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SYNTHESIS OF *LOBESIA BOTRANA* AND *SPODOPTERA LITTORALIS* NATURAL SEX-ATTRACTANTS

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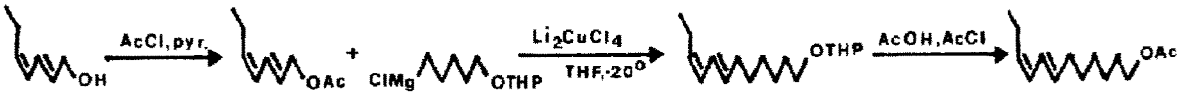
Abstract - Starting from the coupling reaction of alkyl cuprates with 1-alkynyl-2-propenyl acetates, the title compounds were prepared by short convenient syntheses.

In an earlier communication,[1] the coupling reaction of alkyl cuprates with 1-alkynyl-2-propenyl acetates to give (Z)-enynes was described. We now report the application of this reaction in the synthesis of the sex pheromones of the European grapevine moth, *Lobesia botrana*, and the Egyptian cotton leafworm, *Spodoptera littoralis*. (2E,4Z)-2,4-Heptadienol 1, prepared as previously reported,[1] was acetylated and acetate 2 (0.090mol) was coupled with Grignard reagent 3 (0.145mol) in the presence of dilithium tetrachlorocuprate (3.6mmol) in THF (180mol) at -20°. As expected,[2] the reaction (Scheme 1) occurred regio-selectively with no significant allylic rearrangement. Instead, surprisingly, some change in the stereochemistry of the diene system was observed. The crude product 4, after acidic hydrolysis, acetylation, and purification by column chromatography gave (7E,9Z)-7,9-dodecadien-1-yl acetate 5 (50% yield based on 1, containing[3] ca. 20% of the E7,E9 isomer[4]). This synthetic material attracted *L. botrana* males in the field as strongly as the 7E,9Z isomer alone. A similar result of field trapping has already been noted[5].

Scheme 1

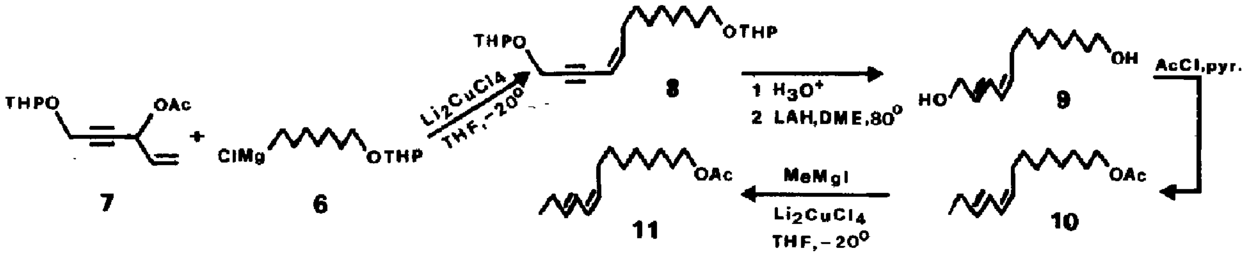


1 2 3 4 5

Scheme 2 shows the synthetic route to (9Z,11E)-9,11-tetradecadien-1-yl acetate 11, the sex pheromone of *S. littoralis*.

A solution of the Grignard reagent 6, prepared from 7-chloroheptyl tetrahydropyranyl ether (29.8g, 0.127mol) and magnesium (3.4g, 0.14g atom) in THF (130ml), was added to a cooled (-20°) solution of the acetate[1] 7 (19g, 0.080mol) in THF(170ml) containing dilithium tetrachlorocuprate (0.0032mol). The mixture was kept at -10° for 1 h, worked up as usual and the crude product 8, after removal of the protecting group, was reduced with 1 equiv. of $LiAlH_4$ in dimethoxyethane at 80°. Pure diol 9 (m.p.42-43°; 7.5g, 0.036mol, 45% yield based on 7) could readily be obtained by crystallization from hexane diethyl/ether(60/40)at -20°. Acetylation of 9, followed by the coupling of the allylic acetate 10 with 2 equiv. of methylmagnesium iodide in the presence of dilithium tetrachlorocuprate(2.7%) in THF at -20° gave, after working-up[6] and purification by column chromatography, the pheromone 11 (7.3g, 0.029mol, 36% yield based on 7). G.l.c. analysis[3] of the product showed it to contain *ca.*5% of 9E,11E isomer[4] and trace amount of Z9,11Z and 9E,11Z isomers. Such a route was scaled up as a practical method of preparing commercial batches of 11.

Scheme 2



References and notes

(1) G.Cassani, P.Massardo, and P.Piccardi, *Tetrahedron letters*,1979,633.

(2) J.F.Normant, A.Commercon, and J.Villieras, *Tetrahedron letters*,1975,1465.

(3) G.l.c. analysis was determined on 50 m glass capillary column filled with Carbovax 20M.

(4) The E,E isomer is easily removed from mixture by the formation of its Diels-Alder adduct with excess tetracyanoethylene in THF.

(5) R.Roehrich, J.P.Carles, Y.Darrioumerle, P.Pargade and B.Lalanne Cassou, *Ann.Zool.-Ecol.anim.*8,473,1976.

(6) During the reaction a partial deacetylation of cross-coupled product 11 to (9Z,11E)-9,11-tetradecadien-1-ol was observed and therefore the crude reactio mixture was acetylated again(AcCl,pyr) before purification by column chromatography.

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