Tetrahedron Letters No. 48, pp 4209 - 4212, 1975 Pergamon Press. Printed in Great Britain.

SYNTHESIS OF (7*E*,9*Z*)-7,9-DODECADIEN-1-YL ACETATE, A SEX PHEROMONE OF *LOBESIA BOTRANA*[1]

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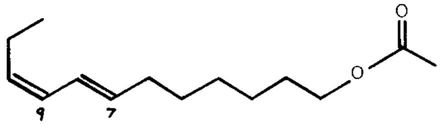
(Received in USA 12 August 1975; received in UK for publication 16 October 1975)

The European grape vine moth, *Lobesia botrana* (Schiff) (Lepidoptera Tortricidae, sub-family Olethreutinae) is a major pest of vineyards in southern Europe and its occurrence is monitored extensively with live virgin female traps[2a] It has recently been proposed that (7*E*,9*Z*)-7,9-dodecadien-1-yl acetate (**1**) is a natural sex pheromone emitted by the virgin female,[2,3] and the synthetic compound has been shown to effectively attract male moths in the field [2-4] We describe here a practical stereoselective route which can be used to prepare **1** on a large scale

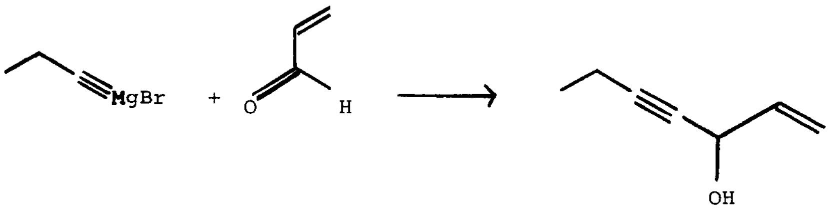


1

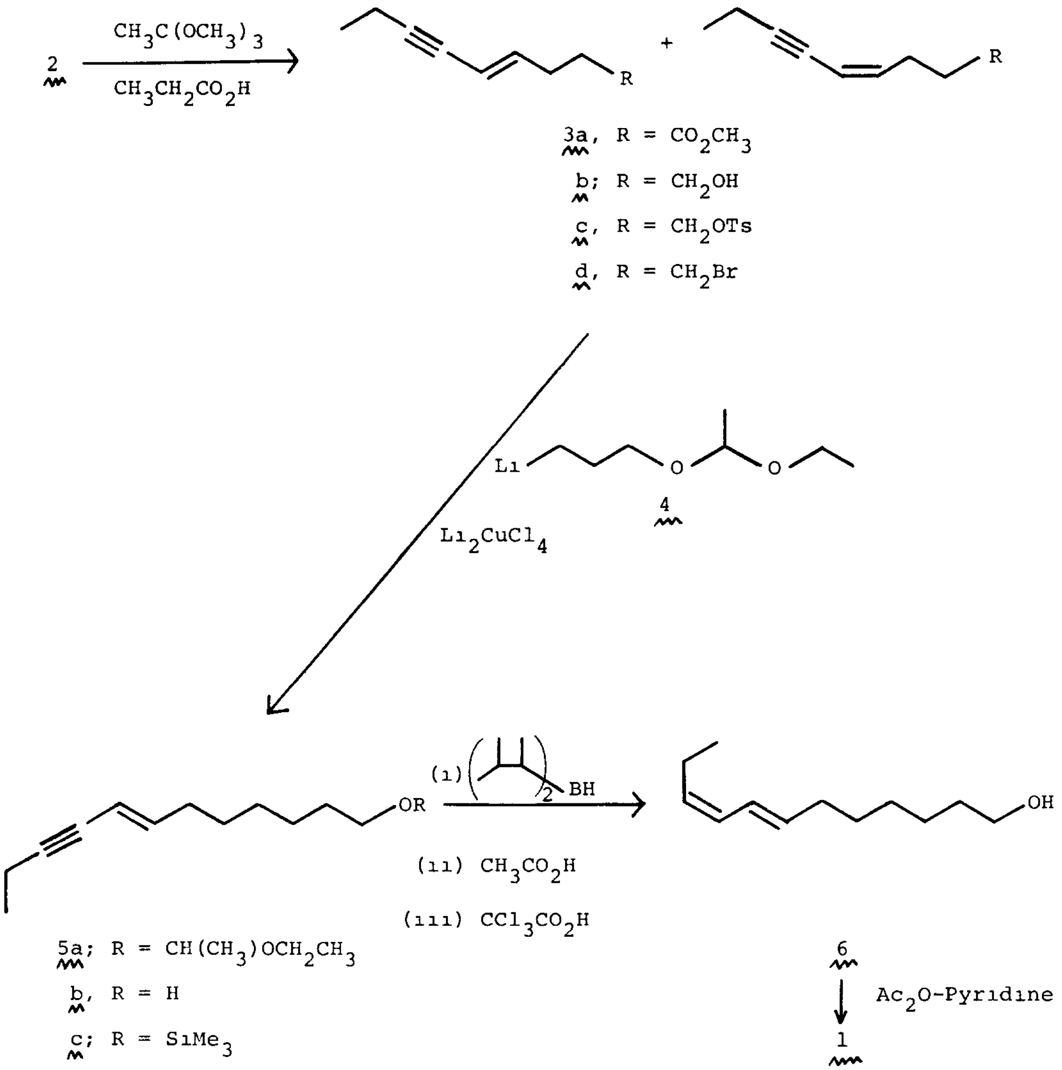
Reaction of 1-butynylmagnesium bromide with acrolein in diethyl ether at -20° gave 1-hepten-4-yn-3-ol (**2**) The crude alcohol **2** was heated for 6 hr with trimethyl orthoacetate in toluene, with propionic acid as the catalyst,[5,6] under conditions of continuous removal of the methanol-toluene azeotrope. Distillation gave (in 50% yield from acrolein) methyl 4-nonen-6-ynoate (**3a**), bp 130° (20 mm) Glc analysis of the product showed it to contain an *E* *Z* ratio of *ca*. 4.1 (*cf* ref 6) The pure *E* isomer can be readily obtained by distillation of the isomer mixture on a spinning-band column, but such a separation is unnecessary at this stage

