

STEREOSELECTIVE SYNTHESIS OF (6Z,9Z)-6,9-NONADECADIENE AND (6Z,9Z)-6,9-HENEICOSADIENE, SEX PHEROMONES OF *Bupalus piniarius* AND *Utethesia ornatrix*

Om P. VIG, Goverdhan L. KAD*, Madan L. SHARMA, Vijay DOGRA, Sanjiv SHARMA, Mohammad A. HUQ and Arun SABHARWAL

Department of Chemistry, Panjab University, Chandigarh-160014, India

Received December 28, 1989

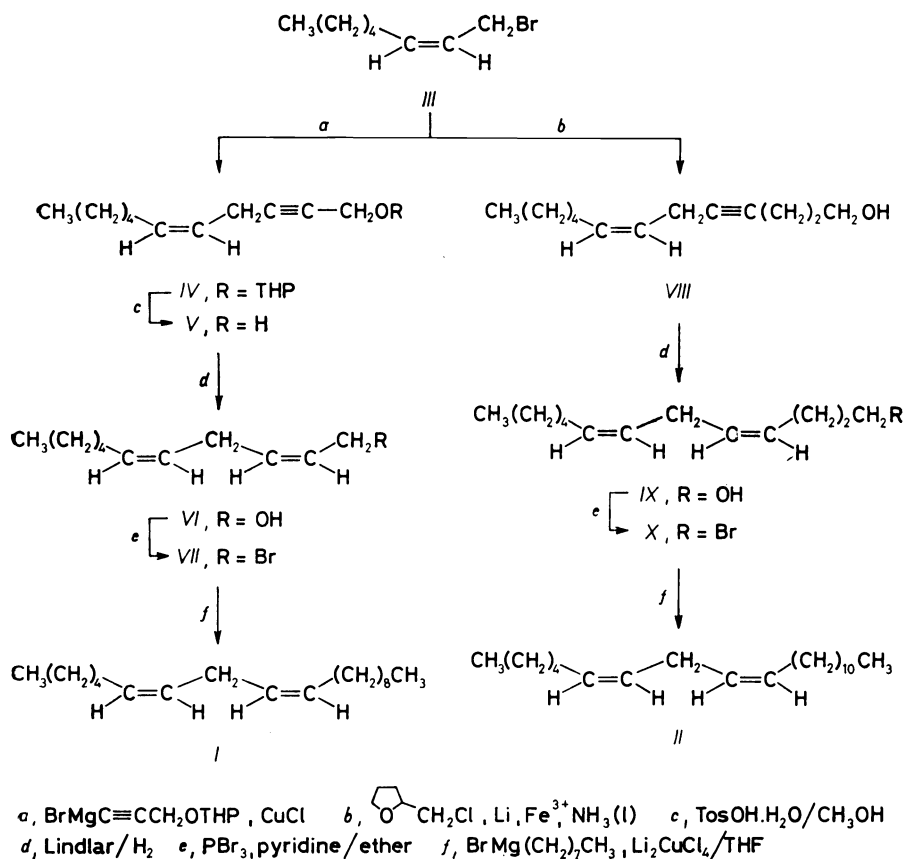
Accepted March 1, 1990

Stereoselective syntheses of (6Z, 9Z)-6,9-nonadecadiene (*I*) and (6Z, 9Z)-6,9-heneicosadiene (*II*), sex attractants of female moths *Bupalus piniarius* and *Utethesia ornatrix*, have been reported.

Electroantennogram active C₁₉- and C₂₁-dienes, (6Z, 9Z)-6,9-nonadecadiene (*I*) and (6Z, 9Z)-6,9-heneicosadiene (*II*) have been isolated from the sex attractant gland secretion of female moths *Bupalus piniarius* and *Utethesia ornatrix* by Bestmann et al.¹ and Meinwald et al.^{2,3}. The presence of two *cis* double bonds at C-6 and C-9 are the important structural features of these diene systems. Literature³⁻⁵ records syntheses of *I* and *II* leading to low yields. Herein, we report simple and stereoselective syntheses of *I* and *II* in good yields (see Scheme 1).

