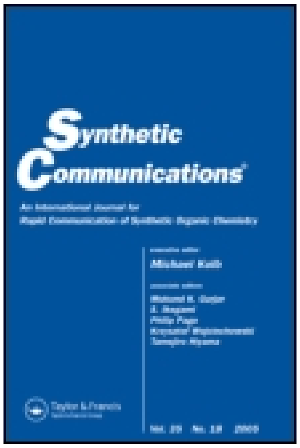

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Synthesis of (*Z*)-5-Decenol and (*Z*)-5-Decenyl Acetate, Components of the Sex Pheromones of a Variety of Lepidoptera

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ABSTRACT

Two simple Wittig procedures for the synthesis of (Z)-5-decenol and (*Z*)-5-decenyl acetate based on the monoacetylation or monobromination of 1,5-pentanediol were followed.

Key Words: Pheromones; Lepidoptera; Wittig reaction.

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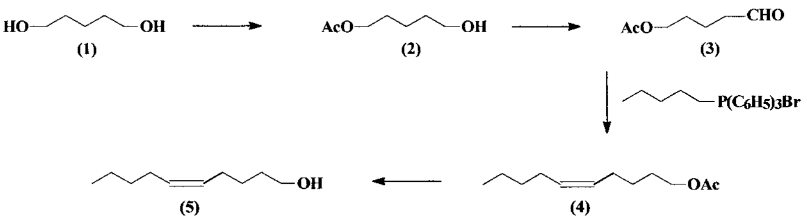
INTRODUCTION

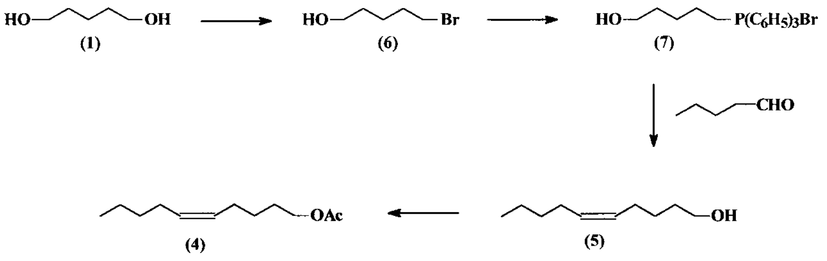
Sex pheromones of Lepidoptera are usually long chain aldehydes, alcohols or esters with one or more double bonds. The presence of the same compound in the sex pheromones of several insects is a common fact.[1] Symmetrical diols are suitable starting material for both the acetylenic[2] or the Wittig[3] routes, which are the most common approaches employed to prepare sex pheromones of Lepidoptera. Both ways usually include monofunctionalization or monoprotection of the symmetrical diol. We now wish to report on the application of simple monoacetylation or monobromination procedures to the Wittig synthesis of (*Z*)-5-decenol and (*Z*)-5-decenyl acetate, which are constituents of the sex attractant mixtures of 22 and 69 insects, respectively.

RESULTS AND DISCUSSION

Treatment of 1,5-pentanediol **1** with NaH in dry THF produced the alkoxyde which on reaction with acetic anhydride led to the monoacetate **2** in 64% after flash chromatography, (See Sch. 1). Oxidation with PCC in $CHCl_3$ produced the aldehyde **3**, which on Wittig olefination with pentyltriphenylphosphonium bromide in THF/DMSO/NaH led to the (*Z*)-5-decenyl acetate **4**. The isomeric purity was verified using GC ($T = 170°C$) Retention Time = 9.66 min. Addition of THF to the solution of the anion of DMSO ($Na^+–CH_2(SO)CH_3$) prior to the addition of phosphonium salt allows the reduction of the amount of dry DMSO, which is usually much more higher than the required for the production of the stoichimetric amount of the base which deprotonates the phosphonium salt. This has allowed us to scale the Wittig procedure up to a 10 mmol amount without significant increases in the volumes of DMSO. Saponification of the alkenol acetate **4** led to the alkenol **5**.



Scheme 1.



Scheme 2.

The second synthetic pathway included monobromination of 1,5-pentanediol with HBr in refluxing benzene under water removal conditions, followed by formation of the ω-functionalized phosponium salt which was treated with the THF solution of two equivalents of (Na^+–$CH_2(SO)CH_3$) and one equivalent of pentanal to produce (*Z*)-5-decenol **5** in moderate yield. Acetylation of the alkenol **5** produced (*Z*)-5-decenyl acetate **4**, (See Sch. 2).

EXPERIMENTAL

IR spectra were recorded on a BIORAD FTS-7 spectrometer. NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using $CDCl_3$ as solvent with TMS (^1H) as references. Gas Chromatograms were recorded on a KNK-300-HRGC KONIC chromatograph using a capillary column DB-5(Long 30 m, Internal Diameter 0.25 mm, Film 0.25 nm Temperature limit 60°C to 325°C, split 1/30).

