

Synthesis of Highly Unsaturated Insect Sex Pheromones. Synthesis of (3Z, 6Z, 9Z)-3,6,9-Nonadecatriene and (3Z, 6Z, 9Z)-3,6,9-Heneicosatriene

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Manuscript received 5 July 1988, revised 24 November 1988, accepted 14 December 1988

(3Z, 6Z, 9Z)-3,6,9-Nonadecatriene and (3Z, 6Z, 9Z)-3,6,9-heneicosatriene, female sex pheromones of *Boarmia selenaria* and *Utetheisa ornatrix* respectively, are synthesised via coupling reaction of Grignard reagents of the appropriate bromides with **11** using Li_2CuCl_4 as catalyst in THF.

THE use of synthetic pheromones to influence the behaviour of insects has been extensively investigated¹. (3Z, 6Z, 9Z)-3,6,9-Nonadecatriene (**1**) and (3Z, 6Z, 9Z)-3,6,9-heneicosatriene (**2**) are the major components of female sex pheromones of *Boarmia ascoties selenaria schiffmuller*² (Lepidoptera: Geometridae), a worldwide distributed pest of important crops and arctiid moth *Utetheisa ornatrix*³. Since these pheromones are highly male attractants and can find practical use in pest management of different crops, a number of synthetic procedures have been reported^{4,5}. We report herein a facile and stereoselective synthesis of **1** and **2** through the use of coupling reaction of the bromide (**11**) with the Grignard reagents of the appropriate bromides in THF in the presence of dilithiumtetrachlorocuprate⁶ as a key step. 1-Bromo-2(Z)-pentene^a (**3**), on alkylation with propargyl pyran in the presence of cuprous chloride⁷ as a catalyst, afforded **4**. Depyration of **4** by refluxing with acidified methanolic solution for 4 h gave the alcohol (**5**). Catalytic hydrogenation⁸ of **5** over Lindlar's catalyst and quinoline in dry hexane afforded the olefinic alcohol (**6**) which was converted into the bromide (**7**). Compound **7** was further subjected to alkylation with propargyl pyran followed by depyranylation and catalytic hydrogenation to furnish (Z, Z, Z)-2,5,8-undecatrien-1-ol (**10**) which was transformed into the bromide (**11**) with PBr_3 in dry ether. Coupling of Grignard reagents (prepared from 1-bromooctane/1-bromodecane and magnesium in THF) with bromide (**11**) in the presence of Li_2CuCl_4 as a catalyst at -10° afforded the title compounds **1** and **2** respectively.



1; R' = C_8H_{17}

2; R' = $\text{C}_{10}\text{H}_{21}$

Experimental

Boiling points are uncorrected. Purity of all the analytical samples was checked by tlc. Ir spectra were recorded on a Perkin-Elmer 337 spectrophotometer and ^1H nmr (90 Hz) spectra on a Varian EM-390 using TMS as an internal reference.

1-Tetrahydropyranloxy-2-yn-5(Z)-octene (**4**): To a solution of ethylmagnesium bromide (prepared from 3.15 g, 30 mmol ethyl bromide and 0.72 g, 30 mmol magnesium) under N_2 in THF (20 ml) was added a solution of 3-tetrahydropyranloxy-prop-1-yne (4.16 g, 30 mmol) in THF (20 ml) over a period of 20 min, and refluxed for 6 h and then cooled to room temperature. Cuprous chloride (0.5 g) was added rapidly to the reaction mixture. After stirring for 15 min, 1-bromo-2(Z)-pentene (**3**; 4.5 g, 30 mmol) in THF (20 ml) was added over 15 min when a yellow precipitate appeared and the reaction mixture was left stirring overnight at room temperature. It was then gently refluxed for 9 h followed by tlc monitoring with hexane-ether mixture (4:1). The reaction mixture was cooled, poured into ice-cold saturated ammonium chloride solution, extracted with ether (4×100 ml) and dried. Solvent evaporation followed by distillation under reduced pressure gave pure **4** (3.72 g, 60%), b.p. $142-45^\circ/7-8$ mm (Found: C, 74.78; H, 9.43. $\text{C}_{15}\text{H}_{20}\text{O}_2$ requires: C, 75.00; H, 9.61%); ν_{max} 3 060, 3 000, 2 260, 1 620, 805 and 700 cm^{-1} ; δ (CCl_4) 1.0 (3H, t, 7.6 Hz, CH_2CH_3), 1.60 (6H, m, $3 \times \text{CH}_2$), 2.03



3; R = Br

4; R = $-\text{C} \equiv \text{C}(\text{OHP})_2\text{OTHP}$

5; R = $-\text{C} \equiv \text{C}(\text{OHP})_2\text{OH}$

6; R = $-\text{CH}=\text{CH}(\text{OHP})_2\text{OH}$

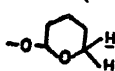
7; R = Br


8; R = $-\text{C} \equiv \text{C}(\text{OHP})_2\text{OTHP}$

9; R = $-\text{C} \equiv \text{C}(\text{OHP})_2\text{OH}$

10; R = $-\text{CH}=\text{CH}(\text{OHP})_2\text{OH}$

11; R = $-\text{CH}=\text{CH}(\text{OHP})_2\text{Br}$

(2H, m, allylic methylene), 2.2 (2H, m, =CHCH₂C=C), 3.5–3.8 (2H, m, ) , 4.2

(2H, s, CH₂-OTHP), 4.79 (1H, s, ) and 5.45

(2H, m, olefinic protons).

