

A Concise Synthesis of the Sex Pheromone of *Phtheochroa cranaodes* (Lepidoptera: Tortricidae)

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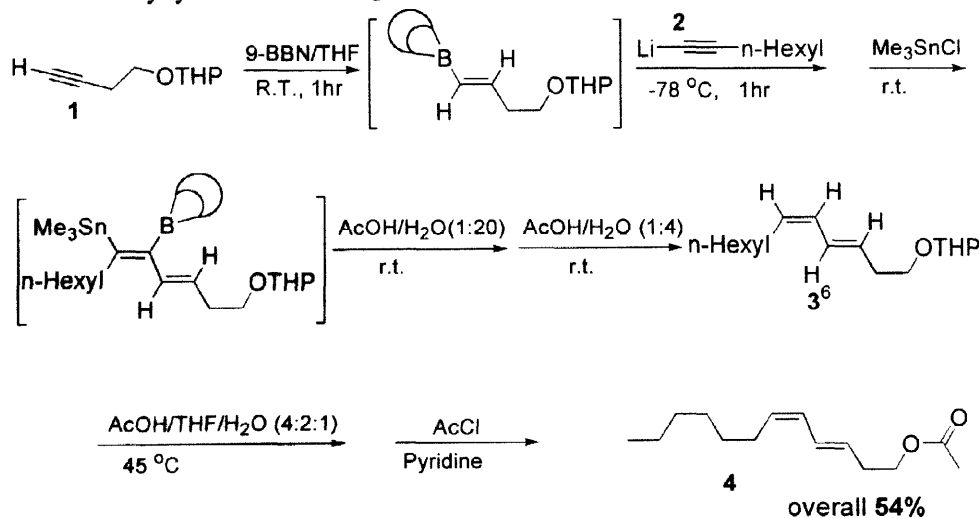
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Abstract: The female sex pheromone (3*E*,5*Z*)-3,5-dodecadienyl acetate of *Phtheochroa cranaodes* was regio- and stereo-selectively synthesized using electrophilic trimethylchlorostannane-induced rearrangement of lithium 1-octynylborate as the main process
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In the course of our continuing research on the area of vinylic metal species, we have reported potentially useful intermediates in the synthesis of natural products¹. We have been also interested in exploring synthetic applications of vinylic metal species, in particular, as routes to stereochemically defined diene systems of several insect sex pheromones². Such regio- and stereo-selective construction of target olefins has received much attention in terms of synthetic problem³.

The leafroller moth *Phtheochroa cranaodes* Meyrick (Lepidoptera: Tortricidae) is economically important insect pest on apples in Southern Brazil. Unelius C.R. *et al.* identified its structure as the (3*E*,5*Z*)-3,5-dodecadienyl acetate by GC-MS analysis of female gland extracts and synthesized it in 1995⁴. A Wadsworth-Horner-Emmons reaction was used to prepare methyl 2,4-dodecadienates which were key synthetic intermediates. However this method suffers from low stereoselectivity and yield. Herein we wish to report a concise and versatile strategy that utilized electrophile-induced rearrangement of suitably prepared lithium 1-octynylborate with Me₃SnCl as outlined in Scheme⁵.



Scheme

The required (3*E*)-stereochemistry of the sex pheromone was easily obtained by regio- and

stereoselective hydroboration of alkyne **1** at r.t.. The alkenylborane was treated with 1-octynyllithium **2** that was *in situ* prepared using *n*-BuLi in THF at -78 °C. The key electrophile-induced rearrangement was accomplished at r.t. with only vinyl group migration using Me₃SnCl as suitably bulk electrophile in highly controlled stereochemistry. Bu₃SnCl was too bulky to be used as electrophile in the electrophile-induced rearrangement. When PhTeI or BuTeI was used as electrophile in the rearrangement step, 1-substituted (1*E*,3*E*)-1,3-butadienyl tellurides were synthesized with excellent stereochemistry and high yield⁷. But there was a problem on conversion of theirs into tellurium-free organic compounds. Generally, detelluration of vinylic tellurides with the formation of new C-H bond takes place by reaction with strong bases⁸. Without isolation, replacements of boron, tin⁹ and THP¹⁰ by hydrogen were accomplished using AcOH/H₂O (1:20, 1:4, 4:1 in volume) step by step. When the sex pheromone was synthesized by acylation using acetyl chloride and pyridine, the reaction product was purified by fresh column chromatography in overall 54% excellent yield. The ¹H NMR spectra of the precursor and the sex pheromone were in good agreements with literature data⁴.

This synthetic strategy successfully led to a target sex pheromone. Considering the nature of the transformation, one would expect such a process for preparing conjugated diene systems such as (7*E*,9*Z*)-7,9-dodecadienyl-1-yl acetate (the sex pheromone of *Lobesia botrana*) regio- and stereoselectively².

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- compound **3** ¹H NMR (CDCl₃) δ 6.36(ddd, J = 15.2; 11.6; 1.2Hz, 1H), 5.90(dd, J = 11.6; 10.9Hz, 1H), 5.65(dt, J = 15.2; 7.1Hz, 1H), 5.36(dt, J = 10.9; 7.6Hz, 1H), 4.59(bs, 1H), 3.71-3.91(m, 2H), 3.38-3.53(m, 2H), 2.34-2.44(m, 2H), 2.06-2.15(m, 2H), 1.53-1.83(m, 6H), 1.23-1.43(m, 8H), 0.86(t, 6.8Hz, 3H).
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