1,5-Pentanediol monoacetate 2: NaH (120 mg, 5 mmol) was added to a solution of 1,5 pentanediol **1** (521 mg, 5.0 mmol) in dry THF (30 mL). The suspension was refluxed and stirred under argon for 5 h, a solution of acetic anhydride (510 mg, 5.0 mmol) in dry hexane (5 mL) was added dropwise and the mixture was stirred for 3 h, followed by carefully addition of water and extraction with ethyl acetate (50 mL). The organic layer was washed with 5% Na_2CO_3 (2×25 mL) and brine (2×25 mL), dried ($MgSO_4$) and the solvent evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate, 3/2) to afford the monoacetate **2** (395 mg, 2.7 mmol, 54%) as a colorless liquid. Elemental analysis: Estimated for $C_7H_{14}O_3$: C, 57.51%; H, 9.65%. Found: C, 57.60%; H 9.72%. IR (cm^{-1}): 3422 (νOH); 2939, 2867 (νCsp_3–H); 1739 (νC=O); 1241, 1036 (νC–O). ^1H NMR (δ, ppm): 3.96

(2H, t, $J = 6.6$ Hz, CH_2OAc); 3.5 (2H, t, $J = 6.6$ Hz, $\underline{CH_2}OH$); 1.94 (3H, s, CH_3COO); 1.5 (6H, m, $(CH_2)_3$).

5-Acetoxypentanal 3: PCC (1.044 g, 4.8 mmol) was added to a solution of 1,5-pentanediol monoacetate **2** (472 mg, 3.2 mmol) in $CHCl_3$ (25 mL) and the mixture was stirred for 4 h. The reaction mixture filtered through a chromatographic column packed with silica gel (10 g) (eluted with hexane/ethyl acetate, 3/2.) and the solvent evaporated to afford pure 5-acetoxypentanal **3** (439 mg, 3.0 mmol, 94%) as a colorless liquid. Elemental analysis: Estimated for $C_7H_{12}O_3$: C, 58.32%; H, 8.39%. Found: C, 58.11%; H, 8.48%. IR (cm^{-1}): 2959 (νCsp_3–H); 1741 (νC=O carboxyl); 1710 (νC=O carbonyl) 1245, 1044 (νC–O). ^{1}H NMR (δ, ppm): 9.76 (1H, t, $J = 1.7$ Hz, $\underline{CH}O$); 4.03 (2H, t, $J = 6.6$ Hz, CH_2OAc); 2.35 (2H, t, $J = 6.9$ Hz, $\underline{CH_2}CHO$); 2.01 (3H, s, CH_3COO); 1.64 (6H, m, $(CH_2)_3$).

(*Z*)-5-Decenyl acetate 4: NaH (80 mg, 3.3 mmol, 1.1 equiv.) was added to dry DMSO (5 mL). The mixture was stirred under argon at 60°C until total dissolution of NaH, dry THF (15 mL) was added and the mixture cooled to 10°C. Pentyltriphenylphoshonium bromide (438 mg, 3.3 mmol, 1.1 equiv.) was added under vigorous stirring and the temperature was allowed to rise to 25°C. After a brilliant red colour developed the mixture was cooled to 0°C and a solution of 5-acetoxypentanal **3** (438 mg, 3.0 mmol, 1 eq.) in dry THF (10 mL) was added. Stirring was continued for 24 h. The resulting suspension was poured into saturated NaCl solution (50 mL), filtered and extracted with diethyl ether (2 × 30 mL). The combined extracts were washed with brine (2 × 25 mL), dried ($MgSO_4$), evaporated and the resulting residue was purified by flash chromatography (hexane/ethyl acetate, 9/1) in silica gel to afford (*Z*)-5-decenyl acetate **4** (389 mg, 1.9 mmol, 65%) as a pale yellow liquid. Elemental analysis: Estimated for $C_{12}H_{22}O_2$: C, 72.68%; H, 11.18%. Found: C, 72.49%; H, 11.27%. IR (cm^{-1}): 3005 (νCsp_2–H); 2957, 2860 (νCsp_3–H); 1742 (νC=O); 1240, 1040 (νC–O). ^{1}H NMR (δ, ppm): 5.33 (2H, dt, $J_1 = 6$ Hz, $J_2 = 2.1$ Hz CH=CH); 4.03 (2H, t, $J = 6.6$ Hz, CH_2OAc); 2.00 (7H, m, $\underline{CH_2}CH{=}CH\underline{CH_2}$, CH_3COO); 1.3 (2H, m, CH_2); 1.3 (6H, m, $(CH_2)_2$); 0.9 (3H, m, CH_3).