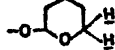
(*Z*)-5-Octen-2-yn-1-ol (5) : Compound 4 (3.72 g, 18 mmol) was refluxed in methanol (100 ml) and *p*-toluenesulphonic acid (0.2 g) for 4 h. The resulting solution was cooled, solvent evaporated and transferred into ice-cooled saturated NaHCO₃ solution. It was then extracted with ether (4 × 50 ml) washed with brine and dried. Evaporation of the solvent followed by distillation afforded 5 (1.5 g, 60%); b.p. 125–28°/6–8 mm (Found : C, 77.32; H, 9.35, C₈H₁₂O requires : C, 77.41; H, 9.67%); ν_{max} 3 350, 3 000, 2 260, 2 100, 1 650, 730 and 700 cm⁻¹; δ (CCl₄) 1.0 (3H, t, *J* 6 Hz, CH₃CH₂), 1.52 (2H, m, allylic methylene), 2.10 (2H, m, =CHCH₂C=), 2.94 (1H, s, OH exchangeable with D₂O), 4.23 (2H, s, CH₂OH) and 5.5 (2H, m, olefinic protons).


(*2Z, 5Z*)-2,5-Octadien-1-ol (6) : Carbinol (5; 5.0 g, 40 mmol) was hydrogenated in presence of Lindlar's catalyst (200 mg) and quinoline (2–3 drops) in dry hexane. When one equivalent of hydrogen was used up, the catalyst was filtered off and the filtrate washed subsequently with dilute acetic acid, water, aqueous NaHCO₃ and water, and dried. Distillation under reduced pressure afforded 6 (4.75 g, 92%); b.p. 130–32°/6–8 mm (Found : C, 75.88; H, 10.85. C₈H₁₄O requires : C, 76.19; H, 11.11%); ν_{max} 3 350, 3 000, 1 650, 1 050, 720 and 705 cm⁻¹; δ (CCl₄) 1.0 (3H, t, *J* 6 Hz, CH₃CH₂), 1.60 (2H, m, allylic methylene), 2.10 (2H, skipped methylene), 3.0 (1H, s, OH exchangeable with D₂O), 4.2 (2H, CH₂OH), 5.5 (4H, m, olefinic protons).

1-Bromo-(*2Z, 5Z*)-2,5-octadiene (7) : PBr₃ (2.7 ml, 25 mmol) was added to a solution of 6 (7 g, 50 mmol) in dry ether (200 ml) containing pyridine (2–3 drops) dropwise at 0°. The solution was stirred for 1 h, refluxed for 1 h and worked up as usual to afford 7 (6.0 g, 57%). Ir spectrum did not show any absorption in the hydroxyl region and used as such in the next reaction.

1-Tetrahydropyranyloxy-2-yn-(*5Z, 8Z*)-5,8-undecadiene (8) : To a solution of ethylmagnesium bromide (prepared from 2.18 g, 20 mmol ethyl bromide and 0.48 g, 20 mmol magnesium) under N₂ in THF (10 ml), was added a solution of 3-tetrahydropyranyloxyprop-1-yne (2.78 g, 20 mmol) in THF (15 ml), and refluxed for 6 h and cooled to room temperature. Cuprous chloride (0.5 g) was then added rapidly and stirred for 15 min followed by addition of 1-bromo-(*2Z, 5Z*)-2,5-octadiene (7; 3.78 g, 20 mmol) in THF (20 ml), and the mixture stirred overnight and worked up in usual manner to yield pure 8 (3.1 g, 62.7%) after chromatography (Found : C,

77.34; H, 9.58. C₁₁H₂₀O₂ requires C, 77.41; H, 9.67%); ν_{max} 3 060, 2 260, 2 100, 1 650, 720 and 705 cm⁻¹; δ (CCl₄) 0.95 (3H, t, CH₃CH₂), 1.1–1.3 (6H, m, 3 × CH₂), 1.5–1.7 (4H, m, allylic protons), 2.1–2.3 (2H, m, skipped methylene), 3.2–3.5 (2H, m,

) , 4.1–4.2 (2H, m, CH₂-O-THP), 4.79

(1H, s, ) and 5.45 (4H, m, olefinic protons).

