

Figure 5.

becomes more (n, π^*) statelike and the fluorescent quantum yield decreases. As shown in Table 2, the fluorescence quantum yields are affected significantly by temperature because of the proximity of $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states. Figure 5 illustrates three possible Jablonski diagrams which can explain the solvent and temperature effect on the fluorescence and phosphorescence.

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

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(Z)-13-Eicosen-10-one (**1**), one of the active components of the female pheromone of the peach fruit moth, *Carposina niponensis* Walsingham, was synthesized from 2-nonanone, succinic anhydride, and n-nonyllithium. The key step involves the preparation of 13-eicosyn-10-one from an epoxyketone via Eschenmoser cleavage.

Introduction

Peach fruit moth, *Carposina niponensis* Walsingham, is a major economic pest of apple, peach, and other fruits in Japan and in Korea.^{1,2} Population monitoring of this species has depended entirely on field observations of injured fruits, since the moths are not captured light traps. Therefore the establishment of a convenient monitoring system for this species by using traps baited with a synthetic sex pheromone is desired.

In 1976, Tamaki and coworkers identified (Z)-13-eicosen-10-one (**1**) and (Z)-12-nonadecen-9-one as the major components of the female sex pheromone of peach fruit moth.¹ A number of different synthetic schemes for the preparation of **1** have since been published,³ the most notable being the addition of (Z)-1-octenyl cuprate reagent to 1-dodecen-3-one.^{3d}

We wish to report an alternative scheme for the synthesis of **1** which employs Eschenmoser cleavage⁴ of an epoxyketone in the preparation of 13-eicosyn-10-one.

Results and Discussion

Simultaneous formation of a triple bond and a ketone can be most elegantly carried out employing Eschenmoser cleavage reaction on epoxyketones⁴ (Scheme 1). Many examples for the cleavage of 2,3-epoxycyclopentanone derivatives are reported and *cis*- γ,δ -unsaturated ketones are easily prepared by hydrogenation of resultant ynones in the presence of Lindlar catalyst.

