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Stereoselective Synthesis of (7Z, 11E)-7, 11-Hexadecadien-1-yl Acetate, Sex Pheromone of the Angoumois Grain Moth

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(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**), the sex pheromone of the female Angoumois grain moth, *Sitotroga cerealella*, was synthesized via the acetylenic intermediate, (11E)-11-hexadecen-7-yn-ol THP ether(**2**). The acetylenic compound was prepared from 7-octyn-1-ol THP ether(**4**) and (3E)-1-bromo-3-octene(**3**). The (E)-homoallylic bromide **3** was synthesized by the Julia olefin synthesis of 1-cyclopropylpentan-1-ol(**6**).

Introduction

(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**) (Figure 1) was identified as the sex pheromone of the Angoumois grain moth, *Sitotroga cerealella*, in 1974 by Vick *et al*[1]. This compound was also identified as a component of the sex pheromone of the female pink bollworm moth *Pectinophora gossypiella*(Saunders), a destructive pest of cotton by Hummel et al[2]. in 1973.

Serious economic losses of stored grains are caused by the Angoumois grain moth. In connection with our work on insect pheromones of agricultural importance, we became interested in the synthesis of this pheromone. Also, Institute of Agricultural Science in Suwon, Korea, needed a fair amount of the Angoumois grain moth pheromone to conduct biological activity tests in Korea.

In the literature, the compound **1** was synthesized via acetylenic intermediates[3-5] or Wittig olefination reactions[6-8]. Here we wish to describe a synthesis of (7Z, 11E)-7, 11-hexadecadien-1-yl acetate(**1**) employing the Julia olefin synthesis[9] to introduce the E-11 double bond.

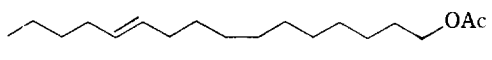

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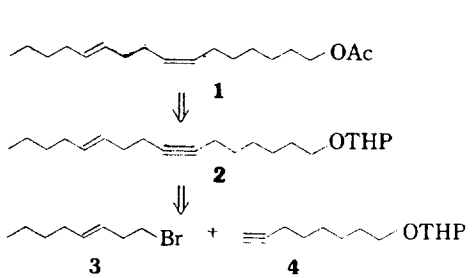
Figure 1

Results and Discussion

A simple retrosynthetic analysis (Scheme 1) reveals that (11E)-11-hexadecen-7-yn-1-ol tetrahydropyranyl ether(**2**) is the penultimate compound which in turn can be prepared from (3E)-1-bromo-3-octene(**3**) and 7-octyn-1-ol THP ether(**4**).

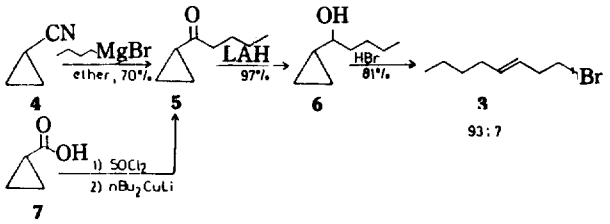
In the literature, (3E)-1-bromo-3-octene(**3**)[4] was prepared from 3-octyn-1-ol by reduction with Na in NH_3 and ether, fractional distillation, and bromination with PBr_3.

The hydrogen bromide promoted rearrangement of secondary cyclopropylmethanols for the preparation of (E)-homoallylic bromide is a useful synthetic reaction.[9]. Thus, cyclopropylcyanide(**4**) was reacted with n-butylmagnesium bromide to give 1-cyclopropylpentan-1-one(**5**)[10]. LAH reduction furnished 1-cyclopropylpentan-1-ol(**6**)[10].



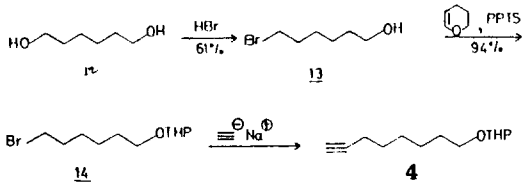
Scheme 1

Treatment of the secondary alcohol **6** with 48% HBr afforded (3E)-1-bromo-3-octene(**3**). The ratio of (E)-and (Z)-isomer was 93:7 by GLC analysis. The ketone **5** was alternatively prepared from cyclopropanecarboxylic acid(**7**) by treatment with $SOCl_2$, followed by acylation[11] with lithium di(n-butyl) cuprate(Scheme 2).



Scheme 2

7-Octyn-1-ol THP ether(**4**)[12] was then reacted with n-butyl lithium in THF to give the lithium acetylide, which was treated with (3E)-1-bromo-3-octene(**3**) in the presence of HMPA to give (11E)-11-hexadecen-7-yn-1-ol THP ether (**2**). The acetylenic intermediate **2** was stereoselectively reduced with H_2 over $Pd/BaSO_2$ to give (7Z, 11E)-7, 11-hexadecadien-1-ol THP ether(**12**). Deprotection by refluxing in the presence of PPTS and ethanol, followed by acetylation with acetic anhydride and pyridine afforded the final product **1**(Scheme 3).



