Note

Convenient Synthesis of Racemic 14-Methy-l-octadecene, Sex Pheromone of the Peach Leafminor Moth

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The peach leafminor moth (Lyonetia clerkella L.) is one of the most serious pests in peach orchards in Japan. 14-Methyl-l-octadecene (1) has been isolated and identified as the sex pheromone of this moth by Sugie et al. in 1984.1) Synthesis of racemic 1 was reported by Sugie et al.2) and by Manabe et al.3) Mori et al. reported a more efficient method for the synthesis of both the enantiomers of 1.2) The synthesized racemic 1, however, had almost the same attractiveness as a crude extract from virgin females of the moth at the same dosage level under field conditions. Therefore, it is very important to establish a synthetic method for a large amount of racemic 1 to utilize the mating disruption technique in peach orchards.

We describe a convenient synthesis of racemic 1, using a coupling reaction with Grignard reagents, prepared from 1-halo-11-methylpentadecane as novel compounds, and allyl halide to synthesize terminal olefinic compounds as the key step. As shown in Fig. 1, 2-chlorohexane (2), was treated with magnesium to give the Grignard reagent (3). Then, a coupling reaction with a 1,10-dihalodecane derivative such as 1,10-dibromodecane (4) or 1-bromo-10-chlorodecane (5) was performed in the presence of dilithium tetrachlorocuprate4) to give 1-halo-11-methylpentadecane. 1-Bromo-11-methylpentadecane (6) and 1-chloro-11-methylpentadecane (7) were isolated in a 65% and 80% yield, respectively. The Grignard reagent (9) prepared from 7 was converted to racemic 1 by treating with allyl chloride in an 80% yield. In the case of Grignard coupling via 8, racemic 1 was obtained in almost the same yield as that already quoted. IR, NMR and MS spectra of the obtained racemec 1 were completely identical with those reported.1 ~3) The overall yield of racemic 1 from the starting material (2) was 64%, which is higher than those of previous methods.1 ~3) As a result, this method is short and efficient for the synthesis of a large amount of racemic 1.

The results of a mating disruption test in Fukushima prefecture showed that the synthesized racemic 1 was effective in a peach orchard.5)

Experimental

All boiling points (bp) were uncorrected. IR spectra were recorded on a JASCO IRA-1, and mass spectra were measured on a HITACHI GC-MS (M-80B). 60 MHz NMR spectra were obtained on a HITACHI R-24A in CDCl3 with TMS as an internal standard.

1-Bromo-11-methylpentadecane (6). A solution of Grignard reagent (3) in THF (300 ml) prepared from 2-chlorohexane (2, 120.5 g, 1.0 mol) and Mg (24.3 g, 1.0 mol) was added dropwise into a solution of 1,10-dibromodecane (4, 375 g, 1.24 mol) and Li2CuCl4 (1.0 g, 4.5 mmol) in THF (500 ml) at 10~20 °C under a nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 1 hr and poured into a mixture of aq. NH4Cl and aq. HCl. The organic layer was separated and concentrated, before the residue was distilled to give 6 (198 g, 65% yield), bp 148~152 °C (4 mm Hg), IR v max (neat) cm⁻¹: 2930, 2860, 1479, 1394, 730. NMR δ: 0.89 (6H, m), 1.23 (25H, br.s), 3.27(2H, t, J=6 Hz). MS (70 eV) m/z: 304 (M⁺, 0.1%), 43 (100%).

1-Chloro-11-methylpentadecane (7). A solution of Grignard reagent (3) in THF (300 ml) prepared from 2-chlorohexane (2, 120.5 g, 1.0 mol) and Mg (24.3 g, 1.0 mol) was added dropwise into a solution of 1-bromo-10-chlorodecane (5, 260 g, 1.0 mol) and Li2CuCl4 (4.5 mmol) in THF (500 ml) at 10~20 °C under a nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 1 hr and poured into a mixture of aq. NH4Cl and aq. HCl. The organic layer was separated and concentrated, before the residue was distilled to give 7 (209 g, 80% yield), bp 148~152 °C (3 mm Hg), IR v max (neat) cm⁻¹: 2930, 2860, 1479, 1394, 730. NMR δ: 0.89 (6H, m), 1.23 (25H, br.s), 3.40(2H, t, J=6 Hz). MS (70 eV) m/z: 260 (M⁺, 0.5%), 85 (100%).

14-Methyl-l-octadecene (1). To a solution of CuCl (0.1 g, 1.5 mmol) and Grignard reagent (9) prepared from 1-chloro-11-methylpentadecane (7, 255 g, 0.98 mol) and Mg (24.3 g, 1.0 mol) in THF (600 ml) was added dropwise allyl chloride (91.8 g, 1.2 mol) at 10 ~ 30 °C under a ni-
trogen atmosphere. The reaction mixture was stirred at 40 °C for 1 hr and poured into a mixture of aq. NH₄Cl and aq. HCl. The organic layer was separated and concentrated, before the residue was distilled to give pure 1 (225 g, 80% yield), bp 131 ~ 135°C (1 mmHg). IR v_max (neat) cm⁻¹: 3090, 2940, 2870, 1640, 1465, 990, 720. NMR δ: 0.89 (6H, m), 1.26 (27H, br. s), 2.04 (2H, m), 4.93 (1H, ddt, J = 10 Hz, 2 Hz, 1 Hz), 4.98 (1H, ddt, J = 17 Hz, 2 Hz, 1 Hz), 5.80 (1H, m). MS (70 eV) m/z: 266 (M⁺, 3%), 43 (100%). These data are identical with those of a previous report.1-3

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References