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STEREOSELECTIVE ACYCLIC SYNTHESIS VIA ALLYLMETALS: AN EFFICIENT SYNTHESIS OF (±)-4-METHYLHEPTAN-3-OL, AN AGGREGATION PHEROMONE OF THE SMALLER EUROPEAN ELM BARK BEETLE[1]

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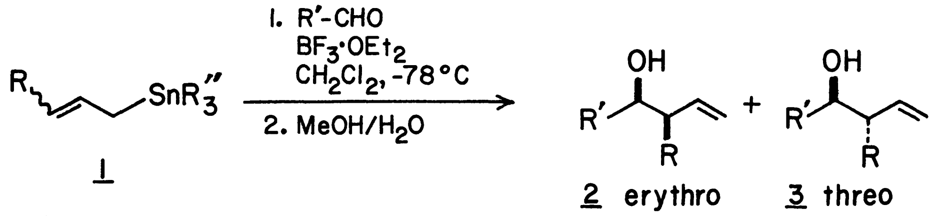
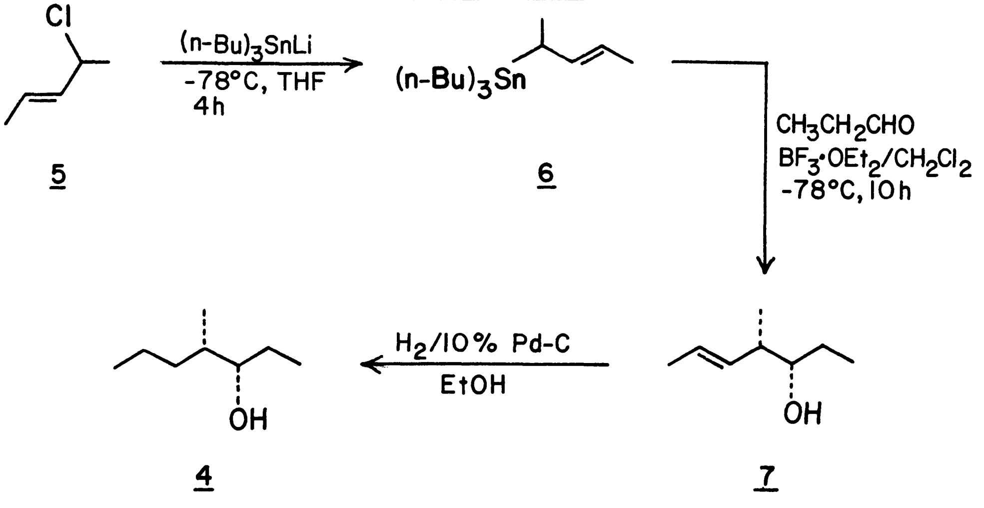
A highly effiecient, stereoselective synthesis of the insect pheromone (±)-4-methylheptan-3-ol, 4 steps from 1,3-pentadiene with an overall yield of 69.3%, has been achieved using a Lewis-acid catalyzed addition reaction of an allyltin and propanal.

The use of allylmetals in the stereoselective synthesis of homoallyl alcohols has attracted considerable interest in recent years.[2] Among the number of allylmetals investigated thus far, allyltins are unique in that the stereochemistry of the products from the Lewis-acid catalyzed addition to aldehyde is dependent upon the structure of allyltins. Thus, both *Z*- and *E*-2-alkenyltins (1: R = R" = alkyl) provided predominantly erythro adducts 2.[3,4] In contrast, *E*-cinnamyltins (1: R = phenyl, R" = alkyl and phenyl) afforded threo adducts 3.[4] We describe in the following an efficient synthesis of the aggregation pheromone 4 of the smaller European elm bark beetle utilizing this highly stereoselective reaction of allyltins.



(-)-4-Methylheptan-3-ol is an aggregation pheromone secreted by the smaller European elm bark beetle, *Scolytus multistriantus* Marsham.[5,6] The requisite



allyltin, 6, for the synthesis of the racemic pheromone 4 was prepared in 95% yield by the treatment of E-2-chloro-3-pentene (5)[7] with tri-n-butyltinlithium. Allyltin 6 produced E-erythro-homoallyl alcohol 7[8] stereoselectively upon its reaction with propanal in 80% yield.[9] Catalytic hydrogenation of 7 provided the pheromone 4 (93% yield), bp 70 - 75°C/14 mmHg (Kugelrohr), diastereomerically pure judged from 360 MHz ^{1}H and 90 MHz ^{13}C nmr and GC (3% SE-30).

The synthesis described herein amply demonstrates the versatility of Lewis-acid catalyzed reactions of allyltins in the stereoselective synthesis of acyclic natural products.[10,11]

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9. The corresponding threo isomer was detected (~3% yield by 360 MHz ^{1}H nmr) in the crude product mixture but was removed during purification by distillation.
10. For another example of the use of an allyltin in the stereoselective synthesis of acyclic natural products, see: K. Maruyama, Y. Ishihara, and Y. Yamamoto, Tetrahedron Lett., 22, 4235 (1981).
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