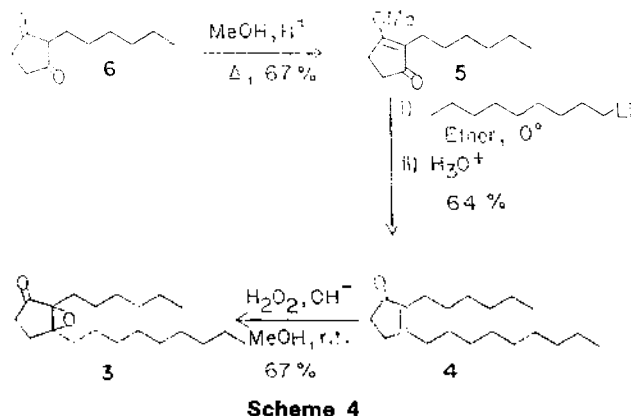
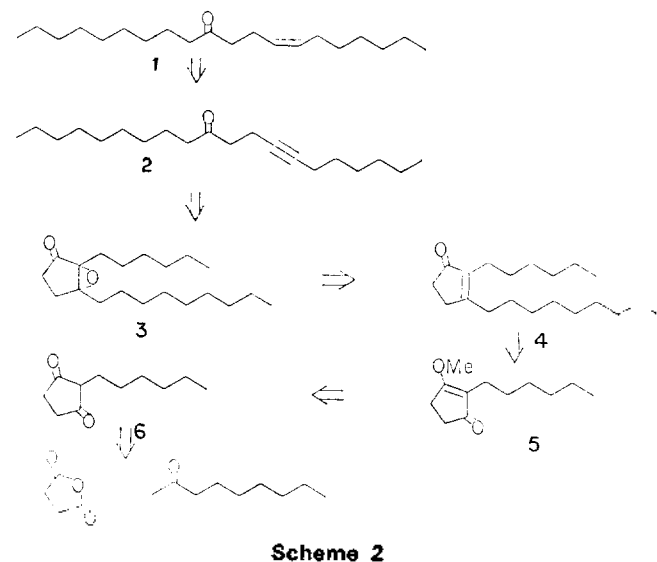
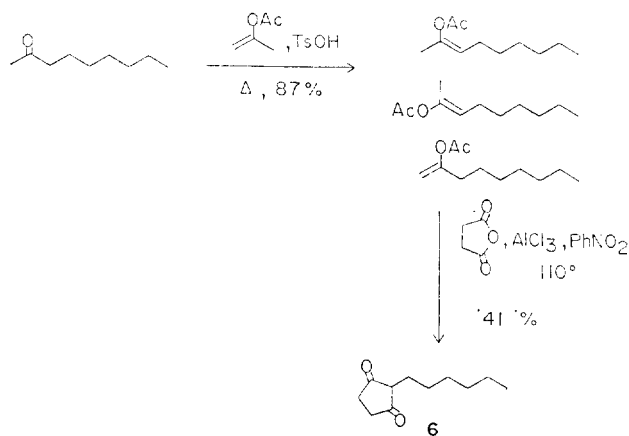
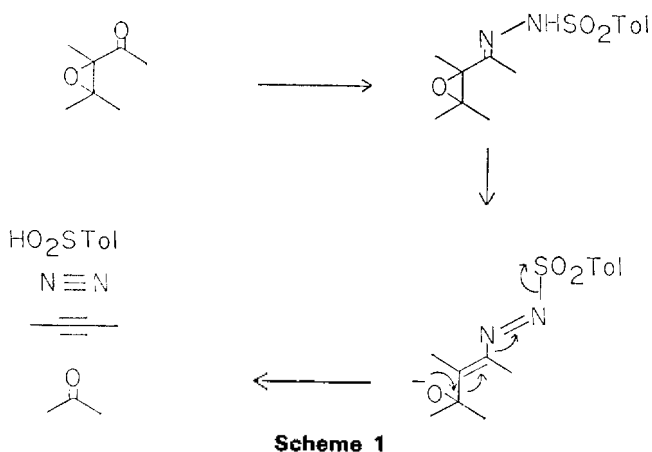
A simple retrosynthetic analysis (Scheme 2) reveals 2-*n*-hexyl-3-*n*-nonyl-2-cyclopenten-1-one (**4**) as the pivotal intermediate, which in turn can be prepared from 2-*n*-hexyl-1,3-cyclopentanedione (**6**). Thus **6** was the first intermediate desired and a literature method was adopted for its preparation.⁵

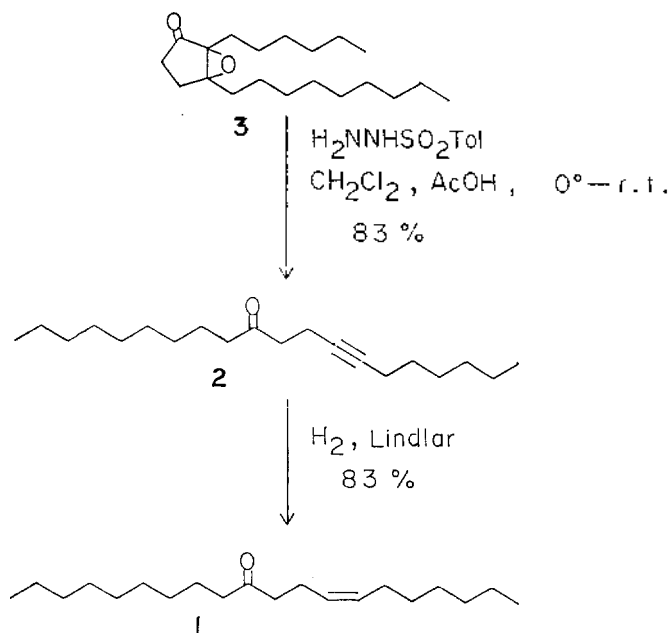
2-Nonanone was heated with 2 equivalents of isopropenyl acetate and a catalytic amount of *p*-toluenesulfonic acid monohydrate under reflux. A mixture of enol acetates of 2-nonanone was obtained in 87% yield after aqueous work-up and Kugelrohr distillation. Succinic anhydride was heated to 120° for 30 min. in dry nitrobenzene containing 3.5 equivalents of anhydrous aluminum chloride and the solution was allowed to cool to room temperature. The enol acetate mixture (1.5 eq.) was added to the nitrobenzene solution and the reaction mixture was allowed to stand at room temperature

