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A Stereoselective Synthesis of (Z,Z)-3,13-Octadecadien-1-yl Acetate, and Its (E,Z)-Isomer, the Sex Pheromone of the Cherry Tree Borer, *Synanthedon hector* Butler

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Received February 2, 1988

A mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(**1**) and its (E,Z)-isomer(**2**), the sex pheromone of the cherry tree borer, *Synanthedon hector* Butler was synthesized. (Z)-11-Octadecen-1-al(**3**) was prepared from 1,10-decandiol. The Wittig reaction of the above aldehyde **3** with carboethoxymethylenetriphenylphosphorane, or the Wadsworth-Emmons reaction of the above aldehyde **3** with the anion of triethylphosphonoacetate gave ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer. Deconjugative protonation of ethyl (Z,Z)-2,13-octadecadienoate and its (E,Z)-isomer with potassium hexamethyldisilazide followed by aqueous ammonium chloride work-up afforded stereoselectively ethyl (E,Z)-3,13-octadecadienoate and its (Z,Z)-isomer, respectively, of which stereoselectivity was adjusted to give the product in the required ratio. Exposure of the above deconjugated ester to excess lithium aluminum hydride resulted in formation of the penultimate (Z,Z)-3,13-octadecadien-1-ol and its (E,Z)-isomer. Acetylation of the desired alcohols afford the final products, (Z,Z)-3,13-octadecadien-1-yl acetate(**1**) and its (E,Z)-isomer(**2**).

Introduction

The sex pheromone of the cherry tree borer, *Synanthedon hector* Butler, was isolated and identified as a mixture of (Z,Z)-3,13-octadecadien-1-yl acetate(**1**) and its (E,Z)-isomer(**2**) (Figure 1) by Yaginuma *et al.*¹ and Voerman *et al.*². The cherry tree borer, *Synanthedon hector* Butler, is one of the most important pests of peach and various deciduous fruit trees in Korea³ and Japan⁴. Also sex pheromones of the less peach tree borer, *Synanthedon pictipes*⁵ Grote Robinson and the peach tree borer, *Sanninodea exitiosa*⁵ Say were identified as (Z,Z)-3,13-octadecadien-1-yl acetate(**1**) and its (E,Z)-isomer(**2**).

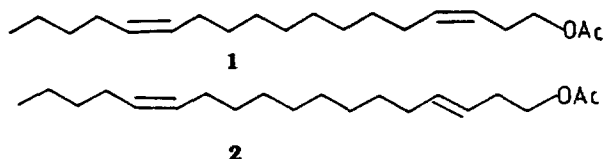


Figure 1

Generally, *Synanthedon* species (Lepidoptera: Sesiidae) were found to be attracted by a mixture of the (Z,Z)-isomer **1** and the (E,Z)-isomer **2**, which suggest that relatively low species-specificity of the pheromone component of Sesiidae. Recently, the highly purified (Z,Z)-isomer **1** was shown to be attractive to the smaller clear wing, *Synanthedon tenus*⁶, which is the pest in Japanese persimmon orchards. Even 0.5% contamination of the (E,Z)-isomer **2** inhibited⁶ the attractancy of the (Z,Z)-isomer **1**.

Several syntheses⁷ of the (Z,Z)-isomer **1** and the (E,Z)-isomer have been reported in the literature.

A mixture (1:1) of the (Z,Z)-isomer **1** and the (E,Z)-isomer **2** was known to be an effective trap bait for the male cherry tree borer, an economic pest in Korean peach orchards. We have devised a convenient synthesis of the mixture of the (Z,Z)-isomer **1** and the (E,Z)-isomer **2** employing the Wittig or Emmons reaction followed by deconjugative protonation as the key step, which were adjusted to give the products in the required ratio.

