

Acyclic Stereocontrol through the Metalla-Claisen rearrangement. Part I

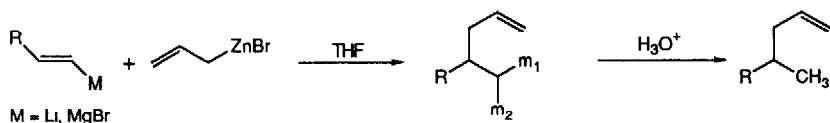
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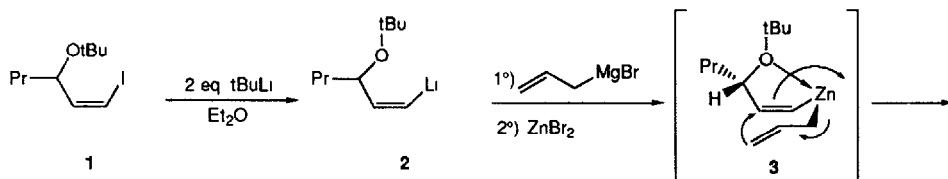
Key Words transmetalation, acyclic stereocontrol, allyl vinyl zinc, 1,1-dimetallic compounds

Abstract (*Z*)- γ -lithio vinylic ethers can be added in a stereoselective way to allyl zinc bromide, leading to 1,1-dimetallic species with two asymmetric carbon atoms

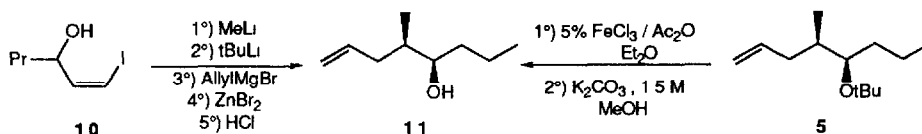
[3,3] Sigmatropic migrations, among which the Cope and Claisen rearrangements, provide a powerful means for constructing carbon-carbon bonds and are increasingly employed in asymmetric synthesis¹. Recent reports have documented the viability and synthetic potential of the carbanion accelerated Claisen rearrangement of allyl vinyl ethers². We have postulated some years ago³ that the addition of allyl zinc bromide to various alkenyl organometallics⁴ could be seen as a metalla-Claisen rearrangement leading to a gem dimetallic species



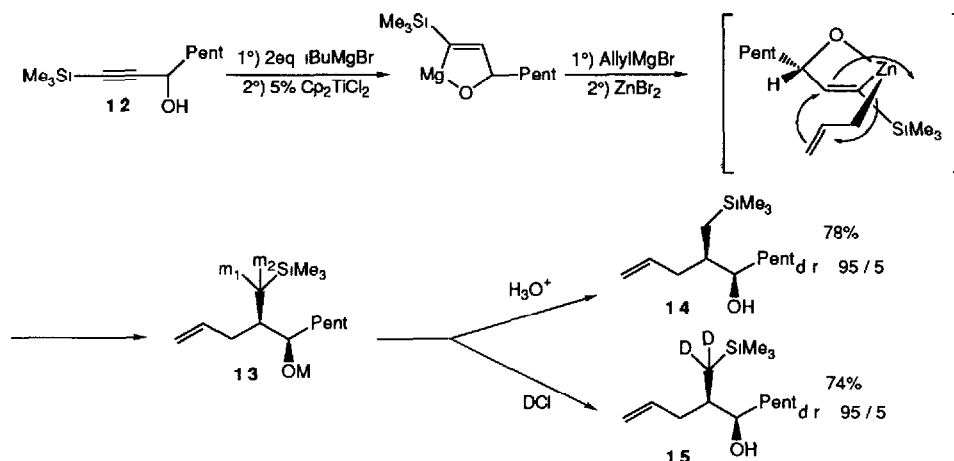
We now report our preliminary results in the area of acyclic stereocontrol by metalla-Claisen rearrangement. The starting materials for this work, are (*Z*)- γ -iodo allylic ethers⁵. Metal-halogen exchange with *t*BuLi affords an alkenyl lithium reagent **2**, which reacts with allylzinc derivatives to give a postulated allyl vinyl zinc compound **3** which then undergoes a [3,3] Sigmatropic rearrangement leading to the stable 1,1-dimetallic species **4**, and after acidic hydrolysis, to the compound **5** with two asymmetric carbon atoms



by comparison with alcohol **11** derived from iodo alcohol⁸ **10** via an analogous metalla-Claisen pathway. In this case, the diastereomeric ratio was lower (80/20) than in the case of the tertbutyl ether



This methodology has been applied to the synthesis of "trimetallic species"



Starting from a γ -trimethylsilyl propargylic alcohol **12**, submitted to the hydromagnesiation reaction⁹, followed by the metalla-Claisen procedure and hydrolysis, alcohol **14** was obtained with a very good diastereoisomeric ratio. The relative configuration of the new asymmetric center has been deduced by comparison of **14** with the alcohol obtained by allylmagnesiation of (E)-1(trimethylsilyl)-but-1-en-3-ol¹⁰ both are identical.

In conclusion, Z γ -iodo allylic ethers (or alcohols) can be metallated and added in a stereoselective way to allyl zinc bromide¹¹, leading to syn-substituted homohomoallylic alcohols, which can be further elaborated, due to the presence of two carbon-metal bonds. The cases of the lithiated E isomers of **2**, and of homologs of allyl zinc bromide will be shortly published.

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- 11 Contrary to our initial reports³ this new approach allows the use of allylic Grignard reagents which are more stable than their zinc counterparts and can be stored at 0°C for longer periods In the absence of zinc halide, no rearrangement takes place between the vinyl lithium and allyl magnesium halide reagents

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