(*Z*)-1-Bormo-2-octene (*III*) on treatment with 3-(2-tetrahydropyranyloxy)-1-propynylmagnesium bromide in the presence⁶ of CuCl, in dry THF under an inert atmosphere at low temperature furnished (*Z*)-1-(2-tetrahydropyranyloxy)undec-5-en-2-yne (*IV*) in 45% yield. Deprotection of *IV* with methanol/*p*-toluenesulfonic acid monohydrate gave pure *V* which on semihydrogenation over Lindlar's catalyst in hexane followed by bromination with phosphorus tribromide/pyridine in anhydrous ether afforded *VII*.

(*Z*)-Tridec-7-en-4-yn-1-ol (*VIII*) was obtained⁷ through the reaction of *III* with tetrahydrofurfuryl chloride using LiNH₂ in liquid NH₃. Carbinol *VIII* was partially reduced using Lindlar's catalyst in hexane quantitatively to *IX*, which on subsequent reaction with phosphorus tribromide/pyridine in anhydrous ether gave *X*. Dilithium tetrachlorocuprate catalysed coupling reaction of *VII* and *X* with octylmagnesium bromide in THF under nitrogen atmosphere at -10° afforded, after silica gel column chromatography, pure *I* and *II* in 40% and 46% yield, respectively. The spectral data (IR, ¹H NMR) of the synthetic samples were found to be in close agreement with the reported values³⁻⁵.



SCHEME 1

EXPERIMENTAL

Boiling points are uncorrected. Progress of all reactions was monitored by TLC using silica gel impregnated with 13% calcium sulfate. Silica gel (Acme, 60–80 mesh) was used for column chromatography. IR spectra were obtained with Perkin-Elmer 377 spectrophotometer (wave-numbers in cm^{-1}) and ^1H NMR spectra (CCl_4) on a Varian EM-390 using tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ -scale), coupling constants (J) in Hz. Unless otherwise mentioned, all organic extracts were dried over anhydrous sodium sulfate.

(Z)-1-(2-Tetrahydropyranyloxy)-undec-5-en-2-yne (IV)

A solution of 7.0 g (50 mmol) 1-(2-tetrahydropyranyloxy)-2-propyne in 30 ml dry THF, was added to the clear solution of ethylmagnesium bromide (prepared from 5.4 g (50 mmol) of bromoethane and 1.2 g (50 mmol) of Mg in 30 ml THF under nitrogen atmosphere), during 30 min and refluxed for 6 h, cooled to room temperature and to this was added 500 mg of CuCl rapidly.

(*Z*)-1-Bromo-oct-2-ene *I*, (7.2 g, 38 mmol) in 30 ml dry THF was added to the reaction mixture slowly and then refluxed gently for 9 h. The well stirred reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution, extracted with ether (4×50 ml). The organic phase was washed with brine and dried. Evaporation of the solvent followed by vacuum distillation gave pure *IV*; 4.32 g (45%), b.p. $144\text{--}148^\circ\text{C}/0.80\text{--}1.07$ kPa. IR spectrum (neat): 3 060, 3 000, 2 330, 2 250, 1 620, 1 460, 905, 860, 805, 725, 700. ^1H NMR spectrum: 5.48 m, 2 H ($2 \times \text{H}-\text{C}=\text{C}$); 4.79 s, 1 H (H-2 of tetrahydropyranyloxy group); 3.80–4.20 m, 4 H (CH_2O and $2 \times \text{H}-6$ of tetrahydropyranyloxy group); 3.00 d, 2 H ($=\text{CH}-\text{CH}_2-\text{C}\equiv$, $J = 7$); 2.08 m, 2 H ($\text{CH}_2-\text{CH}=\text{C}$); 1.36 m, 12 H ($6 \times \text{CH}_2$); 1.00 t, 3 H (CH_3). For $\text{C}_{16}\text{H}_{26}\text{O}_2$ (250.4) calculated: 76.75% C, 10.47% H; found: 76.68% C, 10.38% H.

