

REACTIVITY OF ALLYL-ZINC (AND COPPER) REAGENTS
TOWARDS ALLENIC ETHERS AND α -METALLATED ALLENIC ETHERS

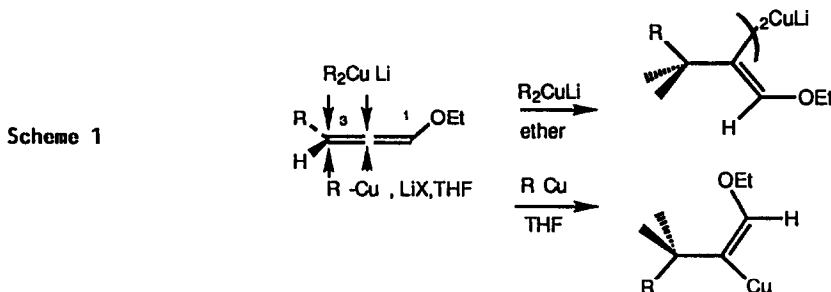
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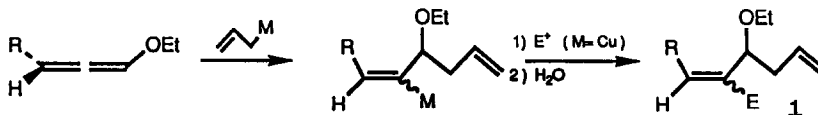
Abstract. Allylzinc (copper) reagents add to alkoxyallenes in a regioselective way, leading to β -alkoxy vinyl metals. Allyl zinc derivatives react with α -lithioalkoxyallenes to generate regioselectively metallated β -allene-enes.

We have already shown¹ that the addition of organocopper species to allenic ethers is highly dependent on the nature of the organometallics and of the solvent.

Lithio cuprates in ether lead to a Z vinyl copper species, whereas alkyl copper or cuprates derived from organolithium reagents, in THF, lead to the corresponding E isomer. However, as far as regio selectivity is concerned, in all the cases studied, the R group of the copper reagent (either primary alkyl, secondary alkyl, vinyl, or phenyl), is delivered exclusively on carbon 3 independent of the substitution pattern of the allene (Scheme 1).



We now report that the addition of allylmetals to the same substrates follows an entirely different pathway (Scheme 2).



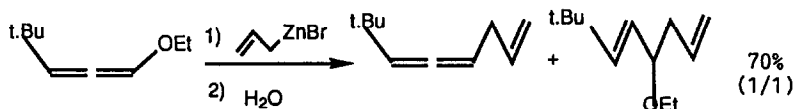
Scheme 2

The allyl moiety now attacks carbon 1 and we end up with a vinyl metallic species bearing an allylic alkoxy group. With allyl zinc bromide in THF, the reaction is not stereoselective, and a 1/1 mixture of Z and E isomers is obtained in high yield : (Scheme 2, R = nBu, M = ZnBr, 90% yield after hydrolysis).

However, treatment of allylzinc bromide with one equivalent of CuBr (better than CuCN, 2 LiCl) prior to the addition to the allenic ether, now leads to a predominant syn addition (Z/E = 91/9) (use of catalytic amounts of copper salts does not bring about any stereoselection).

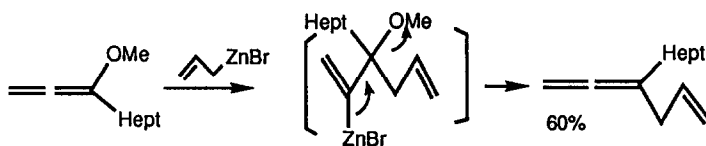
This syn addition occurs from the less hindered side of the C = C bond. The vinyl copper reagent thus formed leads to stereospecifically trisubstituted alkenes by known reactions, for example² : Scheme 2, R = n.Bu, E⁺ = PhSCH₂NEt₂ gives 1 R = n.Bu, E = CH₂NEt₂ yield 60% Z/E = 90/10.

When a bulky substituent is present in the allenic ether, β-elimination of zinc alkoxide takes place :



Scheme 3

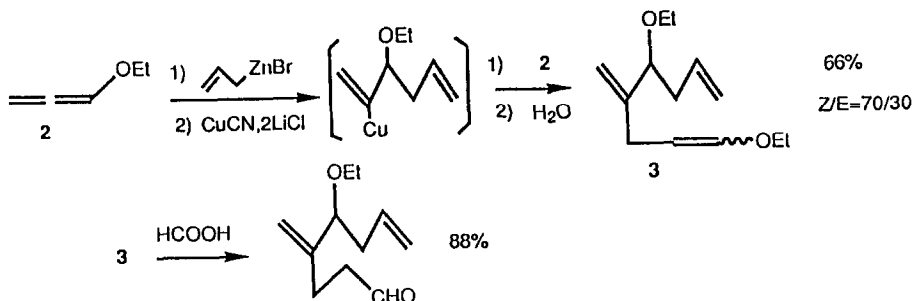
In this case, the allylic ether formed is almost purely of E configuration, pointing to the fact that the syn addition product bearing a tertbutyl and an ethoxy allyl group in cis relationship, is more congested, and more prone to β-elimination than its trans counter part. α-Alkyl alkoxyallenes, leading to a tertiary alkoxy derivative also suffer rapid elimination (Scheme 4).



