

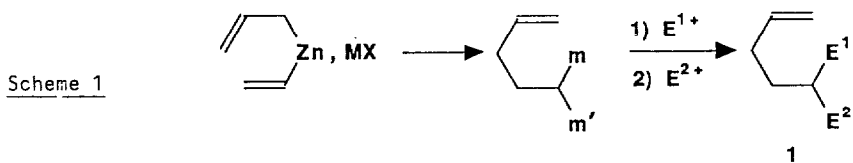
ALLYLIC ORGANOBISMETALLIC REAGENTS - PART 1

J.F. Normant, J.Ch. Quirion, A. Alexakis and Y. Masuda

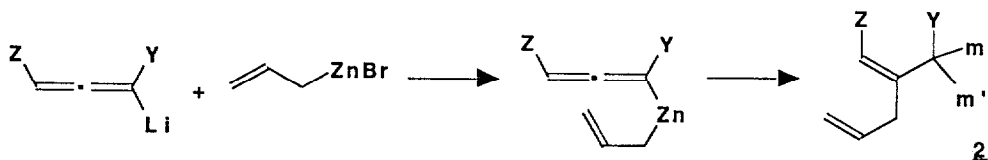
Laboratoire de Chimie des Organo-éléments, Tour 45
 Université P. et M. Curie, 4 Place Jussieu F-75252 PARIS Cedex 05

Summary - Allyl-allenyl zinc reagents undergo a rearrangement leading to allylic bis metallic species. A high regioselectivity is observed when these reagents are treated with a variety of electrophiles. The net result is an access to highly functionalized vinyl zinc reagents.

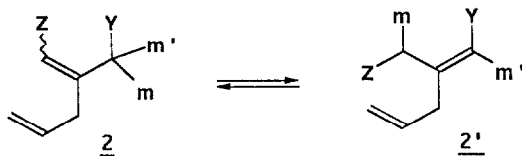
We have recently disclosed a "metalla Claisen" rearrangement of allyl-vinyl zinc reagents leading to bis metallic derivatives, which can react, once or twice, with a variety of electrophiles¹ :



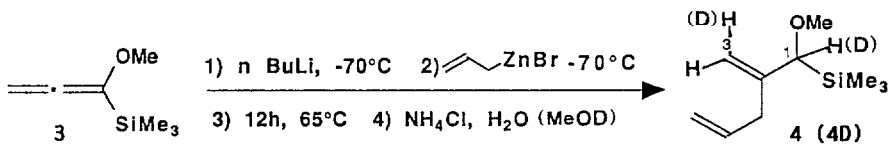
We have now extended this concept to the rearrangement of allyl-allenylzinc reagents. The postulated process is :



As in the case of scheme 1, the real nature of m and m' is unknown, and the corresponding organometallics is probably a nonmonomeric cluster. We have shown that the reactivity of the two C-m bonds in 1 is different¹, but the problem is even more complex here, since the newly-formed reagent 2 may be thought of in terms of a mixture of two equilibrating species :

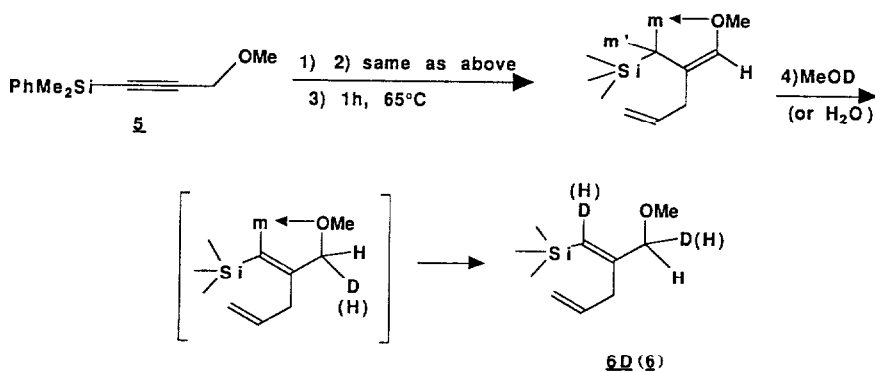


1-Trimethylsilyl-1-methoxyallene is treated sequentially by *n*-butyllithium in THF², and then by allylzinc bromide at -70° , before the mixture is brought to reflux for 12 h and hydrolyzed to give the allylsilane 4 in 60% yield :



In this case, protonation occurs on carbons 1 and 3 almost exclusively. Deuterolysis (MeOD) leads to a single isomer 4D.

A large variety of simple and functionalized lithio allenes are easily available by metallation of allenes or, more simply, of substituted alkynes²⁻⁴. We thus turned our attention to propargylic ethers. When 1-phenyldimethylsilyl-3-methoxyprop-1-yne is treated as above, a single isomer 6D is obtained. This high regio- and stereoselectivity may be accounted for by a favoured chelation of the bimetallic reagent :

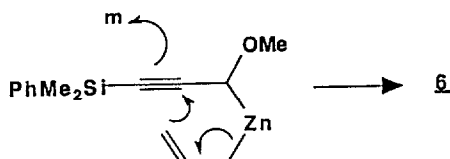


6 has been compared to both *E* and *Z* authentic samples of the product, prepared according to ⁵ and is identical to the former. By analogy, we propose the *Z* structure for 4D.

