Note

Efficient Preparation of \((7E,9Z)\)-7,9-Dodecadienyl Acetate, Sex Pheromone of the European Grapevine Moth \((Lobesia botrana)\)

Akira YAMAMOTO and Takehiko FUKUMOTO

Specialty Chemicals Research Center, Shin-Etsu Chemical Co., Ltd., Niigata 942, Japan

Received March 27, 1989

\((7E,9Z)\)-7,9-Dodecadienyl acetate \((E,Z)-7,9\text{-DDDCA}\) (1) was found by Roelofs et al.\(^1\) in 1973 to be the sex pheromone of the European grapevine moth \((Lobesia botrana)\), one of the most serious pests in the grape orchards of Europe. They\(^2\) then showed the synthetic route of 1, which had 7 steps from sebacic acid. The synthetic pheromone was very effective for attracting the male of Lobesia botrana.

We now describe a short-step synthesis of \((E,Z)-1,9\text{-DDDCA}\) (1) by a Wittig reaction, using 9-halo-(2\(E\))-2-nonen-1-al that can easily be prepared from the diethylacetal of 9-halo-2-nonyn-1-al as the key step. As shown in Fig. 1, an 8-halo-1-octyne\(^3\) such as 8-bromo-1-octyne (3) or 8-chloro-1-octyne (2) was treated with methyl magnesium chloride to give the Grignard reagent 4 or 5. A Grignard reaction with triethyl orthoformate was performed in THF at 80~90°C to give the diethylacetal of 9-halo-2-nonyn-1-al (6 or 7) in a 71% yield. 9-Halo-(2\(E\))-2-nonen-1-al (10 or 11) was easily obtained by partial hydrogenation of 6 or 7 after hydrolysis in a 90% yield. The Wittig reaction of 9-halo-(2\(E\))-2-nonen-1-al (10 and 11) and \(n\)-propylidenetriphenylphosphorane was performed in THF to give 1-halo-(7\(E\),9\(Z\))-7,9-dodecadiene \((E,Z)\)-7,9-DDCA (1) in a 92% yield. Through 5 steps from 2 or 3, the overall yields of 1 were 37.3% and 20.9%, respectively. This synthetic \((E,Z)\)-7,9-DDCA had an 87% purity (containing 13% of the \((E,E)\)-isomer), and was very effective in attracting the male of Lobesia botrana and in the mating disruption test in a grape orchard.

The present method has the following characteristics: 1) Each process gave a high yield and is suitable for industrial production; 2) the bifunctional 9-halo-(2\(E\))-2-nonen-1-al, which could be easily prepared from acetylenic compound, was utilized; 3) 1-halo-(7\(E\),9\(Z\))-7,9-dodecadiene was used as the substrate to conveniently give the corresponding acetate with retention of the stereochemistry.

Experimental

All boiling points (bp) are uncorrected. IR spectra were recorded on a JASCO IRA-1, and mass spectra were measured on a HITACH GC-MS (M-80B). 60 MHz NMR spectra were obtained on a HITACH R-24A in CCl\(_4\) with TMS as an internal standard.

9-Chloro-2-nonyn-1-al diethyl acetal (6). To a stirred THF (400 ml) solution of methyl magnesium chloride (2.1 mol) was added dropwise 8-chloro-1-octyne (2, 289 g) at 50~60°C. After stirring for 1 hr at 60~70°C and diluting the mixture with toluene (200 ml), triethyl orthoformate (325 g) was added to the reaction mixture at 80~90°C. After stirring for 20 hr at 90~100°C, the mixture was poured into a 3\text{m} NH\(_4\)Cl solution (300 ml) and extracted with \(\text{i}-\text{hexane}\). The extract was washed with water, dried over anhyd. Na\(_2\)SO\(_4\) and concentrated in vacuo. The residue was distilled to give 6 (350 g, 71%). bp 155~160°C (5 mmHg). IR \(\nu_{\text{max}}\) (neat) cm\(^{-1}\): 2960, 2915, 2235, 1440, 1350, 1325, 1140, 1080, 1045, 1000. NMR \(\delta\): 1.16 (6H, t, \(J=8\)Hz), 1.35~1.65 (8H, m), 2.22 (2H, t), 3.50 (6H, 2\(X\)-CCH\(_2\)O- -CH\(_2\)-Cl), 5.02 (1H, br. s). MS (70 eV) \(m/z\): 246 (M\(^+\), 1.6%), 201 (100%).

9-Bromo-2-nonyn-1-al diethyl acetal (7). In the same manner, 8-bromo-1-octyne (3, 378 g) was converted to 7 (292 g, 50.2%), bp 158~165°C (5 mmHg). IR \(\nu_{\text{max}}\) (neat) cm\(^{-1}\): 2960, 2915, 2235, 1440, 1350, 1325, 1140, 1080, 1045, 1000. NMR \(\delta\): 1.16 (6H, t, \(J=8\)Hz), 1.35~1.65 (8H, m), 2.22 (2H, t), 3.40 (1H, 2\(X\)-CCH\(_2\)O-), 3.50 (2H, t, \(J=8\)Hz), 5.02 (1H, br. s). MS (70 eV) \(m/z\): 290 (M\(^+\), 1.17%), 245 (100%).

