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A Practical Synthesis of (E)- β -Farnesene, the Alarm Pheromone of Aphids

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(E)- β -Farnesene (**1**), (6E)-methylene-7,11-dimethyl-1,6,10-dodecatriene (Figure 1), was known as a constituent of various essential oils.¹ In 1972, W.S. Bowers identified (E)- β -farnesene as an alarm pheromone of cotton aphid, *Aphis gossypii* Glover and other aphid species.² The damage to crops by aphids either by feeding or by transmitting virus disease can be prevented to some extent by insecticides, but aphids are developing increased resistance, particularly to systemic organophosphates.³ The fast-acting pyrethroids may control.⁴ Of the chemicals that influence aphid behavior, the most active is the alarm pheromone,⁵ (E)- β -farnesene(**1**).

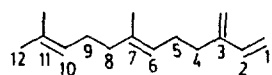
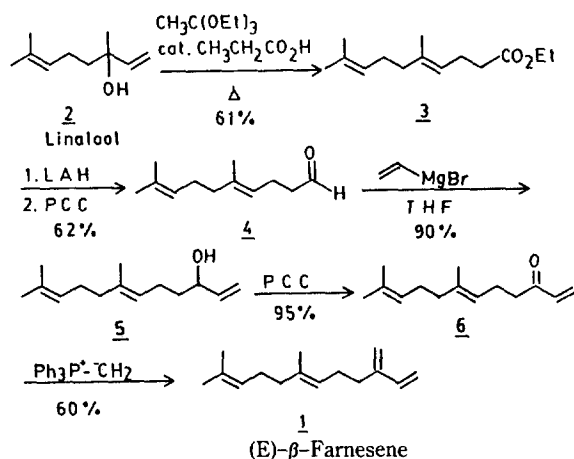
(E)- β -Farnesene

Figure 1.

(E)- β -Farnesene was prepared by dehydration of farnesol and nerolidol with both basic and acidic catalysts.⁶ By dehydration, mixtures including α - and β -farnesene were formed. Several other synthesis have been reported in the literature.⁷



Scheme 1.

Now we wish to report a convenient and practical method to synthesize (E)- β -farnesene using readily available linalool, a monoterpene. The establishment of the (E)-configuration at 6-position of (E)- β -farnesene was accomplished by ortho ester Claisen rearrangement reaction developed by W.S. Johnson.⁸

Ortho ester Claisen reaction of linalool(**2**) with triethylorthoacetate in the presence of a catalytic amount of propionic acid at 140° afforded ethyl (4E)-5,9-dimethyldecanoate(**3**) in 61% yield. The product obtained was distilled on a Kugelrohr under reduced pressure(3mmHg). The ratio of (E)- and (Z)-isomer was 97:3 by HPLC analysis. LAH reduction of the above ester(**3**) followed by PCC oxidation⁹ provided the aldehyde(**4**). The aldehyde was purified by flash chromatography using n-hexane-ethyl acetate(2:1) as eluents. The aldehyde(**4**) was submitted to the addition of vinylmagnesiumbromide in tetrahydrofuran to furnish 7,11-dimethyl-1,6,10-dodecatriene-3-ol(**5**) which was subsequently oxidized with PCC reagent to give α,β -unsaturated ketone(**6**). The α,β -unsaturated ketone(**6**) was purified by flash chromatography using n-hexane-ethyl acetate(1:1) as eluents. This ketone(**6**) was finally subjected to Wittig reaction with methylenetriphenylphosphonium ylide to afford (E)- β -farnesene(**1**) (Scheme 1). The (E)- β -farnesene¹⁰ thus obtained was identical in all respects(TLC,NMR,IR,GC) with the material previously reported in the literature.

This method is considered to be suitable to prepare a fair amount of alarm pheromone to conduct field test experiments.¹¹

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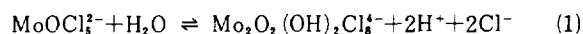
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 - ¹H NMR (80 MHz, CDCl₃) δ 1.60 (m, 9H), 2.08 (m, 8H), 4.90-5.40 (m, 6H), 5.95 (q, J=8Hz, 1H).
 - The biological activity test of the synthetic alarm pheromone for aphids *Lipaphis erysimi* K. and *Myzus persicae* S. has been conducted by Department of Entomology, Institute of Agricultural Science, O.R.D., Suwon 170, Korea with good results. The results will be reported later.

