

matography with hexane and benzene, and purified GLC. The results are illustrated in Scheme and Table 1, respectively.

As shown in Scheme, phenylethyne is metalated preferentially at the  $\alpha$ -position so that quenching the reaction mixture with  $I_2$ ,  $\alpha$ -iodostyrene and  $\beta$ -iodostyrene were produced in 85:15 ratio.

The results in Table 1 show that the catalytic hydroalumination of alkynes is promoted by use of catalytic amounts of  $Cp_2TiCl_2$  to the corresponding alkenes on hydrolysis or alkenyl iodides on iodination in excellent yields. The formation of *cis*- and *trans*-1,2-diphenylethenes in the ratio of 61:39 suggests that the hydroalumination of diphenylethyne with  $LiAlH_4$  catalyzed  $Cp_2TiCl_2$  takes preferentially place in *cis* addition rather than *trans* addition.<sup>7</sup> The formation of the hydrogenated product, 1,2-diphenylethane, is also observed. The result suggests that small amount of dialuminates may be produced during the reaction. However, the detailed mechanism of this reaction is not clear at present, experiments

remain in a lot of parts.

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## A Short Synthesis of (Z)-13-Eicosen-10-one, the Component of the Peach Fruit Moth Pheromone

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(Z)-13-Eicosen-10-one(1), a principal component of the sex pheromone of the peach fruit moth, *Carposina niponensis* Walsingham is the most serious pests on apple, peach in Korea<sup>1</sup> and Japan.<sup>2</sup> In 1977, Y. Tamaki *et al*<sup>2</sup> identified (Z)-13-eicosen-10-one (1) (Figure 1) and (Z)-12-nonadecen-9-one in the ratio of 20:1 as the major components of the female sex pheromone of the peach fruit moth. (Z)-13-Eicosen-10-one (1) alone exerts a similar pheromone activity.<sup>3</sup>

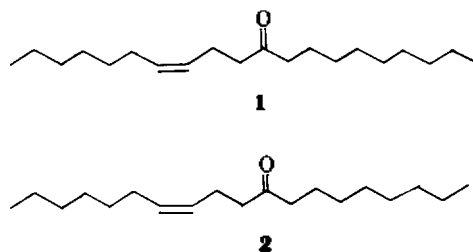
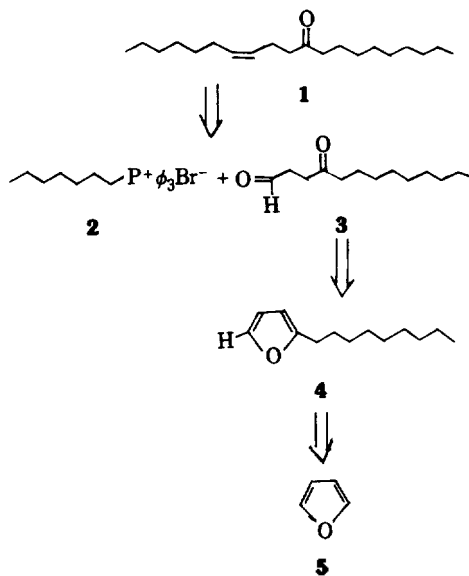


Figure 1

Since the peach fruit moths are hardly attracted by light traps, survey of the trend of their outbreak in the field is difficult.<sup>4</sup> Pheromone vials containing 1-3mg of (Z)-13-eicosen-10-one(1) adhered to rubber or plastic capsule resulted in a good forecasting outbreaks of this insect.<sup>5</sup>

Several synthesis of (Z)-13-eicosen-10-one(1) have been



Scheme 1. Retrosynthetic Analysis of 1

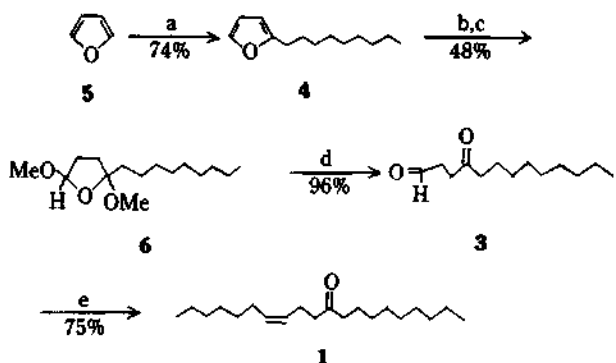
reported in the literature.<sup>6</sup> A search for more efficient and convenient methods for the synthesis of (Z)-13-eicosen-10-one(1) is still very worthwhile. Here we wish to report a short synthesis of (Z)-13-eicosen-10-one(1) from furan, which is

cheap and readily available.