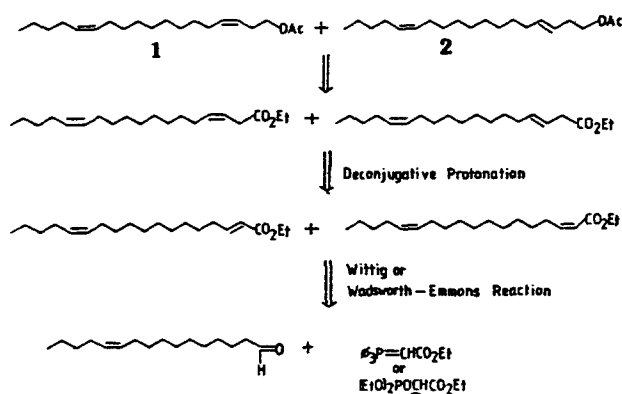
Table 1. Wittig or Emmons reaction of (Z)-11-hexadecen-1-al (3) with $\phi_3P=CHCO_2Et$ or $(EtO)_2P(O)CHCO_2Et$ and deconjugative protonation of the mixture of the compounds unsaturated esters 11 and 12

Wittig or Emmons reaction									Deconjugative protonation					
entry	substrate	ylide or anion formation			olefination		product isomer ratio ^a (11:12)	isolated yield ^b (%)	reaction conditions			product isomer ratio (13:14)	isolated yield ^c (%)	
		base	reaction conditions solvent, temp, °C,	time,h	temp, °C,	time,h			base,	solvent,	temp, °C			
1	(EtO) ₂ POCH ₂ CO ₂ Et	NaH	DME	25	6	85	6	80:20	76	KN(SiMe ₃) ₃	THF	-78	74:26	64
2	Brφ ₂ P ⁺ CH ₂ CO ₂ Et	NaOH	H ₂ O	25	1/2	25	7	64:36	85	KN(SiMe ₃) ₃	THF	-78	57:43	85
3	(EtO) ₂ POCH ₂ CO ₂ Et	KN(SiMe ₃) ₃	THF	-78	1	-75—50	2	20:80	55	KN(SiMe ₃) ₃	THF	-78	17:83	72
4	(EtO) ₂ POCH ₂ CO ₂ Et	KN(SiMe ₃) ₃	THF	-78	1	-78	2	16:84	60	KN(SiMe ₃) ₃	THF	-78	14:86	75

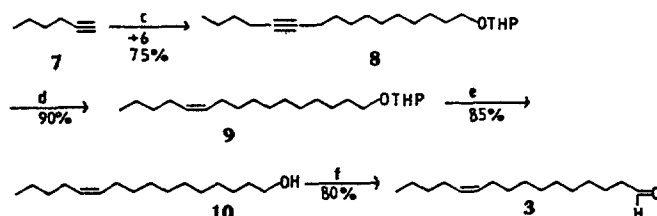
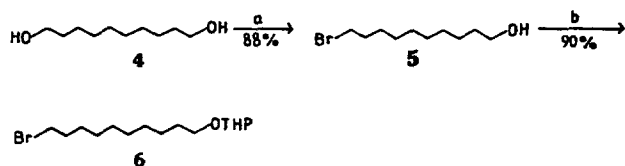
^aThe isomer ratio was determined by gas chromatography (capillary column, ultra 2, 25m × 0.32mm × 0.52μm film, N₂, 50 PSI). ^bThe products were separated by column chromatography.

Results and Discussion

Although the (Z,Z)-isomer 1 and the (E,Z)-isomer 2 were prepared separately, we decided to synthesize the required mixture by a single scheme (scheme 1) involving stereochemical control of the Wittig reaction of (Z)-11-hexadecen-1-al (3) with carboethoxymethylenetriphenylphosphorane or the Wadsworth-Emmons reaction of (Z)-11-hexadecen-1-al (3) with the anion of triethylphosphonoacetate, followed by deconjugative deprotonation as the key step.