Scheme 3

Experimental

^{1}H-NMR spectra were taken in chloroform-d, at 80 MHz on a BRUKER WP 80 SY spectrometer chemical shifts are reported in ppm δ relative to internal tetramethylsilane. Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer and were calibrated with the 1601 cm^{-1} absorption of polystyrene. Gas chromatogram were obtained on a Varian 3700 gas chromatography with Carbowax 20 M Column (1/8 inch × 6ft, 4% OV-101, 100°C). All solvents were distilled before use.

1-Cyclopropylpentan-1-one(**5**). To a stirred suspension of magnesium (0.12g, 4.9 mmol) in diethyl ether (2.0 m*l*) was added 1-bromobutane (0.66g, 4.8 mmol) slowly under nitrogen atmosphere. After the mixture was stirred at room temperature for 1hr, it was treated with cyclopropyl cyanide (0.33g, 4.9 mmol) in dry diethyl ether (2.0 m*l*). The reaction mixture was heated at reflux for 9hr and then allowed to room temperature. After the addition of satd. NH_4Cl (10 m*l*), it was stirred for 24 hr at room temperature. The organic layer was separated and washed with brine and water. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was distilled on Kugelrohr (45°C, 3 mmHg) to give 1-cyclopropylpentane-1-one(**5**) (0.61g, 70%); IR (NaCl, neat) 3000, 2900, 1690, 1460 cm^{-1}; ^{1}H-NMR δ 0.70-1.15 (m, 7H), 1.16-1.75 (m, 4H), 1.75-2.10 (m, 1H), 2.40-2.70 (t, 2H).

1-Cyclopropylpentan-1-ol(**6**). To a stirred solution of LAH (0.076g, 2.0 mmol) in dry ether (5.0 m*l*) was added 1-cyclopropylpentan-1-one(**5**) (0.25g, 2.0 mmol) in dry ether (5.0 m*l*) slowly at 0°C for 20 min. The reation mixture was stirred at reflux for 3hr and allowed to room temperature. After the addition of satd. Na_2SO_4 (0.25 m*l*), the reaction mixture was stirred at 15-20°C for 15 min. The organic layer was washed with brine and water and dried over $MgSO_4$ and concentrated in vacuo. the crude product was distilled on Kugelrohr (48°C, 3 mmHg) to give 1-cyclopropylpentan-1-ol (0.25g, 97%); IR (NaCl, neat) 3350, 3080, 2950, 1460 cm^{-1}; ^{1}H-NMR δ 0.10-0.35 (m, 2H), 0.36-0.65 (m, 2H), 0.70-1.10 (m, 3H), 1.12-1.75 (m, 8H), 2.70-3.05 (m, 1H).

1-Cyclopropylpentan-1-one(**5**). To a stirred solution of cyclopropanecarboxylic acid (1.72g, 2.00 mmol) in dichloromethane (3.0 m*l*) was added thionyl chloride (2.62g, 2.20 mmol) in dichloromethane (5.0 m*l*) slowly. The reaction mixture was stirred at reflux for 7hr. After evaporation of all the volatiles, the crude product was distilled on Kugelrohr (130°C, 760 mmHg) to give cyclopropanecarboxylic acid chloride (1.81g, 87%); IR (NaCl, neat) 3150, 1790, 1360, 690 cm^{-1}; ^{1}H-NMR δ 0.95-1.50 (m, 4H) 1.95-2.30 (m, 1H).

To a suspension of CuI (1.1g, 6.0 mmol) in dry ether (2.0 m*l*) was added n-BuLi (8.00 m*l*, 1.6M in hexane) at-47°C under nitrogen for 30 min. To this reaction mixture was added cyclopropanecarboxylic acid chloride (0.21g, 2.0 mmol) in dry ether (2.0 m*l*) at-78°C and stirred for 30 min. The reaction mixture was quenched with small amounts of methanol and extracted with ether. The organic layer was washed with water, and then brine and dried over $MgSO_4$. After evaporation of the solvents, the crude product was distilled on Kugelrohr (45°C, 3 mmHg) to give 1-cyclopropylpentan-1-one(**5**) (0.23g, 92%).

(3E)-1-Bromo-3-octene(**3**). To a stirred solution of 1-cyclopropylpentan-1-ol(**6**) (0.20g, 1.6 mmol) in benzene (4.0 m*l*) was aded aqueous hydrobromic acid (48%, 0.67 m*l*). The reaction mixture was stirred at room temperature for 2hr and stirred at reflux for 1hr and allowed to room temperature. The reaction mixture was extracted with ether and washed with satd. $NaHCO_3$ solution, water, and then brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was distilled on Kugelrohr (70°C, 4.5 mmHg) to give (3H)-1-bromo-3-octene(**3**) (0.24g, 81%)with a E/Z isomer ratio of 93:7 (by GC analysis); IR (NaCl, neat) 2950, 2850, 1630, 1450, 1260, 970, 640 cm^{-1}; ^{1}H-NMR δ 0.80-1.05(m, 3H), 1.05-1.60(m, 4H), 1.80-2.15(m, 4H), 3.20-3.55(t, 2H), 4.80-5.30(m, 2H).