(*Z*)-5-Decenol 5: KOH (112 mg, 2 mmol) was added to a solution of (***Z***)-5-decenyl acetate **4** (157 mg, 0.79 mmol) in methanol (5 mL), the mixture was stirred for 24 h, NaCl saturated solution (2 mL) was added and methanol was eliminated under reduced pressure. The residue was extracted with ethyl acetate (40 mL) and the organic layer washed with 3% HCl solution (2 × 15 mL) and brine (2 × 15 mL), dried ($MgSO_4$) and evaporated to afford pure (*Z*)-5-decenol **5** (119 mg, 0.77 mmol, 93%) after flash chromatographic purification (hexane/ethyl acetate, 9/1). Elemental analysis: Estimated for $C_{10}H_{20}O$: C, 76.86%; H, 12.90%. Found: C, 76.73%; H, 12.99%. IR (cm^{-1}): 3332 (νOH); 3004 (νCsp_2–H); 2932, 2859 (νCsp_3–H); 1065 (νC–O). ^{1}H NMR (δ, ppm): 7.25 (1H, s, OH); 5.36 (2H, t, $J = 4.35$ Hz, CH=CH); 3.65 (2H, t, $J = 6.3$ Hz, $\underline{CH_2}OH$); 2.00 (4H, m, $\underline{CH_2}CH{=}CH\underline{CH_2}$); 1.6 (2H, m, CH_2); 1.4 (6H, m, $(CH_2)_2$); 0.9 (3H, m, CH_3).

5-Bromopentanol 6: A mixture of 1,5-pentanediol **1**, (10.451 g, 100 mmol) 48% HBr (12.5 mL) and benzene (200 mL) was stirred and refluxed for 24 h under a Dean Stark trap, the resulting solution was washed with 6 N NaOH solution (2 × 30 mL), 5% HCl (2 × 30 mL), water (2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried ($MgSO_4$) and evaporated to afford pure 5-bromopentanol **6** (10.986 g, 65.7 mmol, 66%) as a pale yellow liquid. Elemental analysis: Estimated for $C_5H_{11}BrO$: C, 35.95%; H, 6.64%. Found: C, 35.89%; H, 6.69%. IR (cm^{-1}): 3284 (νOH); 2942, 2810 (νCsp_3–H); 1044 (νC–O); 562 (νC–Br). ^{1}H NMR (δ, ppm): 3.71 (1H, s, OH); 3.64 (2H, t; $J = 6.3$ Hz, CH_2Br); 3.4 (4H, dt, J_1=2.1 Hz, J_2=6.9 Hz, $\underline{CH_2}OH$); 1.9 (2H, q, $J = 7.2$ Hz, $\underline{CH_2}CH_2Br$); 1.5 (4H, m, $(CH_2)_2$)

(*Z*)-5-Decenol 5: A. Preparation of 5-hydroxypentyltriphenylphoshonium bromide: 5-bromopentanol (335 mg, 2 mmol) **6** and triphenylphospine (525 mg, 2 mmol) were refluxed for 48 h in ethyl acetate (20 mL), the solvent was evaporated, the resulting gummy solid was refluxed in benzene for 2 h, the hot liquid was decanted, dry THF (20 mL) was added and the solution was maintained under strong stirring for 3 h. **B.** Wittig olefination: NaH (106 mg, 4.4 mmol, 2.2 equiv.) was added to dry DMSO (5 mL), the mixture was stirred under argon at 60°C until total dissolution of NaH, dry THF (15 mL) was added, the mixture cooled to 15°C and added under strong stirring to a cooled (15°C) THF slurry of the phosphoniom salt prepared above. After a brilliant red colour developed the mixture was cooled to 0°C, a solution of pentanal (172 mg, 2 mmol, 1 equiv.) in dry THF (10 mL) was added and stirring was maintained for 24 h. The resulting suspension was poured into saturated NaCl solution (50 mL), filtered and extracted with diethyl ether (2 × 30 mL). The combined extracts were washed with brine (2 × 25 mL) dried ($MgSO_4$), evaporated and the resulting residue purified by flash chromatography (hexane/ethyl acetate, 9/1) in silica gel to afford (*Z*)-5-decenol **4** (164 mg, 1.1 mmol 52%) identical as described above.

(*Z*)-5-Decenyl acetate 4: Acetic anhydride (102 mg, 1 mmol, 2 equiv.) was added to a solution of (*Z*)-5-decenol **5** (78 mg, 0.50 mmol) in dry pyridine (2 mL) and the mixture was stirred overnight. Ice water (5 mL) was added, the solution was stirred for 30 min, ethyl acetate (20 mL) was added and the mixture was washed with water (2 × 10 mL) 10% solution of $CuSO_4$ (3 × 10 mL) and water (3 × 15 mL). The dried solvent ($MgSO_4$)

was evaporated to afford (*Z*)-5-decenyl acetate **4** (96 mg, 0.49 mmol, 98%) identical as described above.

CONCLUSION

A simple procedure based on the monoacetylation of 1,5-pentanediol was followed for the synthesis of (*Z*)-5-decenol and (*Z*)-5-decenyl acetate. Experiments to improve yields of monoacetylation and to adapt this procedure to longer chain symmetrical diols are on development. Additionally a procedure to obtain the same products based on the preparation of ω-functionalized phosponium salt was developed.

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