Scheme 4

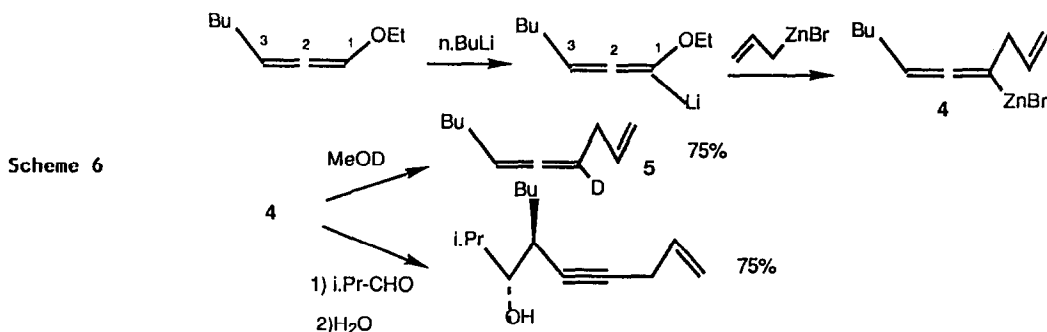
With ethoxyallene, allylzinc bromide in the presence of one equivalent of CuCN, 2LiCl gives the same regioselectivity, but the intermediate vinyl copper species adds rapidly to the starting allene on carbon atom 3 as expected¹, leading to a mixture of E and Z enol

ethers (Z/E = 70/30) which have been hydrolyzed to the corresponding aldehyde (Scheme 5).



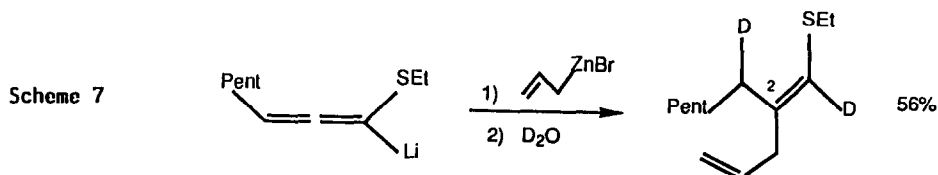
Scheme 5

If one metallates the starting alkoxyallene on carbon atom 1, further addition of allylzinc bromide now leads to a metallated skipped allene-ene **4**. The presence of an allenyl metal has been checked by deuterolysis (to **5**: 95% D) and by reaction with an aldehyde, whereby a single isomer of a homopropargylic alcohol is formed, assumed to be the three one according to literature precedents³⁻⁶ (see scheme 6).



Scheme 6

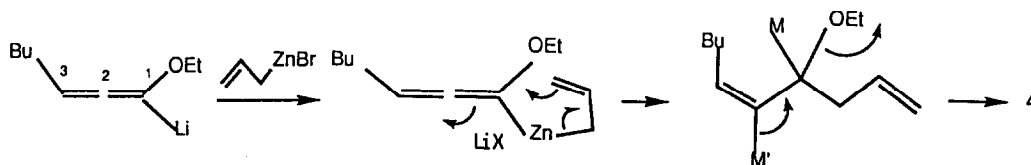
Thus the alkoxy moiety dramatically alters the course of the reaction, as compared with an alkyl thio group: we have previously shown⁷ that in the latter case a "metalla-Claisen" rearrangement led to a 1,3-bismetallated skipped diene, i.e. to an allylation on carbon atom 2 (Scheme 7).



Scheme 7

The mechanism of the reaction will not be discussed here, but the more plausible pathway involves the internal delivery of the allyl group on carbon atom 1. This leads to a bis metallated species, which is highly unstable, since this allylic carbenoid has some carbocationic character⁸⁻¹², and is prone to β -elimination of a metal alkoxide (see scheme 8), in opposition to the vinylic zinc derivative leading to 1 (see Scheme 2).

Scheme 8



In summary, we have described a new stereoselective access to functionalized vinyl copper species from allenic ethers, and a new access to skipped allene-enes regioselectively metallated on the allene moiety.

References

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(Received in France 7 March 1990)