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A STEREOSELECTIVE SYNTHESIS OF (Z,E)-9,11-TETRADECADIENYL-1-ACETATE, A MAJOR COMPONENT OF THE SEX PHEROMONE OF *SPODOPTERA LITURA*

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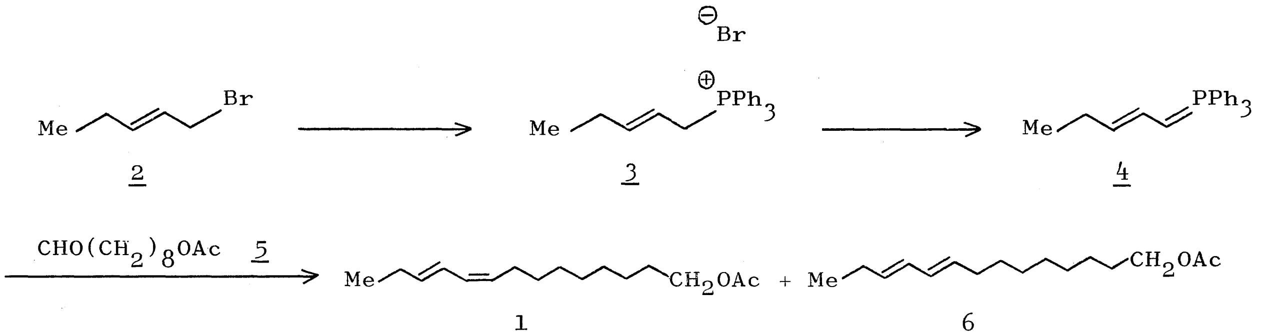
Wittig reaction of 9-acetoxynonyl-triphenylphosphonium bromide (7) with (E)-2-pentenal (8) gave stereoselectively (85-90%) (Z,E)-9,11-tetradecadienyl-1-acetate (1) together with a small amount of the (E,E)-isomer (6) which was removed from the mixture by the formation of the Diels-Alder adduct (13) with tetracyanoethylene. In contrast, Wittig reaction of (E)-2-pentenyl-triphenylphosphonium bromide (3) with 9-acetoxynonyl aldehyde (5) afforded a mixture of 1 and 6.

(Z,E)-9,11-Tetradecadienyl-1-acetate (1) is a major component of the sex pheromone of *Spodoptera litura*[1], a wellknown pest of vegetable crops in Japan. 1 has been also isolated from *Spodoptera littoralis*[2,3] which is a polyphagous pest, especially on cotton plants, in Mediterranean countries. For the studies of insects-controlling, a large amount of pure 1 was required. Present communication describes a convenient stereoselective synthesis of 1.

Wittig reaction of (E)-2-pentenyl-triphenylphosphonium bromide (3), m.p. 209-210°, obtained from (E)-2-pentenyl bromide (2)[4], with 9-acetoxynonyl aldehyde (5)[5] gave a mixture of (Z,E)-9,11-tetradecadienyl-1-acetate (1) and the (E,E)-isomer

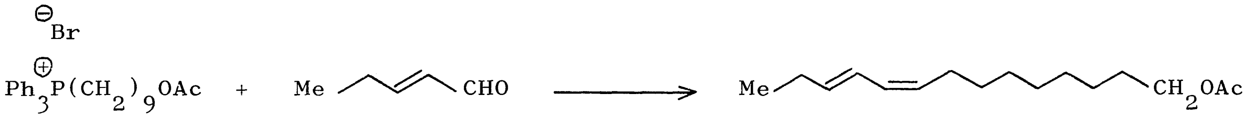


2 3 4

1 6

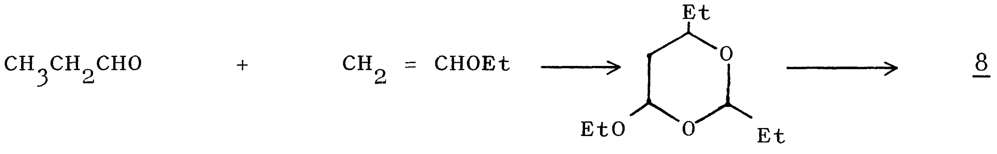
(6)[6] in various ratios depending on the solvent polarity and the base used: in benzene (potassium t-butoxide) 40:60[7], in glyme (n-butyllithium) 50:50, in dimethyl sulfoxide (sodio methylsulfinylcarbanide)[8] 60:40. Preferential formation of trans-olefins (even in polar solvent) in the Wittig reaction of alkylidenetriphenylphosphorane such as 4 has already been reported[10-12].