**Scheme 1.** Retrosynthetic Analysis of the (Z,Z)-isomer 1 and the (E,Z)-isomer 2

The aldehyde, (Z)-11-hexadecen-1-al (3) was prepared from 1,10-decanediol in six steps (scheme 2). 1,10-Decanediol (4) was subjected to monobromination⁸ to yield 10-bromodecan-1-ol (5), which was subsequently protected with DHP and a catalytic amount of PPTS to give 10-bromodecan-1-ol THP ether (6). 1-Hexyne (7) was reacted with n-butyl lithium in THF to give the lithium 1-hexynide, which was alkylated with 10-bromodecan-1-ol THP ether (6) using HMPA as a cosolvent to provide 11-hexadecyn-1-ol THP ether (8). The acetylenic intermediate 8 was stereoselectively reduced with H₂ over Pd/BaSO₄¹⁰ to give (Z)-11-hexadecen-1-ol THP ether (9). Deprotection of the ether 9 by refluxing in the presence of PPTS⁹ and ethanol followed by oxidation with PCC¹¹ provided (Z)-11-hexadecen-1-al (3).

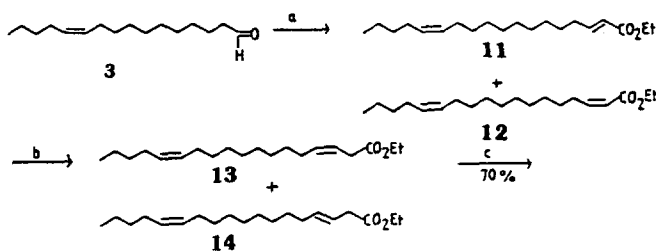


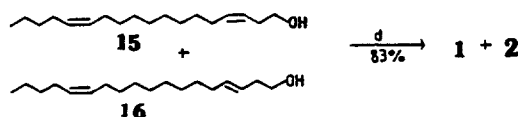
^a(a) 47% HBr, benzen, Δ, 18h; (b) DHP, PPTS, rt, 7h; (c) n-BuLi in hexane, then add 6, HMPA, 0°C, 8h; (d) H₂, Pd/BaSO₄, quinoline, rt, 15h; (e) PPTS, EtOH, 60°C, 5h; (f) PCC, CH₂Cl₂, rt, 3h

Scheme 2^a

(Z)-11-Hexadecen-1-al (3) thus obtained was reacted with carboethoxymethylenetriphenylphosphorane or the anion of triethylphosphonoacetate to furnish ethyl (Z,Z)-2,13-octadecadienoate (11) and ethyl (E,Z)-2,13-octadecadienoate (12) (Scheme 3). The ratios of the (Z,Z)-isomer 11 and the (E,Z)-isomer 12 depended on the reaction conditions and the ratios were analyzed by G.C.. Table 1 summarizes our results on the effect of solvent, temperature, and base on the isomer ratio in the products. In the literature¹², deconjugative protonation of ethyl (E)-2-alkenoate with LDA in THF at -78°C give the corresponding ethyl (Z)-3-alkenoate, whereas ethyl (Z)-2-alkenoate with LDA in THF at -78°C give the corresponding (E)-3-alkenoate. Deconjugative protonation of the mixture of ethyl (E,Z)-2,13-octadecadienoate (11) and its (Z,Z)-isomer (12) with potassium hexamethyldisilazide in THF at -78°C gave a mixture of ethyl (Z,Z)-3,13-octadecadienoate (13) and ethyl (E,Z)-3,13-octadecadienoate (14), respectively (Scheme 3). Our results on the isomer ratios of deconjugative protonation are summarized in table 1.

Exposure of the deconjugated esters to excess lithium aluminium hydride in ether at 0°C for 1h resulted in the formation of the desired mixture of (Z,Z)-3,13-octadecadien-1-ol (15) and its (E,Z)-isomer 16. Acetylation of the alcohols 15 and 16 with acetic anhydride in dry pyridine afforded the final products¹³, (Z,Z)-3,13-octadecadien-1-yl acetate (1) and (E,Z)-3,13-octadecadien-1-yl acetate (2) (Scheme 3).