It has been established that the Wittig reaction when carried out between aliphatic aldehyde and aliphatic non-stabilized triphenylphosphonium ylide in nonpolar solvent in the absence of inorganic ions ("salt-free") gives predominantly (Z)-olefins stereoselectively.<sup>7</sup> The latent 1,4-dicarbonyl nature of the furan nucleus<sup>8</sup> could be successfully exploited to 4-oxo-tridecan-1-al(3). A simple retrosynthetic analysis (Scheme 1) reveals that 2-nonyl substituted furan(4) is the key intermediate, which in turn prepared from furan(5) by alkylation reaction.

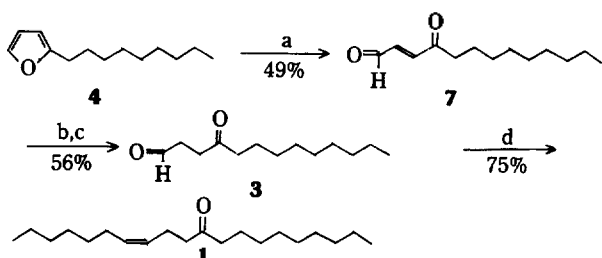
2-Nonylfuran(4) was easily obtained by alkylation reaction of furan(5). Treatment of 4 with bromine in methanol<sup>10</sup> smoothly gave  $\alpha, \alpha'$ -dimethoxydihydrofuran, which was hydrogenated<sup>11</sup> with H<sub>2</sub> on Pd/C to yield  $\alpha, \alpha'$ -dimethoxytetrahydrofuran 6<sup>12</sup> as a mixture of *cis*- and *trans*-in the ratio of 1:1. Acidic hydrolysis provided 4-oxo-4-tridecan-1-al(3),<sup>12</sup> which was reacted with heptylidetriphenylphosphonium ylide in a *cis*-selective Wittig olefination<sup>6c</sup> to afford (Z)-13-eicosen-10-one(1)<sup>12</sup> (Scheme 2).

#### Scheme 2. Synthesis of 1<sup>a</sup>:



<sup>a</sup>Reagents: (a) nBuLi, THF, nC<sub>9</sub>H<sub>17</sub>Br, -15°C-40°C (b) Br<sub>2</sub>, MeOH, NaHCO<sub>3</sub>, -15°C→rt (c) H<sub>2</sub>, Pd/C, 1 atm, rt (d) p-TsOH, H<sub>2</sub>O-CH<sub>3</sub>CN(1:1), rt (e) 2 plus n-BuLi, toluene, 12-crown-4, rt → 80°C; add 3, -35°C→rt

Alternatively, 2-nonylfuran(4) was oxidatively opened<sup>13</sup> by PCC to give enedione 7, which was hydrogenated and oxidized to give 4-oxotridecan-1-al(3). The aldehyde was subsequently converted into the target compound, (Z)-13-eicosen-10-one(1) (Scheme 3).



#### Scheme 3. Alternate Synthesis of 1<sup>a</sup>

<sup>a</sup>Reagent: (a) PCC, CH<sub>2</sub>Cl<sub>2</sub>, reflux (b) H<sub>2</sub>, Pd/C, 1 atm, rt (c) PCC, CH<sub>2</sub>Cl<sub>2</sub>, rt

