Synthesis of (Z)-7-heneicosene and (Z)-7-tricosene via organoboranes—Part V

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(Z)-7-Heneicosene 4a and (Z)-7-tricosene 4b, the main components of the female sex pheromone of staphylinid beetle, Aleochara cartula have been synthesized by hydroboration of 1-octyne with HBBr2.SMe2 followed by esterification with a diol and subsequent treatment with Grignard reagent, I2/MeOH and NaOH.

(Z)-7-Heneicosene1 and (Z)-7-tricosene2, the main components of the female sex pheromone of staphylinid beetle, Aleochara cartula have been synthesized earlier3,4.

It was envisioned that these pheromones be prepared stereospecifically with the desired C=C geometry as the presence of minute quantity of opposite stereoisomer inhibits5 the biological activity in most cases. Vinyl organoboranes have elegantly been used6,7 for general stereospecific synthesis of both (Z)- and (E)-disubstituted alkenes. An alternative general process involving alkenylboronic esters has been described for stereospecific synthesis of both the alkenes where one of the organyl group comes from the Grignard reagent. Consequently, in continuation of our work on pheromones, the applicability of the above methodology has been extended and we report herein a one-pot synthesis of pheromones via alkenylboronic esters (Scheme 1).

Hydroboration of 1-octyne 1 with HBBr2.SMe2 yielded the (E)-complex 2 which on treatment with 1,3-propane diol gave the (E)-2-(1-octenyl)-1,3,2-dioxaborinane 3. This intermediate 3 on treatment with Grignard reagent followed by rearrangement afforded exclusively the (Z)-olefins 4a,4b (Scheme 1).

The peak at 725 cm⁻¹ indicated the presence of a cis-double bond in (Z)-7-heneicosene 4a and a multiplet in 1H NMR ranging from δ 5.3 to 5.5 confirmed the formation of C=C. Similarly, (Z)-tricosene 4b in its IR showed a peak at 720 cm⁻¹ for cis-C=C and olefinic protons in its 1H NMR at δ 5.15 to 5.5.

This methodology for preparing (Z)-disubstituted alkenes via alkenylboronic esters is useful for introducing organyl groups not available via hydroboration, thus, generalizing the synthesis of (Z)-disubstituted alkenes via organoboranes.

Experimental Section

General. The glass apparatus and syringes were dried at 140 °C for 4 hr and assembled hot under nitrogen. Hydroboration and Grignard reaction were carried out under a blanket of nitrogen. THF was refluxed over sodium benzophenone distilled just
before use. \( ^1 \)H NMR spectra were recorded in \( \text{CCl}_4 \) on a Varian EM-390 spectrometer using TMS as internal reference (chemical shifts in \( , \) ppm) and IR spectra as liquid films on a Perkin-Elmer infrared 337 spectrophotometer (\( \lambda_{\text{max}} \) in cm\(^{-1} \)).

Preparation of Grignard reagent. A dried 250 mL round bottomed flask, equipped with a magnetic stirring bar, septum inlet and a reflux condenser was, flushed with nitrogen. The flask was charged with 11 mmoles of activated magnesium followed by the addition of 20 mL of dry ether and 11 mmoles of required alkyl halide. After the commencement of the reaction 60 mL of dry ether was added dropwise until the whole metal disappeared.

Preparation of (E)-2-(1-octenyl)-1,3,2 dioxaborinane 3 from 1. Into a dry 100 mL round bottom flask, equipped with a magnetic bar and a condenser, was taken a solution of 1-octyne (20 mmole) in \( \text{CH}_2\text{Cl}_2 \) (30 mL). To this was added 2.7 mL (20 mmole) of BHBr2.SMe2. The contents were stirred for 4 hr at room temperature for completion of the reaction. The volatile material was then pumped off in vacuum at room temperature. To the above reaction mixture was added ethyl ether (15 mL) followed by the addition of 1,3-propanediol (10 mmole) with stirring at room temperature. The contents were allowed to stir for 2 hr.

Preparation of (Z)-7-heneicosene 4a from 3. The solution of (E)-2-(1-octenyl)-1,3,2 dioxaborinane 3 as prepared above was cooled to \(-78^\circ C\) and the Grignard reagent (\( \text{C}_{15}\text{H}_{31}\text{MgBr} \), 11 mmole) in diethyl ether added dropwise until it disappeared. The reaction mixture was stirred for 0.5 hr at \(-78^\circ C\) and then at 0°C for 1 hr. Iodine (10 mmole) in methanol (40 mL) was added slowly at 0°C and the reaction mixture stirred overnight at room temperature. Sodium hydroxide (10 mL of 3 \( M \) solution) was added and the mixture stirred for 15 min. It was then diluted with water (150 mL), and extracted with hexane (3 x 25 mL). The combined hexane extract was washed with an aqueous solution of sodium thiosulfate (25 mL, 1\( M \)) and water (2 x 50 mL) and then dried over anhydrous sodium sulfate. Evaporation of solvent gave the crude product, which was purified by distillation to afford (Z)-7-heneicosene 4a in 83% yield; IR (Neat) : 2900, 1650, 1470 and 725 cm\(^{-1} \); \( ^1 \)H NMR (\( \text{CCl}_4 \)): \$ 5.3-5.5 (2H, olefinic protons), 1.95-2.1 (4H, allylic methylenes) 0.9-2.0 (b, 30 H, 15 X-CH2), 0.9 (t, 6H, 2 X CH3).

Preparation of (Z)-7-tricosene 4b from 3. In a dry 100 mL flask, equipped with a magnetic stirring bar and septum inlet were added (E)-2-(1-octenyl) -1,3,2 dioxaborinane 3 (10 mmole) as above which was diluted with diethyl ether (20 mL). The mixture was then cooled to \(-78^\circ C\) and Grignard reagent (\( \text{C}_{15}\text{H}_{31}\text{MgBr} \), 11 mmole) in diethyl ether added to it dropwise. The reaction mixture was stirred for 0.5 hr at \(-78^\circ C\) and then at 0°C for 1 hr. Iodine (10 mmole) in methanol (40 mL) was added slowly at 0°C and the reaction mixture stirred overnight at room temperature. Sodium hydroxide (10 mL of 3 \( M \) solution) was added and the mixture stirred for 15 min. It was then diluted with water (150 mL), and extracted with hexane (3 x 25 mL). The combined hexane extract was washed with an aqueous solution of sodium thiosulfate (25 mL, 1\( M \)) and water (2 x 50 mL) and then dried over anhydrous sodium sulfate. Evaporation of solvent gave the crude product, which was purified by distillation to afford (Z)-7-tricosene 4b in 84% yield; IR (Neat) : 2950, 1660, 1470 and 720 cm\(^{-1} \); \( ^1 \)H NMR (\( \text{CCI}_4 \)): \$ 5.5-5.5 (2H, olefinic protons), 2.00-2.2 (4H, allylic methylenes), 0.95-1.95 (b, 34 H, 17 X-CH2), 0.9(t, 6H, 2 X CH3 groups).

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References

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