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ALLYLIC ORGANOBISMETALLIC REAGENTS - PART 2[1]

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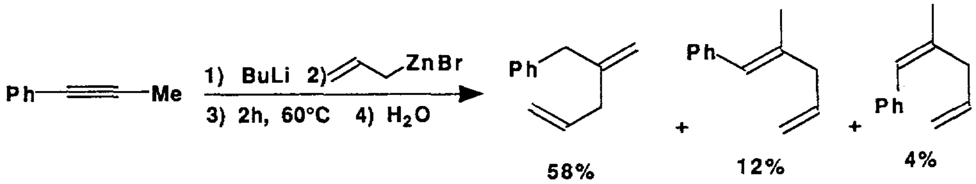
Summary - *The metalla-Claisen rearrangement of allenyl-allyl zinc reagents described in the preceding letter may follow different patterns according to the nature of the allenyl moiety. It is thus possible to promote three consecutive rearrangements leading to cyclic trismetallic species with good stereoselectivity.*

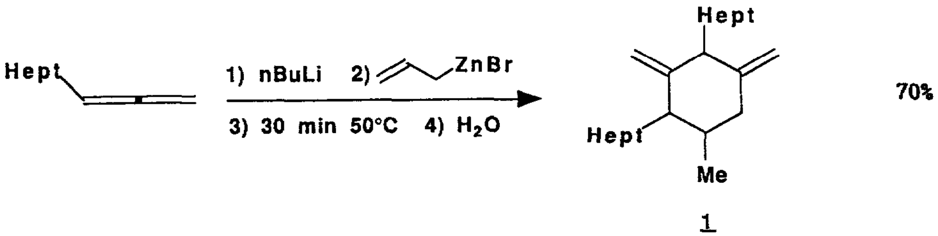
In the preceding letter, we discussed the metalla-Claisen rearrangement of allyl-allenyl zinc reagents derived from silylated alkoxyallenes, silylated propargylic ethers, or alkylthioallenes.

When the reaction is performed with nonsilylated, or nonoxygenated educts, several discrepancies from the general scheme are observed. For example, lithiation of 1-phenyl-1-propyne[2] followed by reaction with allylzinc bromide and heating (60°C 2 h) gives a bismetallic reagent which is protonated nonregioselectively, contrary to what was observed when oxygen or sulfur-substituted substrates were used[1] :



The dramatic influence of O and S atoms on the regio- and stereoselectivity in the previous cases[1] is thus evident.

If one starts from a terminal allene, the reaction takes another course :



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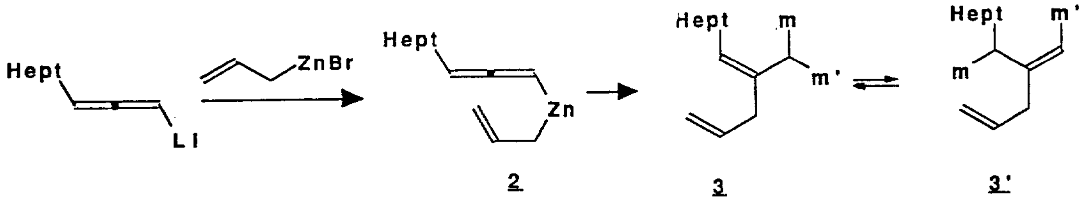
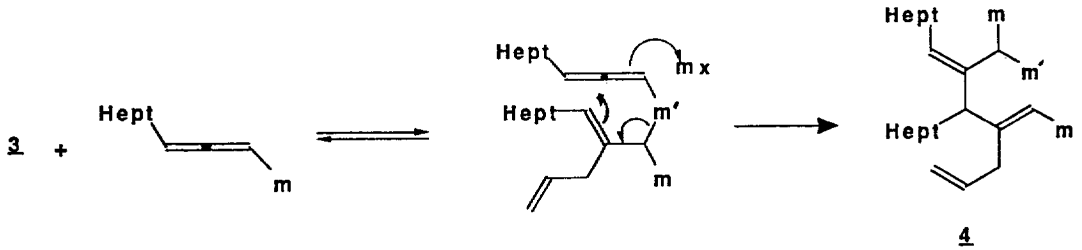
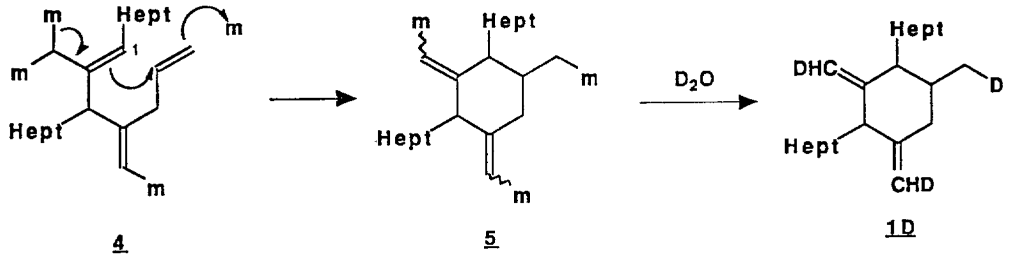
and a cyclic bis-exomethylene cyclohexene is obtained in good yield as a 90/10 mixture of two isomers. Deuterium oxide quench of the reaction mixture shows incorporation (> 90% according to NMR and mass spectra) of three deuterium atoms, namely on the methyl and the two terminal sp$_2$ carbon atoms. We interpret the formation of 1 by three consecutive rearrangements : two sequential metalla-Claisen reactions, followed by a zinc-ene process:



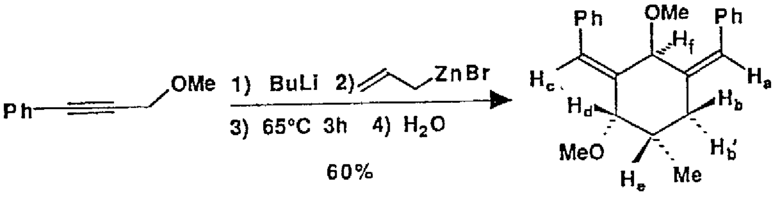




For reasons which require further study, the initially formed bis-metallic species 3 is observed in only trace amounts (3 or 3', m = m' = H) from the beginning to the end of the reaction, and this allylic bis-metallic reagent undergoes a second metalla-Claisen rearrangement with the starting metallated allene.

This pathway could proceed further, leading to polymerisation, but 4 shows a 1-6 relationship between an allylic organometallics and a terminal double bond, allowing cyclisation.

Such metal-ene reactions are better documented in the case of magnesium[3] than zinc, but Lehmkuhl et al[4] disclosed the addition of bis allylzinc species to alkenes, and, more recently, Bickelhaupt, Klumpp et al[5] succeeded in the preparation of metallated heterocycles by zinc-ene reactions. Curiously enough, in the case of 1-methoxy-3-phenylprop-2-yne, we also found such a process namely :



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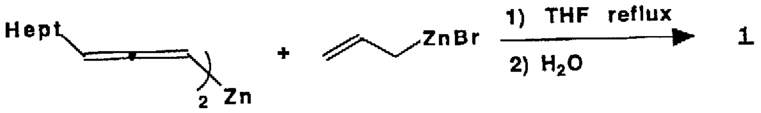
Where a unique isomer is formed. Cristallographic study of 6 (m.p. 100°C) is underway, but NMR 2D experiments favour structure 6. The coupling constants $JH_aH_b = JH_cH_d = 2.0$ Hz are considered as indicative of an axial position of H_b and H_d, located in cis position relative to H_a and H_c respectively[6], H_e and H_f being equatorial ($JH_bH_e = JH_dH_e = 4.6$ Hz, and $JH_{b'}H_f = 1.0$ Hz).

This high stereoselectivity, after three rearrangements, raises a number of interesting problems :

- Only 3 (and not its metallotropic isomer 3') reacts regioselectively with the allenyl metal, and the geometry (E or Z) of the vinyl metal is locked in 4.
- The zinc-ene reaction follows the general pattern described by Oppolzer[3e] in the case of monometallic (magnesium) allylic systems whereby the more substituted C_1 atom is the attacking site.
- The transmetallation leading to 2 is a fast process occuring at low temperature, so that no free allenyl lithium reagent is left for the step 3 → 4. We have checked that the presence of the latter is not required. Heating a mixture of bis allenylzinc and allylzinc bromide leads to 1 as well :



Mixed zincate complexes must be involved, and the equilibria are shifted by the irreversible process 4 → 5.

The corresponding chair- or boat like transition states of these three consecutive reactions will be discussed in the full paper. We are presently studying the scope of these reactions, and the reason why a mono- or bis metalla-Claisen rearrangement takes place according to the structure of the starting allenic substrate.

Acknowledgement.
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References :

1/ Part I preceding letter

2/ P. Klein in "The Chemistry of the carbon-carbon triple bond", Ed. S. Patai, J. Wiley, New York 1978, p. 343

3/ a/ H. Felkin, J.D. Umpleby, E. Hagaman and E. Wenkert, Tetrahedron Lett., 2285 (1972)
b/ H. Felkin, L.D. Kwart, G. Swierczewski and J.D. Umpleby, J. Chem. Soc Chem. Comm., 242 (1975)
c/ H. Lehmkuhl, D. Reinehr, D. Hennenberg, G. Schomburg and G. Schroth, Liebigs Ann. Chem., 119 (1975)
d/ H. Lehmkuhl, D. Reinehr, K. Mehler, G. Schomburg, H. Kötter, D. Hennenberg and G. Schroth. Liebigs Ann. Chem., 1449 (1978)
e/ W. Oppolzer, R. Pitteloud and H.F. Strauss, J. Amer. Chem. Soc., 104, 6476 (1982)
f/ W. Oppolzer and R. Pitteloud, J. Amer. Chem. Soc., 104, 6478 (1982).
g/ W. Oppolzer and K. Bättig, Tetrahefron Lett., 23, 4669 (1982)
h/ W. Oppolzer, H.F. Strauss, D.P. Simmons, Tetrahedron Lett., 23, 4673 (1982)

4/ H. Lehmkuhl and H. Nehl, J. Organomet. Chem., 60, 1 (1973) for a review : H. Lehmkuhl, Bull. Soc. Chim. France II, 87 (1981)

5/ J. Van der Louw, J.L. Van der Baan, H. Stieltjes, F. Bickelhaupt, and G.W. Klumpp, Tetrahedron Lett., 28, 5929 (1987)

6/ R.M. Lett, L.E. Overman, J. Zablocki, Tetrahedron Lett., 29, 6541 (1988).

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