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DIASTEREOSELECTIVE ADDITION OF FUNCTIONALIZED ALLYLIC ZINC BROMIDES TO ALKENYL ORGANOMETALLICS. Part 5

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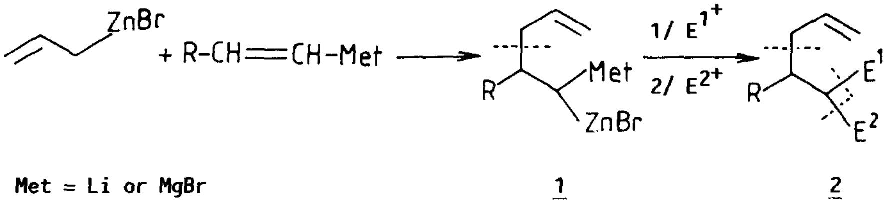
Summary - The addition of functionalized allylic zinc bromides of type 3 to alkenyl-lithium or -magnesium derivatives is always regiospecific and shows a high diastereoselectivity ; it furnishes functionalized gem-dimetallic compounds or a 2-vinylcyclopropylzinc bromide which can be allylated or stannylated.

Scheme 1

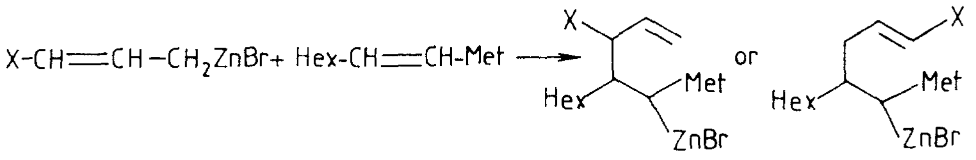


Recently we have reported that allylzinc bromide adds to various alkenyl organometallics to give gem-dimetallic reagents of type 1 which can react selectively with two different electrophiles E^1 and E^2 to furnish a great variety of products of type 2[1,2] (see scheme 1).

We report now our preliminary results about the addition of the substituted or functionalized allylic zinc bromides 3a-3d to octenylmagnesium bromide[3] 4a or octenyllithium[3] 4b. These additions are always regiospecific and lead, depending on the substrate 3, specifically to products of type 5 or 6 (see scheme 2).

Thus the addition of the 2-octenylzinc bromide 3a to the pure (Z)-octenyllithium[4] 4b (THF ; 5°; 19hr) leads after hydrolysis to the alkene 7 as a mixture of two diastereoisomers in a ratio of 88 : 12 in 68% yield. The pure (E)-octenyllithium[4,5] 4b gives the alkene 7 as a

Scheme 2



3a : X=Pent
3b : X=SiMe$_3$
3c : X=OEt
3d : X=SPh

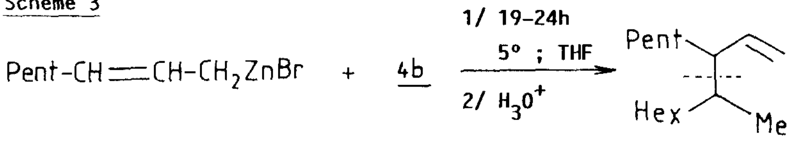
4a : Met=MgBr
4b : Met=Li

5

6

mixture of two diastereoisomers, now in the ratio of 22 : 78 in 47% yield (see scheme 3). This result demonstrates the high diastereoselectivity of the addition reaction[6,7].

Scheme 3[7]



3a

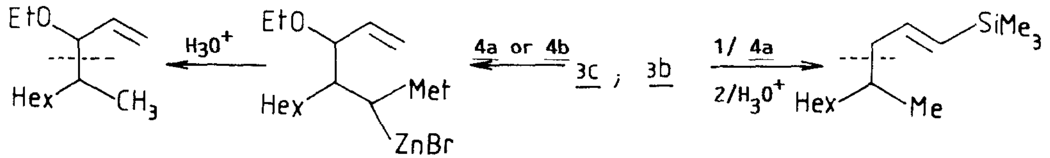
7 : 68% from (Z)-4b ; d.r.=|88:12|

d.r. : diastereomeric ratio

: 47% from (E)-4b ; d.r.=|22:78|

The addition of the trimethylsilyl-substituted[8] allylic zinc bromide 3b to the alkenyl organometallic 4a proceeds with the reverse regioselectivity (attack from the less substituted carbon atom of the allylic system) to give the vinylsilane 8(1eq. of 4a ; 1.8eq. of 3b ; THF ; 4hr at 35°, then 8hr at 25°) in 96% yield as an E:Z mixture of 91:9 (see scheme 4). Whereas the reagents of type 3 where X=SO$_2$Ph, SOPh, OPh do not add to the

Scheme 4[7]



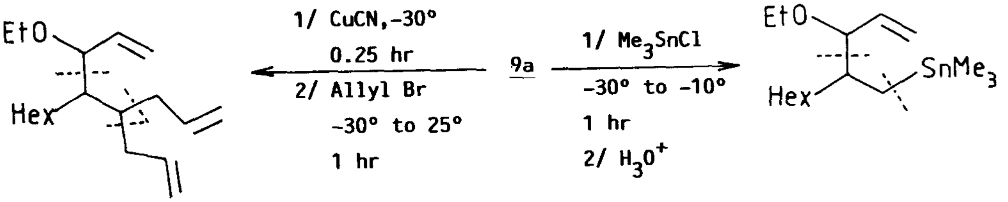
10 : from 9a : 65%
: from 9b : 70%
d.r. = 86:14

