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STEREOCHEMISTRY OF THE $Pd(PPh_3)_4$-CATALYZED CONVERSION OF 1-BROMOALLENES INTO PHENYL SUBSTITUTED ALLENES.

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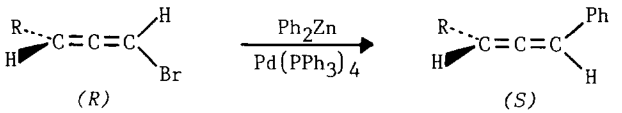
Summary: *1-Bromoallenes* **1** *are converted into the phenyl substituted allenes* **2** *with inversion of configuration in the allenyl moiety by reaction with* Ph_2Zn *using* $Pd(PPh_3)_4$ *as catalyst.*

A number of years ago it was found that 1-bromoallenes are converted into alkylallenes by lithium dialkylcuprates.[1] In a recent study it was reported that such reactions may occur with inversion of configuration in the allenyl moiety.[2]

This paper discloses the stereochemical course of the $Pd(PPh_3)_4$-catalyzed conversion of 1-bromoallenes by Ph_2Zn. Previous work in these laboratories showed that 1-bromoallenes react with organozinc compounds to give substituted allenes in excellent yields when $Pd(PPh_3)_4$ is applied as catalyst.[3] Similar to the Pd(0)-catalyzed conversion of vinylic halides by organometallic species[4] we expected to find retention of configuration for our reaction.

For our study we prepared two optically active 3-substituted-1-bromoallenes, viz, (-)-**1a** and (-)-**1b**, following the procedure which we have described elsewhere.[5] The absolute configuration of both allenes is *R*.[6] Addition of (-)-**1** (3.0 mmol), at -60°C, to a stirred solution of pure Ph_2Zn (2.0 mmol) and the catalyst $Pd(PPh_3)_4$ (0.12 mmol) in THF (21 ml), followed by stirring the resulting mixture during 5 min at 0°C (**1a**) or during 15 min at 20°C (**1b**), resulted in excellent conversions (>98%) of (-)-**1** into the *dextrorotatory* phenyl substituted allenes **2**. The configuration of both allenes **2** is therefore *S*.[6] This means that the conversions of **1a** and **1b** into **2a** and **2b**, respectively, proceed with *inversion* of configuration.[7]

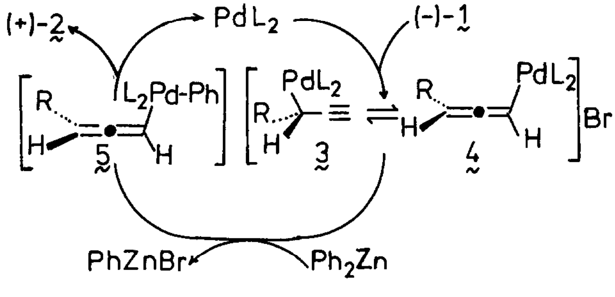


(-)-**1a**: R = Ph
(-)-**1b**: R = *t*-Bu

(+)-**2a**: R = Ph
(+)-**2b**: R = *t*-Bu

The $[\alpha]_D^{20}$-values (EtOH) for **2a** and **2b** amounted to +985° and+268°, respectively. When it is assumed that the values for optically pure **2a**[8a] and **2b**[8b] are +1137° and +370°, respectively, the enantiomeric excess of (*S*)-**2a** amounts to 87% and that of (*S*)-**2b** to 73%.

The obtained stereochemical result can be rationalized as follows. In the first step of the reaction the catalytically active species Pd$(PPh_3)_2$[9] will induce an *anti* S_N2'-reaction in allene **1** to give the 2-propynylic palladium(II) intermediate **3** (see Scheme). A suprafacial [1.3]-shift in **3** then produces the allenic compound **4**. Reaction of compound **4** with Ph_2Zn gives the diorganopalladium(II) species **5**.[10] This process will proceed with retention of configuration in the allenyl moiety. Subsequent reductive elimination of (+)-**2** from complex **5**, also here with retention of configuration in the the allenyl group, completes the catalytic cycle. This rationale is similar to that proposed by us for the reaction of 2-propynylic esters with organozinc reagents in the presence of the same catalyst.[11]



Scheme

References and notes

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3. K. Ruitenberg, H. Kleijn, H. Westmijze, J. Meijer and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 101 (1982) 405.
4. For instance, see A.O. King, N. Okukado and E. Negishi, J. Chem. Soc., Chem. Commun., 683 (1977).
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6. See ref.5 and: C.J. Elsevier, H.J.T. Bos and P. Vermeer, J. Org. Chem., 49 (1984) 379.
7. $[\alpha]_D^{20}$-values (EtOH): -1235° for (*R*)-**1a** and -230° for (*R*)-**1b**. The % ee is not known but is probably very high (cf. ref.5 and 6).
8. (a) P. Rossi and P. Diversi, Synthesis, 25 (1973); (b) C.J. Elsevier, Ph. D. Thesis, Utrecht (1984).
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10. The PhZnBr, which is liberated, can participate in another cycle.
11. C.J. Elsevier, P.M. Stehouwer, H. Westmijze and P. Vermeer, J. Org. Chem., 48 (1983) 1103.

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