with a 5% aqueous solution of NaHCO₃, water and brine in succession, and dried over Na₂SO₄. The solvent was evaporated in vacuo to give the compound 2 as a dark brown viscous liquid, which was purified as a yellow viscous liquid (40 g, 71%) by silica gel (Merck Kieselgel 60) column chromatography with a n-hexane–ether (10:1) mixed solvent. IR νmax cm⁻¹: 3020, 1730, 1710, 1025, 985. NMR δ (CDCl₃): 1.25 (6H, t, J=7.5 Hz), 1.70 (3H, d, J=6.0 Hz), 1.28 (2H, t, J=6.8 Hz), 3.55 (2H, s), 3.68 (1H, t, J=6.8 Hz), 4.18 (4H, q, J=7.5 Hz), 5.05–6.15 (4H, m).

Methyl 5-oxo-(E,E)-8,10-Dodecadienoate (3). A solution of 2 (56.4 g, 0.2 mol) in dry 1,2-dimethoxyethane (DME, 50 ml) was added dropwise to a stirred solution of sodium hydroxide (9.6 g of a 50% mineral oil dispersion, 0.2 mol) in dry DME (150 ml) at room temperature and stirring was continued for 1 hr. Ethyl 3-bromopropionate (43.4 g, 0.24 mol) and finely powdered sodium iodide (8 g) were then added to the solution and the mixture was refluxed for 18 hr with stirring. The reaction mixture was cooled to room temperature, and the solvent was distilled off in vacuo. The residue was heated with a 15% aqueous solution of NaOH (500 ml) under reflux for 20 hr, and the reaction mixture was acidified with conc. HCl, saturated with NaCl and extracted with ether. The ether solution, after being washed with brine and dried over Na₂SO₄, was evaporated in vacuo to give the compound 3 as a yellow liquid, bp 105–120°C (0.4 mmHg), silica gel (Merck Kieselgel 60) column chromatography of which with n-hexane–ether (8:1) gave the methyl ester 3 (20.6 g, 46% yield from 2).

The keto ester 3 via tosylhydrazone was reductively deoxygenated by heating with sodium cyanoborohydride in acidic dimethylformamide-sulfolane⁵ to give an ester (4), which was finally reduced to the desired alcohol 5 with lithium aluminum hydride (38% yield from 3).

Note

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Methyl (E,E)-8,10-dodecadienoate (4). To a mixed solution of 3 (15.7 g, 0.07 mol) and p-toluene-sulfonylhydrazine (16.3 g, 0.0875 mol) in DMF-sulfolane (350 ml, 1:1) was added p-toluenesulfonic acid (1.75 g) and sodium cyanoborohydride (17.6 g, 0.28 mol) at room temperature, and the solution was heated at 100°C for 4 hr. After cooling to room temperature, the reaction mixture was diluted with water (1000 ml) and extracted with cyclohexane. The cyclohexane solution was washed with water, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography of the oily residue over silica gel (Merck Kieselgel 60) with petroleum ether–ether (10:1) gave 4 (5.6 g, 38%) as a pale yellow liquid, bp 107 – 110°C (0.4 mmHg). IR νmax cm⁻¹: 3020, 1735, 1630, 985. NMR δ (CCl₄): 1.35 (8H, m), 1.74 (3H, d, J=6.0 Hz), 1.90–2.45 (4H, m), 3.62 (3H, s), 5.30–6.25 (4H, m). MS m/e: 210 (M⁺, 100), 178 (M⁺–CH₃OH, 46), 82 (28), 81 (45), 68 (62).

(E,E)-8,10-Dodecadien-1-ol (5). A solution of 4 (4.2 g, 0.02 mol) in absolute ether (40 ml) was added dropwise to a slurry of lithium aluminum hydride (0.38 g, 0.01 mol) in absolute ether (60 ml) with stirring at room temperature. Stirring was continued for 1 hr at room temperature. After the mixture was refluxed for 1 hr, the reaction was quenched with 2N H₂SO₄ (30 ml) and the mixture was worked up by the usual procedure to give the alcohol 5, with a nearly quantitative yield, which solidified during storage in a refrigerator, mp 28–29°C (recrystallized from petroleum ether). The purity was 97% on GLC analysis (10% SE-30, 2 m, at 100–220°C, 8°C/min). IR νmax cm⁻¹: 3340, 3020, 1630, 985. NMR δ (CDCl₃): 1.74 (3H, d, J=6.0 Hz), 3.58 (2H, t, J=7.0 Hz), 5.25–6.32 (4H, m). MS m/e: 182 (M⁺, 90).

REFERENCES