9a : Met=MgBr
9b : Met=Li

8 : 96% ;
E/Z : 91/9

organometallics 4a and 4b, the metallated allylic ether[9] 3c adds smoothly to 4a (1.3eq. of 3c for 1eq. of 4a ; THF ; 3hr at 40° ; then 14hr at 30°) and to 4b (1.3eq. of 3c for 1eq. of 4b ; THF ; 30hr at 25°) to give respectively the dimetallic reagents 9a and 9b which after hydrolysis lead to the allylic ether 10 respectively in 65%[10] and 70% yield as a mixture of diastereoisomers (d.r.= 86:14)[3]. Since the starting organometallic 4a occurs a E:Z mixture of 12:88, the diastereoselectivity of the addition reaction is very high. The functionalized dimetalled compound 9a can also be bis-allylated[2] in the presence of copper cyanide (CuCN(1eq.) ; -30° ; 0.25hr ; then excess of allyl bromide ; -30° to +25° ; 1hr) to give in an overall yield[7] of 54% the allylic ether 11 (d.r.=88:12)[3]. Treatment of 9a with trimethyltin chloride (1eq. ; -30° to -10° ; 1hr ; then H_3O^+) furnishes the interesting functionalized tin derivative 12 (d.r.=86:14)[3] in 40% overall yield[7] (see

Scheme 5[7]

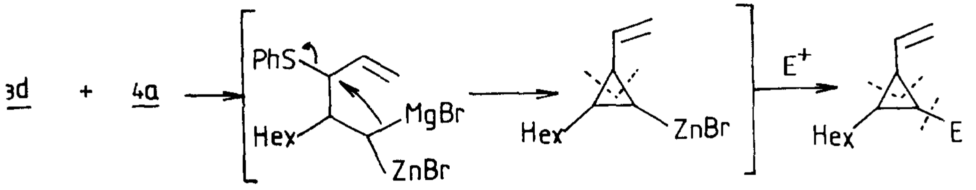


11 : 54% ; d.r.=88:12

12 : 40% ; d.r.=86:14

scheme 5). The addition of the thiophenyl-substituted allylic zinc reagent[11] 3d to the alkenyl Grignard 4a leads to the metallated vinylcyclopropane 13 which is obtained by an intramolecular substitution of the thiophenoxy group of the γ-thiophenoxy gem-dimetallic compound 14. By hydrolysis of 13, the vinylcyclopropane 15 is obtained in 72% yield as a mixture of two diastereoisomers (d.r.=7:3)[3].

Scheme 6[7]



14

13

15 : E=H ; 72% ; d.r.=7:3
16 : E=Allyl ; 72%

The addition of copper cyanide (1eq., -30°) to the cyclopropylzinc derivative 13 followed by an excess of allyl bromide (-30° to 25° ; 1hr) gives the allylated vinylcyclopropane 16 in 72% yield as a mixture of all four diastereoisomers (see scheme 6).

The regiospecific and diastereoselective addition of the substituted allylic bromide 3a and of the functionalized allylic zinc bromides 3b-3d enhances considerably the scope and the synthetic applications of our method. Further developments are currently studied.

Acknowledgements -

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References and Notes -

1. P. Knochel and J.F. Normant, Tetrahedron Lett. 27, 1039, 1043 (1986)
2. Copper and zinc mixed gem-dimetallic organic compounds. Synthesis and reactivity. Part 3 ; Reactivity of the 1-lithio-1-zincaalkenes. A formal regiospecific addition of allylzinc bromide to alkenes. Part 4.
   P. Knochel and J.F. Normant, submitted for publication in Tetrahedron Letters
3. The E:Z ratio of the octenyllithium 4b and the octenylmagnesium bromide 4a used are respectively 82:18 and 88:12.
4. G. Cahiez, D. Bernard and J.F. Normant, Synthesis (1976), 245.
5. G. Zweifel and C.C. Whitney, J. Amer. Chem. Soc. 89, 2753 (1967).
6. The determination of the relative stereochemistry of the two diastereoisomers is currently studied in our laboratory.
7. All the experiments were performed on a 10 or 20 mmol scale. The yields indicated are those of isolated pure compounds which show correct spectroscopic data (I.R., ^{1}H NMR and ^{13}C NMR)
8. T.H. Chan and K. Koumaglo, J. Organomet. Chem. 285, 109 (1985)
9. D.A. Evans, G.C. Andrews and B. Buckwalter, J. Amer. Chem. Soc. 96, 5560 (1974)
10. In addition to 9, the vinylcyclopropane 13, which is obtained as a pure diastereoisomer, is also isolated in 8% yield if the organometallic 4a is used, whereas with the alkenyllithium 4b no vinylcyclopropane is detected.
11. K. Oshima, H. Takahashi, H. Yamamoto and H. Nozaki, J. Amer. Chem. Soc. 95, 2693 (1973).
12. For other synthesis of cyclopropane derivatives using gem-dimetallic reagents see : Y. Frangin and M. Gaudemar, C.R. Acad. Sc. Paris, 278, 885 (1974) ; F. Bernadou and L. Miginiac, C.R. Acad. Sc. Paris, 280, 1473 (1975) ; F. Bernadou and L. Miginiac, J. Organomet. Chem., 125, 23 (1977).

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