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12. Satisfactory physical properties and spectroscopic data (<sup>1</sup>H-NMR, IR) were obtained for the compounds: 2-n-nonylfuran (4); bp 68-72°C/3mmHg; TLC; Rf=0.67, n-hexane: ether (4:1), SiO<sub>2</sub>; IR (NaCl, neat) 2955, 2925, 1595, 1505, 1145, 1010 cm<sup>-1</sup>; H-NMR (80MHz, CDCl<sub>3</sub>) 0.85-1.69 (m, 17H), 2.61 (t, 2H), 5.79 (m, 1H), 6.28 (m, 1H), 7.29 (m, 1H). 2-n-nonyl-2,5-dimethoxy-2,5-dihydrofuran; TLC; Rf = 0.67, n-hexane: ether = 4:1, SiO<sub>2</sub>; IR (NaCl, neat) 2955, 2925, 1620, 1450, 1370, 1110, 1015 cm<sup>-1</sup>; H-NMR (80MHz, CDCl<sub>3</sub>) 0.88-1.35 (m, 17H), 1.72-1.84 (m, 2H), 3.21 (s, 3H), 3.52 (s, 3H), 5.46 (m, 1H), 5.90 (m, 1H), 6.02 (m, 1H) (major isomer); 0.88-1.35 (m, 17H), 1.32-1.84 (m, 2H), 3.13 (s, 3H), 3.46 (s, 3H), 5.75 (m, 1H), 5.90 (m, 1H), 6.03 (m, 1H) (minor isomer). 2-n-nonyl-2,5-dimethoxytetrahydrofuran (6); TLC; Rf=0.56, hexane: ether = 7:3, SiO<sub>2</sub>; IR (NaCl, neat) 2955, 2925, 1470, 1375, 1100, 1015 cm<sup>-1</sup>; <sup>1</sup>H-NMR (80MHz, CDCl<sub>3</sub>) 0.88-1.25 (m, 17H), 1.75-2.05 (m, 6H), 3.18-3.22 (two singlets, 3H), 3.30-3.40 (two singlets, 3H), 4.90 (t, 1H). 4-oxotridecan-1-al (3); TLC; Rf = 0.58, n-hexane: ether = 7:3, SiO<sub>2</sub>; IR (NaCl, neat) 2930, 2850, 2750, 1720, 1710 cm<sup>-1</sup>; <sup>1</sup>H-NMR (80MHz, CDCl<sub>3</sub>) 0.90-1.85 (m, 17H), 2.40 (m, 2H), 2.72 (m, 4H), 9.80 (t, 1H). 4-Oxo-2-tridecen-1-al(7); TLC; Rf=0.62,

n-hexane: ether = 7:3, SiO<sub>2</sub>; IR (NaCl, neat) 2950, 2850, 2750, 1700, 1690, 1620 cm<sup>-1</sup>; <sup>1</sup>H-NMR (80MHz, CDCl<sub>3</sub>) 0.90-1.40 (m, 17H), 2.70 (t, 2H), 6.78 (dd, 1H), 6.88 (dd, 1H), 9.80 (d, 1H). 4-oxotridecan-1-ol; TLC; R<sub>f</sub> = 0.25, n-hexane: ether = 7:3, SiO<sub>2</sub>; IR (NaCl, neat) 3100-3400, 2955, 2850, 1720 cm<sup>-1</sup>; <sup>1</sup>H-NMR (80MHz, CDCl<sub>3</sub>)

0.88-1.80 (m, 17H), 2.50-3.00 (m, 6H), 3.80 (t, 4H). (Z)-13-eicosen-10-one (**1**); IR (NaCl, neat) 2960, 1715, 1620, 1450 cm<sup>-1</sup>; <sup>1</sup>H-NMR (80MHz, CDCl<sub>3</sub>) 0.90 (t, 6H), 1.15-1.50 (m, 22H), 1.80-2.50 (m, 8H), 5.30 (m, 2H).  
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## A Short Synthesis of (±)-Callosobruchusic Acid, the Copulation Release Pheromone(Erectin) of the Azuki Bean Weevil

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In 1981, Yamamoto *et al.*<sup>1</sup> isolated and identified the copulation release pheromone of the azuki bean weevil, *Callosobruchus chinensis* L., as (E)-3,7-dimethyl-2-octene-1,8-dioic acid(**1**) (Callosobruchusic acid) (Figure 1). In 1983, Mori *et al.*<sup>2</sup> synthesized two enantiomers. Both were biologically active<sup>2</sup> as the copulation release pheromone of *Callosobruchus chinensis* L.. This pheromone induces the male to extrude his genital organ and to attempt copulation.