for 40 min. After aging at 120° for 2 hours, the reaction mixture was cooled to room temperature and water was added with vigorous mechanical stirring. Crude solid product was obtained in 41% yield from the heterogeneous mixture upon standing at 5° for 3 hours (Scheme 3).

Crude 2-*n*-hexyl-1,3-cyclopentanedione (**6**) was heated under reflux for 36 hours in methanol containing 7% sulfuric acid for the conversion to the corresponding methyl enol ether (**5**). Thus 2-*n*-hexyl-3-methoxy-2-cyclopenten-1-one (**5**) was obtained in 67% yield after Kugelrohr distillation. The enol ether **5** was added to *n*-nonyllithium in ether at 0° and the mixture was allowed to stand at room temperature for 1 hour. The reaction mixture was worked up in dilute hydrochloric acid to produce 64% yield of 2-*n*-hexyl-3-*n*-nonyl-2-cyclopenten-1-one (**4**) after column chromatographic separation. Reaction with *n*-nonyl Grignard reagent was sluggish and produced little enone. The enone **4** was converted to the epoxyketone **3** upon treatment with basic hydrogen peroxide in methanol in 67% yield. (Scheme 4). It should be noted that the epoxyketone **3** had a slightly higher *R_f* value than that of the enone **4** on silica gel TLC analysis.

The penultimate product 13-icosyn-10-one (**2**) was obtained in 83% yield when the epoxyketone **3** was stirred in dichloromethane-acetic acid (2:1) containing 1 equivalent of *p*-toluenesulfonylhydrazide for 3 hours at 0° and for 3 hours at room temperature. Hydrogenation of **2** with Lindlar catalyst and trace pyridine in methanol produced 83% yield of (*Z*)-13-icosen-10-one (**1**), with identical spectral cha-





characteristics as reported earlier^{3f} (Scheme 5).

The above synthetic scheme involves routine reaction conditions which are amenable to large-scale preparations, and represents another useful application of Eschenmoser cleavage.

Experimental

¹H-NMR spectra were recorded on a Varian EM-360A spectrometer at 60 MHz with an internal standard of tetramethylsilane and IR spectra on Perkin Elmer 283 IR spectrophotometer. Gas chromatograms were obtained on a Hitachi Model 164 T gas chromatograph. TLC plates were made by dipping microscopic slide glasses in the chloroform-methanol (2:1 v/v) slurry of Merck 7739 Kieselgel 60 HF₂₅₄ and drying in the air. Spots were viewed under a UV light or by charring after spraying with 2% ceric ammonium sulfate solution in 1M sulfuric acid.

Crude products were purified by distillation on Kugelrohr under reduced pressure, or on a chromatographic column prepared with silica gel (Merck 7734 Kieselgel 60 at normal pressure, or Merck 9385 Kieselgel 60 at elevated pressure). Hydrogenation was conducted using Parr hydrogenation apparatus 3911.