(*Z*)-Undec-5-en-2-yn-1-ol (*V*)

A mixture of 4.32 g (17 mmol) of *IV* and 400 mg *p*-toluenesulfonic acid monohydrate in 100 ml methanol was stirred for 6 h at 55°C , cooled and neutralised with solid NaHCO_3 . Methanol was removed under reduced pressure to afford a residue which was diluted with water, extracted with ether (3×25 ml) and dried. Solvent was evaporated and residue was distilled under vacuum to yield 1.9 g (66%) of *V*, b.p. $128\text{--}130^\circ\text{C}/0.80\text{--}1.07$ kPa. IR spectrum (neat): 3 350, 3 090, 2 980, 2 330, 2 240, 1 650, 1 460, 1 035, 730, 700. ^1H NMR spectrum: 5.45 m, 2 H ($2 \times \text{H}-\text{C}=\text{C}$); 4.20 s, 2 H (CH_2OH); 3.87 s, 1 H (OH; exchangeable with D_2O); 3.00 d, 2 H ($\text{CH}_2-\text{C}\equiv$); 2.04 m, 2 H ($\text{CH}_2-\text{CH}=\text{C}$); 1.32 m, 6 H ($3 \times \text{CH}_2$); 0.97 t, 3 H (CH_3). For $\text{C}_{11}\text{H}_{18}\text{O}$ (166.3) calculated: 79.46% C, 10.91% H; found: 79.35% C, 10.90% H.

(2*Z*, 5*Z*)-2,5-Undecadien-1-ol (*VI*)

Acetylenic alcohol *V* (1.9 g, 12 mmol) was partially hydrogenated in the presence of 100 mg Lindlar's catalyst and 3 drops of quinoline in dry hexane (20 ml). Hydrogen pressure (276 kPa) was applied and stirred mechanically. When one equivalent of hydrogen was taken up, the catalyst was filtered off. The solution was washed with dilute acetic acid, water and dried. Solvent removal followed by chromatography of the residue over silica gel gave TLC pure *VI*; 1.77 g (92%). IR spectrum (neat): 3 350, 3 060, 3 000, 1 650, 1 460, 1 050, 720, 705. ^1H NMR spectrum: 5.35 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 4.20 d, 2 H (CH_2OH); 3.20 s, 1 H (OH, exchangeable with D_2O); 2.70 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.00 m, 2 H ($\text{CH}_2-\text{C}\equiv$); 1.20–1.58 s, 6 H ($3 \times \text{CH}_2$); 0.88 t, 3 H (CH_3). For $\text{C}_{11}\text{H}_{20}\text{O}$ (168.3) calculated: 78.51% C, 11.98% H; found: 78.40% C, 11.85% H.

(2*Z*, 6*Z*)-1-Bromo-2,5-undecadiene (*VII*)

To 1.77 g (10 mmol) of alcohol *VI* in 75 ml dry ether containing two drops of dry pyridine, 0.5 ml freshly distilled phosphorus tribromide in 10 ml dry ether was added and allowed to stand overnight. After refluxing for 2 h, the reaction mixture was cooled, poured into iced water, extracted with ether (4×25 ml), washed with 5% NaHCO_3 , brine and dried. Evaporation of the solvent furnished 1.70 g (70%) of bromide *VII*. IR spectrum (neat): 3 000, 2 950, 1 650, 1 470, 1 380, 1 260, 800, 710. ^1H NMR spectrum: 5.40 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 3.97 d, 2 H (CH_2Br); 2.70 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.03 m, 2 H ($\text{CH}_2-\text{C}\equiv$); 1.20–1.55 s, 6 H ($3 \times \text{CH}_2$); 0.90 t, 3 H (CH_3).

(4*Z*, 7*Z*)-4,7-Tridecadien-1-ol (*IX*)

The alcohol (*IX*) was prepared from 6.0 g (31 mmol) of (*Z*)-7-tridecen-4-yn-1-ol⁷ (*VIII*) by hydrogenation on 600 mg of Lindlar's catalyst in 20 ml hexane as reported for *VI*. Yield 5.45 g (90%).

IR spectrum (neat): 3 380, 3 000 1 645, 1 050, 720, 705. ^1H NMR spectrum: 5.26–5.30 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 4.00 d, 2 H (CH_2OH , $J = 4.5$); 3.40 s, 1 H (OH, exchangeable with D_2O); 2.78 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.1 m, 4 H ($2 \times \text{CH}_2-\text{CH}=\text{C}$); 1.15–1.45 m, 8 H ($4 \times \text{CH}_2$); 0.86 t, 3 H (CH_3). For $\text{C}_{13}\text{H}_{24}\text{O}$ (196.3) calculated: 79.53% C, 12.32% H; found: 79.46% C, 12.29% H.