Kinetic Studies on Dimerization of Pentachlorooxomolybdate(V) in Hydrochloric Acid

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It is known that basic structures of molybdenum(V) such as Mo₂O₂(OH)₂(aq)⁴⁺, Mo₂O₃(aq)⁴⁺, and Mo₂O₄(aq)²⁺, in solution are obtained as hydrogen ion concentration of pentachlorooxomolybdate(V) solution decreases. However, the nature of the dimers in solution is not secure and may be Mo₂O₂(OH)₂(OH)₂Cl₈⁴⁻.^{1,2} Paramagnetic dimer, Mo₂O₂(OH)₂(aq)⁴⁺, is predominate species in the region of [HCl] = 4-6M, and diamagnetic Mo₂O₃(aq)⁴⁺ and Mo₂O₄(aq)²⁺ are predominate species at lower acidity (<4M HCl).² Monomeric MoOCl₅²⁻ in concentrated hydrochloric acid changes to brown species and its magnetic moments decrease by addition of water.³ This fact indicates that two MoO_(aq)³⁺ ions dimerize to diamagnetic Mo₂O₃(aq)⁴⁺ or Mo₂O₄(aq)²⁺ by way of paramagnetic Mo₂O₂(OH)₂(aq)⁴⁺ at low acidity. We describe here the results of our investigation of the dimerization (1) of MoOCl₅²⁻ when concentration of hydrochloric acid is lowered to 5-6M.



The dihydroxo-bridged oxomolybdenum(V) produced^{4,5} when concentration of hydrochloric acid is lowered to 2M undergoes further condensation with a water molecule,⁶ yielding a single oxygen-bridged oxomolybdenum(V) dimer. With solutions of pH 2-5 and low [Cl⁻], Mo₂O₄(aq)²⁺ is the predominate species and in more basic media further polymerization occurs, resulting in a gelatinous hydroxide.¹

Excess chloride, in the form of lithium chloride, was added to this solution to convert Mo₂O₂(OH)₂Cl₈⁴⁻ to MoOCl₅²⁻. It is obtained that electronic spectrum of oxomolybdenum(V) in solution containing 4M LiCl and 6M HCl is identical to that obtained in 12M HCl. This result indicates that a predominant oxomolybdenum(V) species in 10 M HCl or Cl⁻ is MoOCl₅²⁻

and Mo₂O₂(OH)₂Cl₈⁴⁻ is highly stable in 5-6 M hydrochloric acid. We attempted to isolate a paramagnetic oxomolybdenum(V) dimer in 5M HCl, but could not obtain a crystal from solutions because of its remarkable solubility.

Second-order rate constants for dimerization of MoOCl₅²⁻ in 5-6M HCl were observed with the equation: $-\text{[MoOCl}_5^{2-}]/\text{dt} = k_2[\text{MoOCl}_5^{2-}]^2$. Graph of $(A_0 - A_t)/(A_t - A_\infty)$ vs. time⁷ was linear for at least three half-lives as shown in Figure 1. From this slope (slope = $k_2 [\text{MoOCl}_5^{2-}]_0$, R = 0.998) we can obtain a second-order rate constant (k_2). Figure 2 shows that the second-order rate constants depend on concentrations of hydrochloric acid and chloride ion according to rate equation (1).

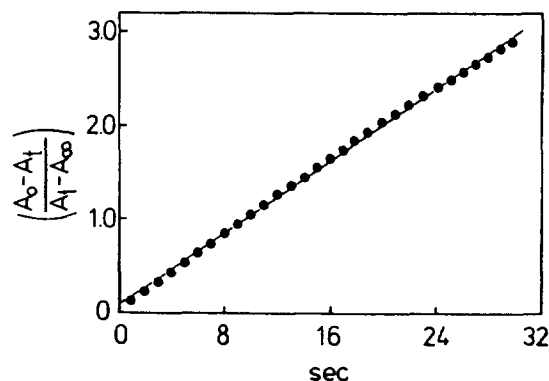


Figure 1. Plot of $(A_0 - A_t)/(A_t - A_\infty)$ vs. time for dimerization of $[\text{MoOCl}_5^{2-}]$ at 5°C. $[\text{MoOCl}_5^{2-}] = 3.10 \times 10^{-3}\text{M}$, $[\text{HCl}] = 3.0\text{M}$, $[\text{LiCl}] = 3.0\text{M}$.