Organic solvents were used without further purification unless specified. For reactions requiring anhydrous conditions, they were dried as follows. After dilute sulfuric acid treatment, nitrobenzene was steam distilled, dried over anhydrous calcium chloride and distilled under reduced pressure; ether and tetrahydrofuran from lithium aluminum hydride; dichloromethane from phosphorous pentoxide. Anhydrous reactions were carried out under nitrogen or argon atmosphere unless mentioned otherwise. In the routine work-up, anhydrous sodium sulfate or magnesium sulfate was used as the drying agent.

2-Nonanone Enol Acetates. Isopropenyl acetate (24.6 g, 246 mmole), 2-nonanone (16.4 g, 115 mmole) and 1.25 g of

p-toluenesulfonic acid monohydrate were put in a 100 ml flask. The reaction mixture was heated under reflux for 14 hours. The reaction mixture was cooled, diluted with hexane, washed with saturated sodium bicarbonate solution and distilled water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Product was distilled on Kugelrohr to yield 20.6 g (87% yield) of enol acetates.

2-*n*-Hexyl-1,3-cyclopentanedione (6). Dry nitrobenzene (180 ml) was filled in a 1.0 l three-neck flask fitted with a stirrer, a condenser, and a thermometer under nitrogen atmosphere. Anhydrous aluminum chloride (25.5 g, 0.19 mmole) and succinic anhydride (5.6 g, 56 mmole) were added with stirring, the temperature being allowed to rise to 80°. The solution was heated at 110° for 20 min, and cooled to room temperature. An aliquot of enol acetates (15 g, 81 mmole) was added over 15 min while the temperature was maintained near 25° with cooling. After aging 30 min, the reaction mixture was reheated and aged at 110° for 2 hours. The solution was cooled to room temperature and poured into 200 ml of water maintained at 5~10°. The addition was carried out with vigorous stirring over 30 min period. The dark brown gum-like product was filtered and purified on a column of silica gel. First, nonpolar compounds were eluted with sufficient hexane, and the product (6) (40g, 41 % yield) was obtained by using ethyl acetate as the eluent. Very small amount of the product was obtained from nitrobenzene layer by steam distillation. NMR (DMSO + CDCl₃); δ 11 (broad, enolic H), 2.37 (m, 4H), 1.03~1.84 (m, 10H), 0.70~1.03 (3H), IR; 1550 cm⁻¹.

2-*n*-Hexyl-3-methoxy-2-cyclopenten-1-one-(5). A dry methanol solution (150 ml) containing 3.6g of 6 (19.7 mmole) and 10 ml concentrated sulfuric acid was heated under reflux for 36 hours. The reaction mixture was concentrated on a rotary evaporator after neutralization with saturated sodium bicarbonate solution, diluted with hexane and ethyl acetate, and washed with brine. The product (5) was distilled on Kugelrohr under reduced pressure (2.6g, 67% yield). NMR (CDCl₃); δ 3.85 (s, 3H), 2.26~2.70 (m, 4H), 1.00~1.44 (m, 10H) 0.70~1.00 (t, 3H).

2-*n*-Hexyl-3-*n*-nonyl-2-cyclopenten-1-one (4). 1-Bromononane (9.49g, 45 mmole) was added dropwise to lithium (0.59g, 85 mmole) in 150 ml of dry ether with vigorous stirring at 0°. After addition was complete, the reaction mixture was stirred for 1 hour at room temperature. To the prepared *n*-nonyllithium solution, enol ether (5, 2.1g, 10.6 mmole) was added at 0°, and the reaction mixture was stirred for 1 hour at room temperature, and poured into 100 ml of dilute hydrochloric acid. The ether layer was separated, washed with 2×50 ml of saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate and concentrated. Column chromatographic purification afforded the pure product 4 (2.2g, 64% yield), NMR (CDCl₃); δ 1.74~2.64 (m, 8H), 1.08~1.70 (m, 22H), 0.70~1.08 (t, 6H).