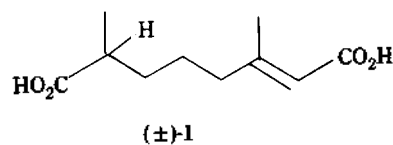
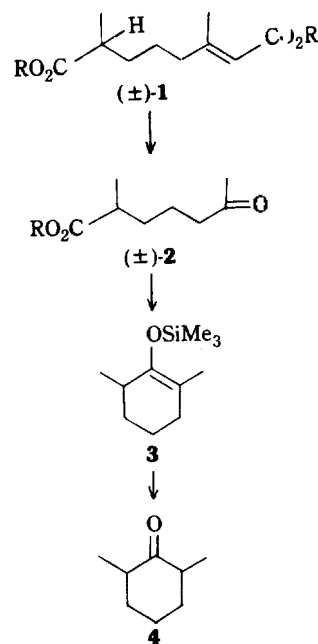


Figure 1

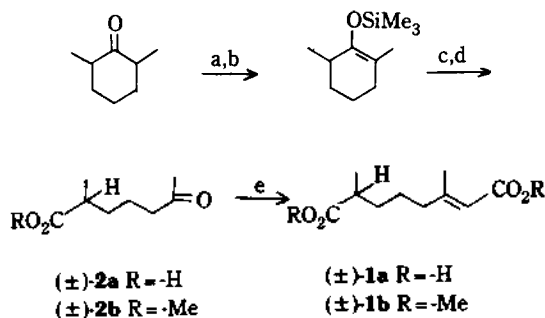
The azuki bean weevil is a persistent pest insect of the azuki bean, cowpea and other important beans. The Institute of Agricultural Sciences in Suwon Korea needed a fair amount of this pheromone to conduct field test experiments, therefore we undertook to synthesize (±)-callosobruchusic acid, (±)-**1**, (±)-(2E)-3,7-dimethyl-2-octene-1,8-dioic acid.

It has been well known that the Emmons olefination reaction of the ketone **2** with the anion of dimethylmethoxycarbonylmethylphosphonate gives predominantly (E)-olefin ester stereoselectively<sup>3</sup>. A simple retrosynthetic analysis(Scheme 1) reveals that methyl 2-methyl-6-oxo-heptanoate **2** is the key intermediate. The ketone **2** can be easily prepared from silyloxyalkene **3** by ozonization reaction<sup>4</sup>. Silyloxyalkene **3** can be obtained by silylation<sup>5</sup> of the enolate of commercially available 2,6-dimethylcyclohexanone, **4**.

2,6-Dimethylcyclohexanone(**4**) was silylated by treating with LDA followed by addition of Me<sub>3</sub>SiCl to give silyloxyalkene **3**<sup>7</sup> in 95% yield. Ozonolysis of **3** in methanol followed by Me<sub>2</sub>S work up afforded (±)-2-methyl-6-oxo-heptanoic acid **2a** in 60% yield. Esterification of the acid **2a** with diazomethane<sup>6</sup> gave the methyl ester **2b**<sup>7</sup> in 95% yield. Emmons olefination reaction of the ketone **2b**<sup>7</sup> with the anion of dimethylmethoxycarbonylmethylphosphonate furnished the unsaturated ester (±)-**1b**<sup>7</sup> in 80% yield. The diester **1b** was treat-



Scheme 1



Scheme 2. Synthesis of (±)-**1a**<sup>a</sup>

<sup>a</sup>(a) LDA, THF, -78°C (b) Me<sub>3</sub>SiCl (c) O<sub>3</sub>, MeOH, -78°C (d) Me<sub>2</sub>S, -78°C→rt (e) (MeO)<sub>2</sub>POCH<sub>2</sub>CO<sub>2</sub>Me, NaH, DME, 50-60°C.