(*5Z, 8Z*)-5,8-Undecadien-2-yn-1-ol (9) : Compound 8 (3.1 g) was refluxed in methanol (100 ml) and *p*-toluene sulphonic acid (0.5 g) for 3 h. Usual work up followed by column chromatography gave pure 9 (1.2 g, 60%) (Found : C, 80.39; H, 9.68. C₁₁H₁₈O requires : C, 80.48; H, 9.75%); ν_{max} 3 350, 2 240, 1 035, 730 and 700 cm⁻¹; δ (CCl₄) 1.0 (3H, t, *J* 7.5 Hz, CH₃CH₂), 1.52 (2H, m, allylic methylene), 2.01 (2H, m, skipped methylene), 2.95 (2H, s, CH₂C=), 3.34 (2H, s, CH₂OH), 3.90 (1H, s, OH) and 5.5 (4H, m, olefinic protons).

(*2Z, 5Z, 8Z*)-2,5,8-Undecatrien-1-ol (10) : Hydrogenation of 9 (1.2 g) in presence of Lindlar's catalyst and quinoline (2–3 drops) followed by similar workup gave 10 (1.1 g, 94%), b.p. 138–40°/6–8 mm (Found : C, 79.44; H, 10.92. C₁₁H₁₈O requires : C, 79.51; H, 10.84%); ν_{max} 3 350, 1 460, 1 050, 720 and 705 cm⁻¹; δ (CCl₄) 1.0 (3H, t, *J* 7.5 Hz, CH₃CH₂), 2.1 (2H, m, allylic methylene), 3.0 (4H, m, skipped methylenes), 3.35 (1H, s, OH exchangeable with D₂O), 3.95 (2H, m, CH₂OH) and 5.5 (6H, m, olefinic protons).

1-Bromo-(*2Z, 5Z, 8Z*)-2,5,8-undecatriene (11) : The alcohol (10; 1.1 g, 10 mmol) was treated with PBr₃ (0.3 ml, 5 mmol) in the presence of pyridine and dry ether followed by similar workup afforded the bromide (11; 1 g, 71%). Ir spectrum showed no peak in hydroxyl region, and used in the coupling reaction.

(*3Z, 6Z, 9Z*)-3,6,9-Nonadecatriene (1) : To a cooled solution of Grignard reagent (prepared from 0.965 g, 5 mmol 1-bromo-octane and 0.12 g, 5 mmol magnesium) in anhydrous THF (20 ml) under N₂, was added 1-bromo-(*2Z, 5Z, 8Z*)-2,5,8-undecatriene (11; 1.1 g, 5 mmol) in THF (15 ml) over 20 min, stirred for 45 min at –10°, thereafter, a catalytic amount of Li₂CuCl₄ (1.5 ml) was added, stirred for 4 h at –10° and left overnight. The reaction mixture was then quenched with a saturated solution of NH₄Cl, extracted with ether, washed with water and dried. Evaporation of solvent followed by column chromatography over silica gel afforded pure 1 (0.45 g, 35%) (Found : C, 85.79; H, 12.70. C₁₉H₃₄ requires : C, 87.02; H, 12.97%); ν_{max} 2 900, 2 860, 1 490, 1 370, 1 230, 1 090, 1 035, 1 015, 930, 875, 815 and 730 cm⁻¹; δ (CCl₄) 0.86 (6H, t), 1.0–1.3 (14H, m, 7 × CH₂), 1.8 (4H, m, allylic methylenes), 2.6 (4H, m, skipped methylenes), 5.1–5.3 (6H, m, olefinic protons).

(3Z,6Z,9Z)-3,6,9-Heneicosatriene (2): To a cooled solution of Grignard reagent (prepared from 1.09 g, 5 mmol 1-bromo decane in 15 ml anhydrous THF and 0.12 g, 5 mmol dry magnesium) in THF under N₂ was added 1-bromo-(2Z, 5Z, 8Z)-2,5,8-undecatriene (11; 1.07 g, 5 mmol) in THF (20 ml) over 20 min, stirred for 45 min at -10°, thereafter, a catalytic amount of Li₂CuCl₄ (1.5 ml) was added, stirred for 4 h at -10° and left overnight. The reaction mixture was then worked up as usual followed by chromatography over silica gel to give pure 2 (0.52 g, 41%) (Found: C, 86.77; H, 12.92. C₂₁H₃₈ requires: C, 86.89; H, 13.10%); ν_{\max} 2900, 2860, 1485, 1370, 1280, 1230, 1130, 1085, 1040, 920, 875 and 730 cm⁻¹; δ (CCl₄) 0.85 (6H, t), 1.0-1.25 (18H, m, 9 × CH₂), 1.7-1.82 (4H, m, allylic methylenes), 2.70 (4H, m, skipped methylenes) and 5.2-5.35 (6H, olefinic protons).

Acknowledgement

One of the authors (V.D.) is thankful to C.S.I.R., New Delhi, for the award of a Senior Research Fellowship.

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