(a) $\phi_3P = CHCO_2Et$ or $(EtO)_2POCH_2CO_2Et$ + base (table 1); (b) $KN(SiMe_3)_2$, THF, $-78^\circ C$, 2h, then satd NH_4Cl ; (c) LAH, ether $0^\circ C$, 1h; (d) Ac_2O , pyridine, rt, 28h

Scheme 3^a

Experimental

Infrared spectra were recorded with Shimadzu IR-440 spectrophotometer. 1H -NMR spectra were taken on a Bruker WP 80 SY 80MHz NMR spectrophotometer, using tetramethylsilane as an internal standard. Gas chromatograms were obtained on a Spectra-Physics 7100 gas chromatography. Preparative thin-layer chromatography (PTLC) was in general carried out on 20cm $\times$ 20cm glass plates coated with 1mm thickness of Merk silicagel PF-254. All solvents and liquid compounds were distilled before use.

10-Bromodecan-1-ol(5). To a stirred solution of 1,10-decanediol(4) (1.3g, 7.6×10^{-3} mol) in benzene (30 ml) was added 48% aqueous hydrobromic acid (1.17 ml) at room temperature. The reaction mixture was stirred at reflux for 18 hr while trapping the water formed using a Dean-Stark water separator. The reaction mixture was washed with 6N NaOH solution, 10% HCl solution, water, and brine. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The crude product was distilled on Kugelrohr (125 $^\circ C$, 3mmHg) to give 10-bromodecan-1-ol (1.4g, 88%); TLC $R_f = 0.27$, CH_2Cl_2 , SiO_2 ; IR (neat) 3300, 2900, 1460, 1260, 1050, 640 cm^{-1} ; 1H -NMR δ 1.1-2.2 (m, 17H), 3.4 (t, 2H), 3.6 (t, 2H).

10-Bromodecan-1-ol THP ether (6). To a stirred solution of 10-bromodecan-1-ol(5) (1.4g, 6.1×10^{-3} mol) in dry dichloromethane (10ml) was added PPTS (0.01g) and dihydropyran (0.66ml). The reaction mixture was stirred at room temperature for 7hr. After methylene chloride was evaporated, the residue was extracted with ether and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was distilled on Kugelrohr (115 $^\circ C$, 5mmHg) to give 10-bromodecan-1-ol THP ether (1.8g, 90%); TLC $R_f = 0.47$, CH_2Cl_2 , SiO_2 ; IR (neat) 2900, 1460, 1360, 1200, 640 cm^{-1} ; 1H -NMR δ 1.2-2.3 (m, 22H), 3.3-3.9 (m, 6H), 4.6 (s, 1H).

11-Hexadecyn-1-ol THP ether (8). To a stirred solution of 1-hexyne(7) (1.3 ml) in dry THF (4.0 ml) was added $n-BuLi$ (7.0 ml, 1.5M in hexane) slowly at $-18^\circ C$. The solution was stirred at $0-10^\circ C$ for 30 min and then 10-bromodecan-1-ol THP ether (6) (1.7g, 5.5×10^{-3} mol) in dry HMPA (1.0 ml) was added at $0^\circ C$ for 8hr. The reaction mixture was extracted with n -hexane. The organic layer was washed with water and brine and dried over $MgSO_4$. Concentration and distillation on Kugelrohr (135 $^\circ C$, 4mmHg) gave 11-hexadecyn-1-ol THP ether(8) (1.3g, 75%); TLC $R_f = 0.59$, CH_2Cl_2 , SiO_2 ; IR(neat) 2900, 1460, 1350, 1200, 1100, 860 cm^{-1} ; 1H -NMR δ 0.8 (t, 3H), 1.2-1.9 (m, 26H), 2.0-2.3 (m, 4H), 3.2-4.1 (m, 4H), 4.6 (m, 1H).

(Z)-11-Hexadecan-1-ol THP ether (9). To a stirred solution of 11-hexadecyn-1-ol THP ether (8) (1.3g, 4.1×10^{-3} mol) in methanol (5.0ml) were added 5%-Pd/ $BaSO_4$ (50mg)

and quinoline (3 drops). The mixture was stirred under hydrogen atmosphere for 15hr and filtered on florisil 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 $MgSO_4$. Concentration and distillation on Kugelrohr (130 $^\circ C$, 4mmHg) gave (Z)-11-hexadecan-1-ol THP ether (9) (1.2g, 90%); TLC $R_f = 0.62$, CH_2Cl_2 , SiO_2 ; IR(neat) 2900, 1460, 1340, 1230, 1030, 960 cm^{-1} ; 1H -NMR δ 0.8 (t, 3H), 1.0-1.7 (m, 26H), 1.8-2.0 (m, 4H), 3.2-4.1 (m, 4H), 4.5 (m, 1H), 5.3 (m, 2H).