2-*n*-Hexyl-3-*n*-nonyl-2,3-epoxycyclopentan-1-one (3). To a solution of enone (4) (2.0g, 6.8 mmole) in 60 ml of methanol were added 30% H₂O₂ (3.7 ml, 36 mmole) and 3.7

ml of 6*N* NaOH. The reaction mixture was stirred at room temperature for 24 hours, diluted with 130 ml of water, and extracted with 2×60 ml of hexane. The combined hexane layer was washed with 2×20 ml of water, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified on a silica gel column to afford the epoxyketone (**3**, 1.7g, 67% yield). NMR (CDCl₃); δ 1.9~2.4 (*m*, 2H) 1.09~1.80 (*m*, 28H), 0.70~1.09 (*t*, 6H).

13-Eicosyn-10-one (2). To a magnetically stirred solution of the epoxyketone (**3**, 394 mg, 1.28 mmole) in 4 ml of dichloromethane and 2 ml of acetic acid at 0° was added *p*-toluenesulfonylhydrazide (238 mg, 1.28 mmole) in one portion. After stirring for 3 hours at 0° and 3 hours at ambient temperature, the mixture was poured into 10 ml of water and the organic layer was washed with 3×10 ml of water followed by 5 ml of saturated sodium bicarbonate solution. The dichloromethane solution was dried over anhydrous magnesium sulfate and concentrated in vacuo to give a pale yellow oil which consisted of two major products by TLC. Less polar product turned out to be the desired acetylenic ketone (**2**) (344 mg, 83% yield) after column chromatographic separation. NMR (CDCl₃); δ 1.88~2.61 (*m*, 6H), 1.14~1.80 (*m*, 24H), 0.70~1.14 (*t*, 6H).

(Z)-13-Eicosen-10-one (1). A solution of the ynone (**2**, 200mg, 0.68 mmole) in 25 ml of methanol containing 500 μl of pyridine was shaken under a slight positive pressure of hydrogen gas over 175 mg Lindlar catalyst (5% Pd on CaCO₃ poisoned with Pb). The hydrogenation was complete in about 1 hour as checked by TLC analysis. The catalyst was removed by filtration and the solution was diluted with hexane, washed with 2×10 ml of 2*N* HCl, water, and brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Pure product (**1**, 167 mg, 83% yield) was obtained by column chromatographic separation.

IR; 1450cm⁻¹, 1710cm⁻¹. NMR (CDCl₃); δ 5.18~5.45 (*m*, 2H), 1.66~2.39 (*m*, 8H), 1.05~1.66 (*m*, 22H), 0.73~1.05 (*t*, 6H).

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cis-trans Isomeric and Substituent Effects on the Lanthanide Induced Shifts in 2-Phenylcyclopropanic System

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LIS's of *cis* and *trans*-methyl-2-phenylcyclopropanecarboxylate, *cis* and *trans*-*t*-butyl-2-phenylcyclopropanecarboxylate, *cis* and *trans*-N,N-dimethylcyclopropanecarboxamide, *trans*-2-phenylcyclopropyl methyl ketone and *trans*-2-phenylcyclopropyl *t*-butyl ketone have been studied. The LIS's hold the McConnell-Robertson relation and are mainly influenced by the steric effect. LIS's of *trans* isomers are larger than those of *cis* isomers. In *trans* isomers, the LIS's decrease in the following order: methyl ketone > methyl ester > N, N-dimethyl amide > *t*-butyl ketone ~ *t*-butyl ester.

Introduction

Since Hinckley¹ reported on the use of a lanthanide shift reagent (LSR) to analyze NMR spectra, literally hundreds of papers²⁻⁷ have appeared, dealing with both theoretical and practical aspects of reagents. LSR's have proved to be a

valuable development in the use of NMR spectroscopy for organic structure determination. While LSR's can be used qualitatively to simplify and interpret spectra patterns, more recent works⁸⁻¹⁴ are directed at a quantitative comparison of experimental lanthanide induced shifts (LIS) with values predicted *via* the pseudocontact equation¹⁵ such as given