(11E)-11-Hexadecen-7-yn-1-ol THP ether(**2**). To a stirred solution of 7-heptyn-1-ol THP ether(**4**) (0.32g, 1.5 mmol) was added n-BuLi (1.5 m*l*, 1.5 M in hexane) slowly at 0°C. The solution was stirred at 0-10°C for 30 min and then (3H)-1-bromo-3-octene(**3**) (0.34g, 1.8 mmol) was added at 0°C. The reaction mixture was stirred at 0-10°C for 4hr and extracted with ether. The organic layer was washed with satd. $NaHCO_3$ solution, water and brine and dried over $MgSO_4$. Concentration in vacuo gave (11E)-11-hexadecen-7-yn-1-ol THP ether(**2**) (0.38g, 80%); IR (NaCl, neat) 2900, 2850, 1630, 1450, 1350, 1200, 1140, 1120, 1040, 970, 900 cm^{-1}; H-NMR δ 0.85(t, 3H), 1.10-2.30(m, 26H), 3.20-4.05(m, 4H), 4.50 (bs., 1H), 5.50-5.80(m, 2H).

(7Z, 11E)-7, 11-Hexadecadien-1-ol THP ether(**12**). To a stirred solution of (11E)-11-hexadecen-7-yn-1-ol THP ether (**2**) (0.22g, 0.68 mmol) in methanol (3.0 m*l*) were added 5%-palladium on barium sulfate (28 mg) and quinoline (2 drops). The mixture was stirred under hydrogen atmosphere for 12hr and filtered to remove the catalyst. Methanol was evaporated in vacuo. The residue was extracted with ether and washed with 6N-HCl, water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give (7Z, 11E)-7, 11-hexadecadien-1-ol THP ether(**15**)(0.19g, 85%); IR (NaCl, Neat) 2900, 2850, 1630, 1450, 1350, 1200, 1140, 1120, 1040, 970, 900 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H), 1.10-2.30 (m, 26H), 3.20-4.05 (m, 4H), 4.55(bS., 1H), 5.50-5.80 (m, 4H).

(7Z, 11E)-7, 11-Hexadecadien-1-yl acetate(**1**). To a stirred solution of (7Z, 11E)-7, 11-hexadecadien-1-ol THP ether (**12**)(0.14g, 0.43 mmol) in ethanol(10 m*l*) was added PPTS (11mg). The mixture was stirred at 55°C for 6hr. Ethanol was evaporated in vacuo and the residue was extracted with ether. The organic layer was washed with 6N-HCl, water and brine and dried over $MgSO_4$. Concentration in vacuo gave (7Z, 11E)-7, 11-hexadecadien-1-ol (0.10g, 93%); IR (NaCl, neat) 3300, 2900, 2850, 1635, 1450, 1050, 970 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H), 1.10-1.80 (m, 12H), 1.81-2.30 (m, 8H), 2.40 (s, 1H), 3.55 (t, 2H, J=6Hz), 5.10-5.70 (m, 4H).

To a stirred solution of (7Z, 11E)-7, 11-hexadecadien-1-ol (0.070g, 0.29 mmol) in dry pyridine (2.0 m*l*) was added anhydrous acetic anhydride (0.036g). The mixture was stirred overnight at room temperature and poured into ice-water and extracted with ether. The organic layer was washed with satd. $NaHCO_3$ solution and brine and dried over $MgSO_4$. Concentration in vacuo and distillation on Kugelrohr (200°C, 3 mmHg) afforded (7Z, 11E)-7, 11-hexadecadien-1-yl acetate (**1**) (0.045g, 55%); IR (NaCl, neat) 2900, 2850, 1740, 1460, 1360, 1240, 1040, 970, 700 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H), 1.10-1.80 (m, 20H), 2.05 (s, 1H), 3.99 (t, 2H, J=6Hz), 5.20-5.70 (m, 4H).

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Thermodynamic Analysis of the Hammett Reaction Parameter and Free Energy Relationship for the Pressure Change

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Pressure dependance of Hammett reaction parameter was analyzed and the free energy relationship for the pressure change derived thermodynamically. There are insufficient data in the literature to test the relation derived but from some limited previous data it could be concluded that the parameter ρ is dependent on pressure and increase or decrease as pressure increase for a given reaction series.

Introduction

The empirical successes of the Hammett equation in correlating a wide variety of equilibrium and rate data are well known. Considerable progress has been made[1-6] in gaining some understanding of why the Hammett equation work as well as it does, and also elucidating its thermodynamic consequences. Among the problems, temperature dependance of Hammett reaction parameter (ρ) was analyzed thermodynamically by Hepler[7] and influence of pressure of ρ-parameter was discussed by Ellis and his coworkers.

In this study, probable effect of pressure on the Hammett