(Z)-11-Hexadecan-1-ol (10). To a stirred solution of (Z)-11-hexadecan-1-ol THP ether (9) (1.2g, 3.7×10^{-3} mol) in ethanol (10 ml) was added PPTS (69mg). The mixture was stirred at $60^\circ C$ for 5hr. 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 and distillation on Kugelrohr (125 $^\circ C$, 4mmHg) gave (Z)-11-hexadecan-1-ol(10) (0.79g, 85%); TLC $R_f = 0.39$, CH_2Cl_2 , SiO_2 ; IR(neat) 3300, 2900, 1460, 1080, 960 cm^{-1} ; 1H -NMR δ 0.8 (t, 3H), 1.0-2.0 (m, 21H), 2.1-2.3 (m, 4H), 3.4 (t, 2H), 5.3 (m, 2H).

(Z)-11-Hexadecan-1-al (3). To a stirred solution of (Z)-11-hexadecan-1-ol(10) (0.7g, 3.3×10^{-3} mol) in methylene chloride (4.0ml) was added PCC (0.61g) in methylene chloride (4.0ml). The mixture was stirred at room temperature for 3h. The reaction mixture was filtered through florisil pad. After solvent was evaporated and the crude product was distilled on Kugelrohr (128 $^\circ C$, 4mmHg) to give (Z)-11-hexadecan-1-al(3) (0.63g, 80%); TLC $R_f = 0.68$, CH_2Cl_2 ; benzene = 10:1, SiO_2 ; IR(neat) 2900, 2850, 2750, 1720, 1460, 980 cm^{-1} ; 1H -NMR δ 0.9 (t, 3H), 1.0-1.7 (m, 18H), 1.8-2.1 (m, 4H), 2.3 (t, 2H), 5.3 (m, 2H), 9.8 (t, 1H).

Ethyl (E,Z)-2,13-octadecadienoate(11) and its (Z,Z)-isomer(12). General Procedure for Reaction of $(EtO)_2POCH_2CO_2Et$ and Base with Aldehyde 3: The reaction of the $(EtO)_2POCH_2CO_2Et$ and base with the aldehyde 3 (Table 1, entry1) is described as an illustrative case. To a stirred suspension of NaH (0.64g) (prewashed with dry n -hexane) in dry dimethoxyethane (4.0ml) was added in small portion diethyl ethylcarbonylmethylenephosphonate (0.35g) at room temperature. After the mixture was stirred at room temperature for 6hr under nitrogen, it was treated with (Z)-11-hexadecan-1-al(3) (0.41g, 0.17×10^{-3} mol) in dry dimethoxyethane (2.0ml). The reaction mixture was stirred at reflux for 6hr. A large excess of water and ether was added and the ether layer was separated, washed with brine and dried over $MgSO_4$. The organic layer was evaporated and concentrated in vacuo. The crude product was separated by column chromatography using CH_2Cl_2 : n -hexane = 5:2 as eluent ($R_f = 0.83$) to give ethyl (E,Z)-2,13-octadecadienoate (11) and its (Z,Z)-isomer(12) (0.44g, 85%); IR (neat) 2900, 1740, 1640, 1460, 1060, 960, 820 cm^{-1} ; 1H -NMR 0.9 (t, 3H), 1.1-1.6 (m, 21H), 1.8-2.2 (m, 6H), 4.2 (q, 2H), 5.3 (m, 2H), 5.8 (m, 1H), 6.9 (m, 1H). The ratio of the isomers was analyzed by capillary GLC at $220^\circ C$.

In the case of $\phi_3P = CHCO_2Et$ (entry 2, Table 1), the ylide, ethoxycarbonylmethylenetriphenylphosphorane was used in dry dimethoxyethane.

