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NEW SIMPLE SYNTHESIS OF INTERNAL CONJUGATED (Z)-ENYNES

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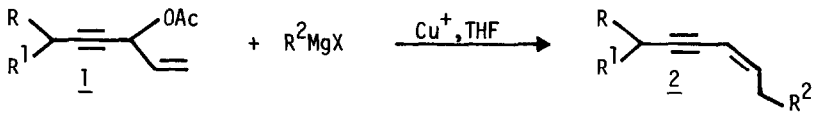
The conjugated enyne unit is characteristic of the key intermediates of a number of synthetic routes developed recently for the preparation of some natural insect sex-attractants.[1]

We report herein a stereoselective procedure for the synthesis of conjugated (Z)-enynes , which not only proceeds under very mild conditions but appears to be an efficient route to certain types of dienes not readily accessible.[2]

The method simply involves the coupling of the 1-alkynyl-2-propenyl acetate 1 [Cu(I) catalysis] with an alkylmagnesium halide to give, after acid hydrolysis, the (Z)-enyne 2 in good yield (ca.80%) as the only reaction product [equation (1)].



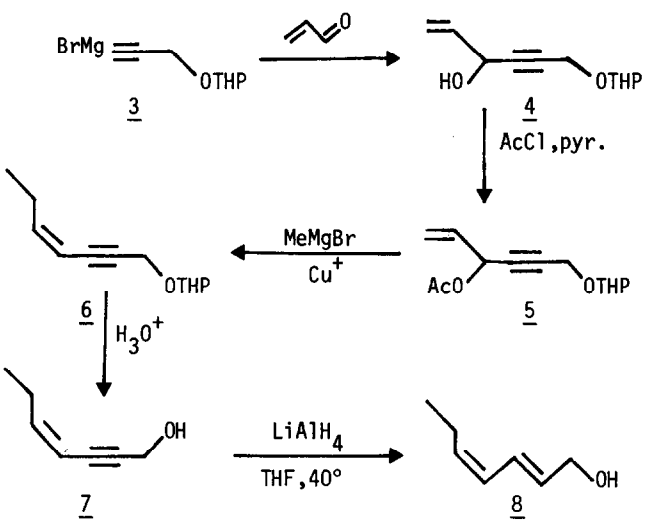
(1)

It has already been shown[3] that the reaction of lithium dialkylcuprates with 3-acetoxy-pent-1-en-4-yne gave mainly the β-addition product to the triple bond and a few percent of the adduct to the double bond . Also in this case the configuration of 2 was Z.

Compounds 2 are readily convertible into the corresponding conjugated (Z,Z)-dienes by known procedures,[4] and have been used by us also in the preparation of (E,Z)-dienes. For example, the Scheme 1 shows an efficient synthesis of (2E,4Z)-2,4-heptadienol a key intermediate for the preparation of the pheromone of the European grapevine moth, Lobesia botrana, an important pest of vineyards.[1,2]

Reaction of 3-(2-tetrahydropyranyloxy)-1-propynylmagnesium bromide 3 with 2-propenal in THF at -10° gave the alcohol 4, which was then converted directly to the acetate 5 with acetyl chloride and pyridine. Coupling of methylmagnesium bromide with 5 (molar ratio 1.5:1) in THF at -15° in

Scheme 1



the presence of a catalytic amount (3 mol%) of CuCl in HMPT (6 mol%) gave (Z)-2-(hept-4-en-3--ynyloxy)tetrahydropyran 6 (80% yield) [n.m.r.($CDCl_3$) δ: 5.6 $-\overset{H_B}{C}=\overset{H_A}{C}-C\equiv C-$, J_{AB} ca. 11Hz].After hydrolysis,the alcohol 7 was reduced with $LiAlH_4$ in THF at 40° for 30 minutes[5] to (2E,4Z)-2,4--heptadienol 8 containing[6] ca. 7% of the E,E-isomer.The E,E-contaminant was easily removed by the formation of its Diels Alder adduct with tetracyanoethylene in THF.

References

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(4) E.Truscheit and K.Eiter,Annalen,1962,658,65 ; A.Butenandt,E.Hecker,M.Hopp,and W.Koch, ibid.,1962,658,39 ; E.Negishi,G.Lew and T.Yoshida,J.C.S.Chem.Comm.,1973,874.

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(6) G.l.c. analysis was determined on 50 m glass capillary column filled with Carbowax 20M. Satisfactory n.m.r.,i.r. and mass spectra were obtained for all new compounds.

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