9-Bromo-2-nonyn-1-al diethyl acetal (7). In the same manner, 8-bromo-1-octyne (3, 378 g) was converted to 7 (292 g, 50.2%), bp 158~165°C (5 mmHg). IR \(\nu_{\text{max}}\) (neat) cm\(^{-1}\): 2960, 2915, 2235, 1440, 1350, 1325, 1140, 1080, 1045, 1000. NMR \(\delta\): 1.16 (6H, t, \(J=8\)Hz), 1.35~1.65 (8H, m), 2.22 (2H, t), 3.40 (1H, 2\(X\)-CCH\(_2\)O-), 3.50 (2H, t, \(J=8\)Hz), 5.02 (1H, br. s). MS (70 eV) \(m/z\): 290 (M\(^+\), 1.17%), 245 (100%).
44.4 mmol), sodium borohydride (2.3 g, 60 mmol) was slowly added in an N₂ atmosphere. After adding ethylene diamine (7.3 g, 0.12 mol), the reaction mixture was stirred for 30 min at room temperature. To this was added 9-chloro-2-nonyl-1-al diethyl acetal (6, 350 g, 1.42 mol), and the mixture was stirred under a hydrogen atmosphere (5 kg/cm²) in an autoclave at 20–30°C. At the end of a hydrogen uptake of 1 equiv., the reaction mixture was poured into water (500 ml) and extracted with n-hexane (500 ml). The extract then was concentrated in vacuo. The residue, methylene chloride (400 ml) and 20% hydrochloric acid (300 ml) were mixed and stirred for 1 hr at room temperature. After stirring, the methylene chloride solution was washed with brine and a sodium bicarbonate solution, dried over anhyd. Na₂SO₄ and concentrated in vacuo. The residual aldehyde (10) (223.8 g, 1.28 mol, 90.3%) was employed for the next step without further purification, the purity of the desired isomer (E-isomer >99%) being determined by GC analysis. MS (70 eV) m/z: 174 (M⁺, 1%), 41 (100%). IR vmax (neat) cm⁻¹: 1690, 985. NMR S: 1.15–1.55 (8H, br. s); 2.20 (2H, m); 3.52 (2H, t); 6.08 (1H, dd, J = 15 Hz, 7.5 Hz); 6.85 (1H, dt); 9.45 (1H, d, J = 7.5 Hz).

9-Bromo-(2E)-2-nonen-1-al (11). In the same manner, 9-bromo-2-nonen-1-al diethyl acetal (7, 400 g, 1.37 mol) was converted to crude aldehyde 11 (258.3 g, 1.18 mol, 86.1%), which was employed for the next step without further purification. The purity of the desired isomer (E-isomer >99%) was determined by GC analysis. MS (70 eV) m/z: 218 (M⁺, 1%), 41 (100%). IR vmax (neat) cm⁻¹: 1695, 990. NMR δ: 1.17–1.60 (8H, br. s); 2.20 (2H, m); 3.50 (2H, t); 6.05 (1H, dd, J = 15 Hz, 7.5 Hz); 6.85 (1H, dt); 9.45 (1H, d, J = 7.5 Hz).

1-Chloro-(7E,9Z)-7,9-dodecadiene (12). To rc-propyltriphenylphosphonium bromide (270 g, 0.68 mol) suspended in dry THF (500 ml) at room temperature under an N₂ atmosphere was added potassium /e/-butoxide (76 g, 0.68 mol). The mixture was stirred for 30 min, and co-halo-aldehyde 10 (122 g, 0.70 mol) was added at 10–20°C for 50 min. The reaction mixture was concentrated in vacuo, and the residue was mixed with water and n-hexane. The n-hexane layer was washed with brine and concentrated in vacuo. The residue was distilled to give 12, containing 12% of the E,E-isomer (85 g, 0.42 mol, 63.3%), bp 112–118°C (3 mmHg). IR vmax (neat) cm⁻¹: 3010, 2960, 2920, 2851, 1740, 1470, 1415, 1380, 980, 790. NMR δ: 0.99 (3H, t, J = 7 Hz), 1.20–1.85 (8H, br. s); 2.05 (3H, s); 4.20 (2H, t); 5.42 (1H, dt, J₀,1 = 7.5 Hz), 5.75 (1H, dt, J₁,₁₂ = 7 Hz), 6.05 (1H, dd, J₁,₁₂ = 10 Hz), 6.50 (1H, dd, J₁,₁₂ = 10 Hz), 6.85 (1H, dt); 9.45 (1H, d, J = 7.5 Hz).

1-Chloro-(7E,9Z)-7,9-dodecadienyl acetate (1). 1-Chloro-(7E,9Z)-7,9-dodecadiene (12, 60 g, 0.3 mol) or 1-bromo-(7E,9Z)-7,9-dodecadiene (13, 73.5 g, 0.3 mol) were added to a stirred solution of anhyd. potassium acetate (90 g, 0.92 mol) in acetic acid (90 g, 1.5 mol). The reaction mixture was stirred at 160°C for 7 hr in an N₂ atmosphere, before the reaction mixture was poured into water and extracted with n-hexane. The extract was washed with a sodium bicarbonate solution and concentrated in vacuo. The residue was distilled to give 1, containing 13% of the E,E-isomer (62.5 g, 0.28 mol, 92%), bp 112–118°C (3 mmHg). IR vmax (neat) cm⁻¹: 3010, 2960, 2920, 2851, 1740, 1470, 1415, 1380, 980, 790, 725. NMR δ: 0.99 (3H, t, J = 7 Hz), 1.20–1.85 (8H, m); 2.05 (3H, s); 4.20 (2H, t); 5.42 (1H, dt, J₀,₁₂ = 7.5 Hz), 5.75 (1H, dt, J₁,₁₂ = 7 Hz), 6.05 (1H, dd, J₁,₁₂ = 10 Hz), 6.50 (1H, dd, J₁,₁₂ = 10 Hz), 6.85 (1H, dt); 9.45 (1H, d, J = 7.5 Hz).

Acknowledgments. We wish to thank Professor K. Mori and Associate Professor T. Kitahara of the University of Tokyo for their helpful discussions.

References