Ethyl (Z,Z)-3,13-octadecadienoate (13) and its (E,Z)-isomer(14). Potassium (0.60g) was added to a solution of hexamethyldisilazane (4.8ml) in THF (10ml) at room temperature. The resulting dark red solution was stirred at room

temperature. To a stirred solution of the mixture of ethyl (E,Z)-2,13-octadecadienoate (**11**) and its (Z,Z)-isomer (**12**) (0.30g, 0.97×10^{-3} mol) in dry THF (6.0 ml) at -78°C was added the above solution of KN(SiMe₃)₂ (2.0 ml) at -78°C . The reaction mixture was stirred at -78°C for 2hr, and then quenched with saturated aqueous ammonium chloride solution at -78°C . The reaction mixture was extracted with ether. The combined organic layers were washed with water and brine, and then dried over MgSO₄. Concentration in vacuo and separation by column chromatography using CH₂Cl₂: n-hexane = 1:1 as eluent (R_f = 0.38) gave ethyl (Z,Z)-3,13-octadecadienoate (**13**) and its (E,Z)-isomer (**14**) (0.19g, 64%); IR(neat) 2900, 1710, 1460, 1060, 960, 820cm⁻¹; ¹H-NMR δ 0.9 (t, 3H), 1.1-1.5 (m, 19H), 1.7-2.3 (m, 6H), 3.1 (d, 2H), 4.2 (q, 2H), 5.3-5.6 (m, 4H). The ratio of isomers was analyzed by capillary GLC at 220°C.

(Z,Z)-3,13-Octadecadien-1-ol(15) and its (E,Z)-isomer (16). To a stirred solution of the deconjugated ester (**13** and **14**) (0.20g, 0.66×10^{-3} mol) in dry ether (1.0ml) was added LAH (38mg, 0.99×10^{-3} mol) in dry ether (1.0ml) at 0°C. The reaction mixture was stirred at 0°C for 1hr and quenched with 2N-HCl solution. The ether layer was washed with water and brine, and then dried over MgSO₄. Concentration in vacuo gave (Z,Z)-3,13-octadecadien-1-ol(**15**) and its isomer (**16**) (0.12g, 70%); TLC R_f = 0.41, CH₂Cl₂, SiO₂; IR(neat) 3300, 2900, 1460, 1100, 960cm⁻¹; ¹H-NMR δ 0.9 (t, 3H), 1.2-1.4 (m, 16H), 1.8-2.4 (m, 9H), 3.5 (t, 2H), 5.3-5.6 (m, 4H).

(Z,Z)-3,13-Octadecadien-1-yl acetate (1) and (E,Z)-3,13-Octadecadien-1-yl acetate (2). To a stirred solution of (Z,Z)-3,13-octadecadien-1-ol and its (E,Z)-isomer (**15** and **16**) (0.12g, 0.45×10^{-3} mol) in dry pyridine (2.0ml) was added anhydrous acetic anhydride (55mg). The mixture was stirred at room temperature for 28hr and then poured into ice-water and extracted with ether. The organic layer was washed with 5%-HCl solution, satd, NaHCO₃ solution and brine and dried over MgSO₄. Concentration in vacuo afforded (Z,Z)-3,13-octadecadien-1-yl acetate (**1**) and (E,Z)-3,13-octadecadien-1-yl acetate (**2**) (0.11g, 83%); IR(neat) 2900, 1740, 1460, 1370, 1240, 1080cm⁻¹; ¹H-NMR δ 0.9 (t, 3H), 1.1-1.5 (m, 16H), 2.0 (s, 3H), 2.1-2.5 (m, 8H), 4.2 (t, 2H), 5.3-5.6 (m, 4H). The ratio of isomers was analyzed by capillary GLC at 220°C.

Acknowledgement. This research was supported by a generous grant (1987) from the Korea Science and Engineering Foundation.

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13. The field test on the attractiveness of the synthetic sex pheromone for 57:43 mixture of the (Z,Z)-isomer **1** and its (E,Z)-isomer **2** (entry 2 in Table 1) was conducted with good results by Department of Entomology, Institute of Agricultural Science, O. R. D., Suwon 170, Korea.