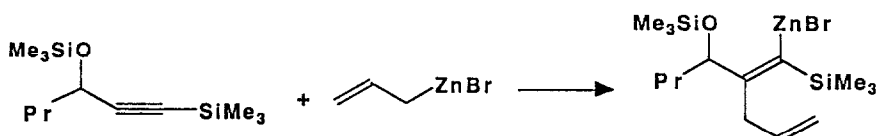
Following the course of the metallation of 5 by G.L.C. shows a mixture of 5 and its metallatropic allenic isomer :



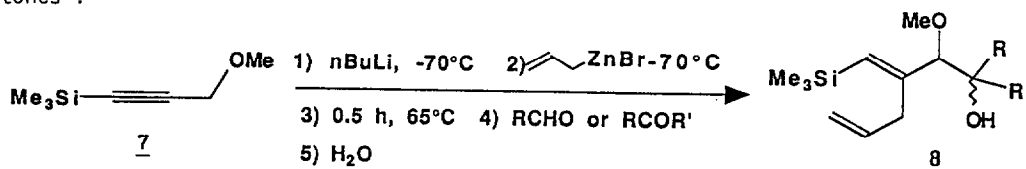
In this case, the carbometallation can be viewed either as a metalla-Claisen rearrangement, or alternatively, internal delivery of the allyl moiety of the mixed propargylic-allylic reagent :



Recently Negishi et al⁶, showed that addition of allyl zinc bromide to silylated alkynes proceeded in 83% yield, although much more slowly than in our case (18-24 h at 60°), and Molander⁷ showed that this preferential Syn addition (85/15) became an anti addition when an ether function was located at the propargylic position on the substrate :

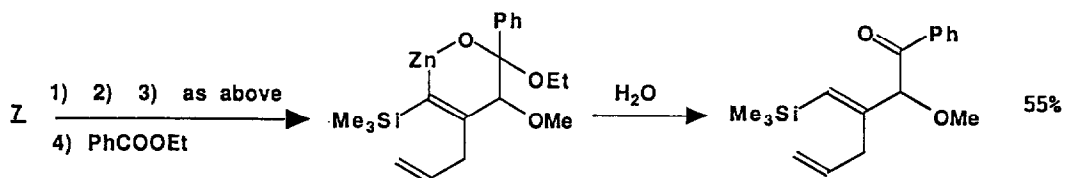


The bis metallic reagents display the same regio selectivity when added to aldehydes or ketones :

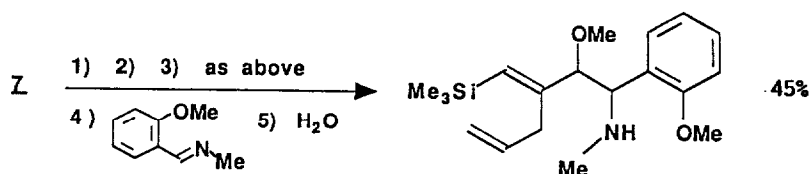


8a R = Ph, R' = H 55% ; 8b R = iPr, R' = H 55% ; 8c R = Ph, R' = Me 55%. A 1/1 ratio of diastereoisomers is observed.

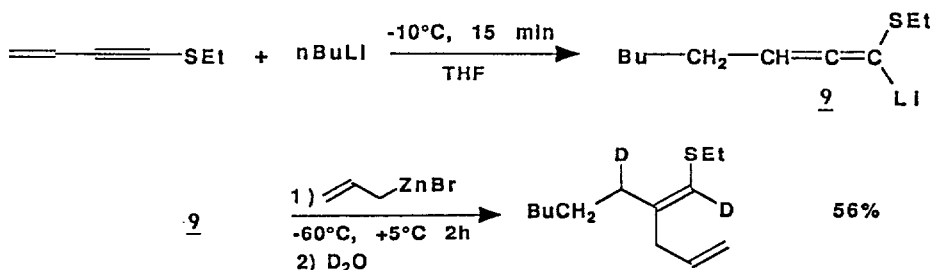
Esters can be reacted as well, but contrary to the usual reactivity of allylic lithium - or zinc reagents, which lead directly to the bis allylic carbinols, this reaction stops at the keto-stage. We interpret this fact by the interaction of the second metal, stabilizing the hemiketalate intermediate :



Imines can also be used :



Metallated allenes can also be prepared by the addition of alkyllithium reagents to activated enynes ; for example, treatment of 1-ethylthio-3-buten-1-yne with butyl lithium^{3b}, followed by allylzinc bromide gives the desired rearrangement without heating :



In this case, a mixture of geometric isomers (Z/E = 88/12) is formed.

Although yields of purified products are presently only modest⁸, the high regioselectivity of these reactions is promising, and the highly functionalized vinyl zinc reagents at hand before hydrolysis are good candidates for further reactions, particularly cyclisations. Work is under way in this direction, as well as the delineation of the scope of this general scheme : the nature of various alkynes, allenes, and functionalized allylic zinc reagents.

Acknowledgements.

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- 8 - In all these experiments, the raw product was obtained with yields in the 60-80% range and fair purity (according to NMR). Purification on silica dramatically diminished the yields for unknown reasons.

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