Reduction of the ester 3a (*E*:*Z* isomers in ratio 4:1) with $LiAlH_4$ in tetrahydrofuran gave the alcohol 3b, bp 65° (0.20mm), which was converted to the bromide 3d, bp 52-55° (0.15mm) (*via* the *p*-toluenesulfonate 3c) in 70% overall yield from 3a. The bromide 3d was then coupled in tetrahydrofuran with 3-[(1-ethoxy)-ethoxy]propyllithium (4)[7] using catalytic quantities (*ca* 0.1 equiv) of dilithium tetrachlorcuprate (-5°, 1 hr),[8] to give 5a. Acid hydrolysis (trichloroacetic acid in aqueous tetrahydrofuran, 60° for 1 hr) then gave the crude alcohol which was *crystallized from pentane at -35°* to give (*E*)-7-dodecen-9-yn-1-ol (5b) (98.6% purity by glc analysis) in 50% overall yield from 3d.

The pure *E* enyne alcohol 5b was converted to the trimethylsilyl ether 5c, bp 90-92° (0.13mm), (Me_3SiCl-Et_3N in CH_2Cl_2). Selective hydroboration of the acetylene group of 5c with an equimolar amount of bis(3-methyl-2-butyl)borane (0°, 2 hr in tetrahydrofuran) followed by protonolysis of the vinylboron intermediate with acetic acid (65°, 5 hr),[9] and then alkaline H_2O_2 treatment to remove boron containing impurities, followed by acid hydrolysis of the protecting group (CCl_3CO_2H in methanol, 25° 1 hr) gave the 7*E*,9*Z* diene 6, bp 85° (0.16mm), in 70% yield from 5b.[10] Acetylation of 6 then gave the sex pheromone 1, bp 86-86.5° (0.2mm).[11,12]



2



3a, R = CO_2CH_3
b; R = CH_2OH
c, R = CH_2OTs
d, R = CH_2Br

5a; R = $CH(CH_3)OCH_2CH_3$
b, R = H
c; R = $SiMe_3$

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(1) Contribution No. 40 from the Research Laboratory of Zoecon Corporation

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(10) The diene alcohol **6** can be purified by crystallization from pentane at -50° but the enyne alcohol **5b** crystallizes much more readily.

(11) Glc analysis was determined at 130° on 4-m x 2-mm (i.d.) glass columns packed with 3% PDEAS on 100/120 mesh Chromosorb W-AW-DMCS (*cf*. ref 2b) The pheromone synthesized by this route was shown to contain 97.5% of the 7*E*,9*Z* isomer and 1.8% of the 7*E*,9*E* isomer A sample of the 7*E*,9*E* isomer was prepared using the general procedure of E. Negishi and T Yoshida, *J Chem Soc.*, *Chem. Comm.*, 606 (1973).

(12) Satisfactory nmr, ir and mass spectra, and also elemental analyses, were obtained for all new compounds.