(4Z, 7Z)-1-Bromo-4,7-tridecadiene (*X*)

To a well stirred and cooled solution of 5 g (25 mmol) of *IX* in 200 ml dry ether containing 3 drops of pyridine was added 1 ml (10 mmol) of phosphorus tribromide in 10 ml dry ether during 15 min. The reaction mixture was kept overnight and then refluxed for 2 h. Working up as described for *VII* afforded 4.5 g (68%) of bromide *X*. IR spectrum (neat): 3 010, 2 910, 1 645, 1 460, 725. ^1H NMR spectrum: 5.3 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 3.46 t, 2 H (CH_2Br); 2.75 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.05 m, 4 H ($2 \times \text{CH}_2-\text{CH}=\text{C}$); 1.3 bs, 8 H ($4 \times \text{CH}_2$); 0.85 t, 3 H (CH_3).

(6Z, 9Z)-6,9-Nonadecadiene (*I*)

To the Grignard reagent (prepared from 2.31 g (12 mmol) octylbromide and 0.28 g (12 mmol) activated Mg in 20 ml dry THF under nitrogen) was added dropwise at -10°C 2.77 g (12 mmol) *VI* in 10 ml anhydrous THF and the mixture was stirred for 30 min. To the resulting mixture a catalytic amount (1.5 ml) of Li_2CuCl_4 , (prepared from 0.85 g LiCl and 0.135 g CuCl_2 in 10 ml anhydrous THF) was added and stirred for 5 h at -10°C . The reaction was quenched with saturated NH_4Cl solution, extracted with ether (4×50 ml), washed with brine and dried. Removal of the solvent followed by chromatography over silical gel using ether (4%) in petroleum ether as eluent afforded the pure title compound. Yield 1.26 g (40%). IR spectrum (neat): 3 010, 2 960, 2 920, 2 850, 1 640, 1 460, 1 375, 1 260, 720. ^1H NMR spectrum: 5.25–5.55 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 2.65 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.05 m, 4 H ($2 \times \text{CH}_2-\text{C}=\text{C}$); 1.32 s, 20 H ($10 \times \text{CH}_2$); 0.87 t, 6 H ($2 \times \text{CH}_3$). For $\text{C}_{19}\text{H}_{36}$ (264.5) calculated: 86.28% C, 13.72% H; found: 86.24% C, 13.76% H

(6Z, 9Z)-6,9-Heneicosadiene (*II*)

Compound *II* was prepared from 2.68 g (10 mmol) of *X*, 2 g (10 mmol) octylbromide and 0.24 g (10 mmol) Mg, as reported above for *I*. Yield 1.39 g (46%). IR spectrum (neat): 3 010, 2 945, 2 920, 2 840, 1 640, 1 570, 1 460, 1 260, 720. ^1H NMR spectrum: 5.40–5.60 m, 4 H ($4 \times \text{H}-\text{C}=\text{C}$); 2.60–2.85 m, 2 H ($=\text{CH}-\text{CH}_2-\text{CH}=\text{C}$); 2.00–2.30 m, 4 H ($2 \times \text{CH}_2-\text{C}=\text{C}$); 1.36 bs, 24 H ($12 \times \text{CH}_2$); 0.87 t, 6 H ($2 \times \text{CH}_3$). For $\text{C}_{21}\text{H}_{40}$ (292.6) calculated: 86.22% C, 13.78% H; found: 86.18% C, 13.82% H.

The financial support from the CSIR, New Delhi is highly acknowledged.

REFERENCES

1. Bestmann H. J., Vostrowsky O.: *Naturwissenschaften* 9, 457 (1982).
2. Conner W. E., Eisner T., Vander R. K., Guerrero A., Ghiringhelli D., Meinwald J.: *Behar. Ecol. Sociobiol.* 7, 55 (1980).
3. Jain S. C., Dussourol D. E., Conner W. E., Eisner T., Guerrero, A., Meinwald J.: *J. Org. Chem.* 48, 2266 (1983).

4. Bestmann H. J., Dotzer R., Manero-Alvarez J.: *Tetrahedron Lett.* 1985, 2769.
5. O'Conner B., Just G.: *J. Org. Chem.* 52, 1801 (1987).
6. Jain S. C., Dussourol D. E., Conner W. E., Eisner T., Gurrero A., Meinwald J.: *J. Org. Chem.* 48, 2266 (1983).
7. Yadav J. S., Reddy P. S.: *Synth. Commun.* 16, 1119 (1986).