The alternative Wittig reaction of 9-acetoxynonyl-triphenylphosphonium bromide (7) with (E)-2-pentenal (8) in dimethyl sulfoxide using sodio methylsulfinylcarbanide[8] under nitrogen at 5° gave 1 together with a small amount of 6 (10-15%) in 74% yield. The C_9-Wittig reagent (7) was prepared as follows. Monobromination of diol (9) with 48% HBr in n-heptane[13] followed by acetylation gave the bromoacetate (11) (96% yield), b.p. 122-123° (0.5 mmHg) and the treatment of 11 with triphenylphosphine in acetonitrile afforded 7 in 94% yield (amorphous powder), IR ν_{max} (KBr) 1730 (OAc), 1600 cm^{-1} (Ar). C_5-Aldehyde (8) (98% pure), b.p. 42° (35 mmHg), was obtained by hydrolysis of cyclic acetal (12),[14,15] readily available from propionaldehyde and ethyl vinyl ether.



7 8 1

$$\underset{\underline{9}}{HO(CH_2)_9OH} \longrightarrow \underset{\underline{10}}{Br(CH_2)_9OH} \longrightarrow \underset{\underline{11}}{Br(CH_2)_9OAc} \longrightarrow \underline{7}$$



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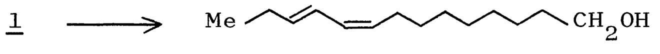
Separation of the (E,E)-isomer (6) from the mixture was effected by treatment with excess tetracyanoethylene[16,17] in tetrahydrofuran at 30° to result in the formation of the Diels-Alder adduct (13), m.p. 87° (from n-hexane-ether 5:1), IR ν_{max} (KBr) 2250 (CN), 1720 (OAc), 850 cm^{-1} (C=C); NMR δ_{ppm} (CCl_4) 1.23 (3H, t, J=7Hz, CH_3), 2.02 (3H, s, OAc), 4.03 (2H, t, J=6Hz, CH_2O), 5.93 (2H, s, vinyl H); Mass m/e 380 (M^+), 320 (-60), which was easily removed by chromatography on silica gel with n-hexane-ether (5:1) to afford pure 1, b.p. 147-148° (0.2 mmHg), UV λ_{max}

(EtOH) 231.5 nm (ε 20000)[18]; IR ν_{max} (film) 1730 (OAc), 985, 950 cm^{-1} (cis, trans-conjugated diene)[18]; NMR δ_{ppm} (CCl_4) 1.02 (3H, t, J=7Hz, CH_3), 1.94 (3H, s, OAc), 3.94 (2H, t, J=6Hz, CH_2O), 5.0-6.4 (4H, m, vinyl H); Mass m/e 252 (M^+), 192 (-60). In order to test the biological activity of the parent alcohol, 1 was hydrolyzed with sodium carbonate in methanol to give 14, b.p. 158-160° (0.2 mmHg), UV λ_{max} (EtOH) 232 nm (ε 19500); IR ν_{max} (film) 3350 (OH), 985, 950 cm^{-1} (cis, trans-conjugated diene); NMR δ_{ppm} (CCl_4) 1.03 (3H, t, J=7Hz, CH_3), 3.52 (2H, t, J=6Hz, CH_2O), 5.0-6.4 (4H, m, vinyl H); Mass m/e 210 (M^+), 192 (-18). Biological activities of 1 are now in testing in the field against *S. litura*.



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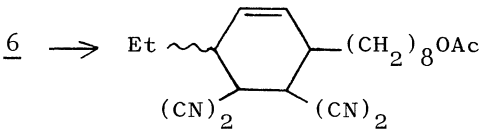

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References and Footnotes

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6. On the basis of the gas chromatographic analysis, the (E,E)-isomer previously reported[1,3] appears to be impurity.
7. The analysis of the products was performed by gas chromatography on a capillary column with 15% PEGA (200 feet, 180°). The relative retention times[9] (internal standard: myristyl acetate) of 1 and 6 were 1.47 and 1.56, respectively.
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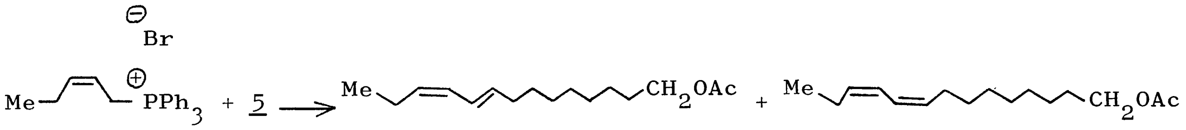
9. Wittig reaction of (Z)-2-pentenyl-triphenylphosphonium bromide (15) with 5 gave also a mixture of the (E,Z)- and (Z,Z)-isomers (16 and 17). The relative retention times of them were 1.50 and 1.54, respectively.



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18. The (E,E)-isomer (6) has UV λ_{max} (EtOH) 229 nm (ε 22000) and IR ν_{max} (film) 1735 (OAc), 990 cm^{-1} (cis, trans-conjugated diene).

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