Pergamon

Tetrahedron Letters 40 (1999) 6567–6568

TETRAHEDRON LETTERS

Catalytic Asymmetric Hydrosilylation of Butadiynes: A New Synthesis of Optically Active Allenes

Annegret Tillack*, Dirk Michalik, Cornelia Koy and Manfred Michalik

Institut für Organische Katalyseforschung an der Universität Rostock e.V., Buchbinderstr. 5-6, D-18055 Rostock, Germany.

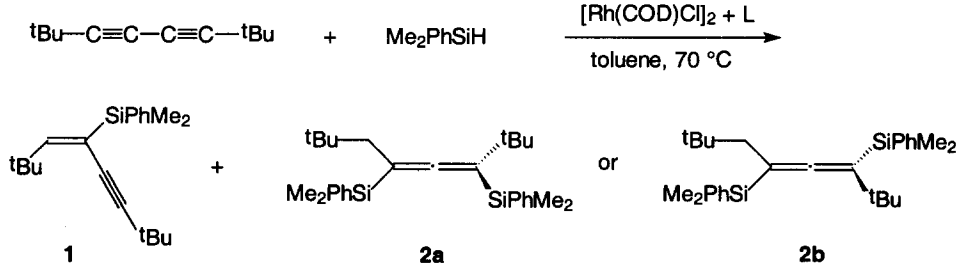
Received 28 June 1999; accepted 15 July 1999

Dedicated to Professor Rüdiger Selke on the occasion of his 65th birthday

Abstract: The Rh-catalyzed hydrosilylation of butadiynes to chiral allenes in the presence of chiral phosphine ligands is described. For the first time an enantiomeric excess of 22% was achieved using PPM ligand ((2*S*,4*S*)-(-)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine).

Keywords: *Asymmetric hydrosilylation; Butadiynes; Chiral allenes; Rhodium phosphine complexes.*

Allenes are of great importance in organic chemistry, their synthesis and application are described in detail in the literature.[1] Many syntheses of chiral allenes of high enantiomeric purity start from chiral precursors, but relatively few syntheses are known in which the chirality is induced by a chiral catalyst.[2] To the best of our knowledge the palladium-catalyzed cross-coupling reaction of 4,4-dimethyl-1,2-pentadiene and iodobenzene in the presence of chiral phosphine ligands is the only example of a transition metal catalyzed enantioselective allene synthesis.[3] Here we report on a further example of a transition metal catalyzed synthesis of chiral allenes *via* asymmetric hydrosilylation. In general, allenes can be synthesized in high yields by hydrosilylation of butadiynes in the presence of achiral catalysts such as Rh-, Pt-[4] and Ni-complexes.[5] Among the various possible catalysts chiral Rh-phosphine complexes turned out to be the best catalysts so far for the asymmetric hydrosilylation of butadiynes (Scheme 1).



L = chiral phosphine ligands

Scheme 1

As a model reaction the hydrosilylation of 2,2,7,7-tetramethyl-3,5-octadiyne with dimethylphenylsilane was

0040-4039/99/$ - see front matter
PII: S0040-4039(99)01403-3

studied. Depending on the reaction conditions the hydrosilylation gives two reaction products, the monohydrosilylation product **1** and the dihydrosilylation product (allene) **2**. With diphenylsilane we observed the formation of disilane under hydrogen elimination, but no reaction to allene **2**. The following chiral ligands were tested with $[Rh(COD)Cl]_2$ *in situ* as catalysts: monophosphine ((*S*)-NMDPP[6]) and chelate diphosphine ligands ((2*S*,3*S*)-Norphos,[6] (2*S*,3*S*)-Chiraphos,[6] (2*S*,3*S*,4*S*,5*S*)-Rophos-benzene,[7] (3*R*,4*R*)-Pyrphos,[6] (2*S*,3*S*)-BDPP,[6] (4*R*,5*R*)-DIOP,[6] (*R*)-BINAP,[6] (2*S*,4*S*)-BPPM,[6] (2*S*,4*S*)-PPM,[6] (3*R*,4*R*)-POP-BZ[6]). The results are given in Table 1. Monophosphine and five- and six-membered chelates favour the formation of **1**. Allene **2** is obtained by using ligands forming seven-membered chelates. For the first time an enantiomeric excess of 22% was obtained in the presence of ligand PPM. In contrast to PPM no enantioselection was obtained with BPPM, a ligand with an electron-withdrawing substituent at the pyrrolidine nitrogen atom. The role of this *N*-substituents must still be clarified. The yield of allene was drastically lowered, if THF or $CHCl_3$ are used as solvents compared to toluene. In contrast, an addition of Et_3N increased the yield up to 41%, but the extent of chiral induction was not affected. In conclusion, we developed a new catalytic asymmetric synthesis of allenes. Further work to elaborate scope and limitation of this method as well as to optimize the enantioselectivity is in progress.

Table 1. Results of catalytic hydrosilylation[a] of $^tBu–C{\equiv}C–C{\equiv}C–^tBu$ with Me_2PhSiH

Entry	Ligand	Yield[b] [%]		*ee*[c] [%] (Conf.)[d]
		1	**2**	
1	(3*R*, 4*R*)-Pyrphos	67	4	n. d.
2	(4*R*,5*R*)-DIOP	53	25	rac.
3	(*R*)-BINAP	41	30	rac.
4	(2*S*,4*S*)-BPPM	56	21	rac.
5	(2*S*,4*S*)-PPM	66	27	22
6	(*R*,*R*)-POP-BZ	56	35	5

a) General procedure: under inert atmosphere, a mixture of 1mmol of butadiyne, 0.02 mmol of the ligand and 0.01 mmol of $[Rh(COD)Cl]_2$ were dissolved in 1 ml of toluene and stirred for 10 min at r. t.. Then 4 mmol of silane were added and the mixture was stirred for 24 h at 70 °C. Afterwards toluene and silane were removed *in vacuo*. The residue was purified by column chromatography (eluent: *n*-hexane; silica gel 60 (Merck)). b) The yield was determined by GC using an internal standard (dodecane). c) The *ee* values were determined by NMR using chiral lanthanide shift reagents ($Yb(hfc)_3$/Ag(fod)). d) The absolute configuration was not determined; optical rotation sign of crude product: (–) (THF).

Acknowledgement. The authors thank the Deutsche Forschungsgemeinschaft for financial support, Prof. Dr. M. Beller for helpful discussions, Dr. V. Tararov and Dr. J. Holz for a gift of ligand POP-Bz and Rophos, resp., Mrs. Ch. Mewes and Mrs. B. Harzfeld for technical assistance.

References

1. a) D. J. Pasto, *Tetrahedron* **1984**, *40*, 2805; b) H. F.Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, 1984; c) C. Bruneau, P. H. Dixneuf, *Allenes and Cumulenes*, in Comprehensive Organic Functional Group Transformations, Eds. A. R. Katritzky, O. Meth-Cohn, C. W. Rees, Pergamon, Oxford, 1995, Vol. 1, Ch. 20; d) I. Ikeda, K. Honda, E. Osawa, M. Shiro, M. Aso, K. Kanematsu, *J. Org. Chem.* **1996**, *61*, 2031; e) R. Lunkwitz, K. Zab, C. Tschierske, *J. Prakt. Chem.-Chem. Ztg.* **1998**, *340*, 662; f) M. Franck-Neumann, D. Martina, D. Neff, *Tetrahedron: Asymmetry* **1998**, *9*, 697.
2. C. J. Elsevier, in Houben-Weyl, series Methods of Organic Chemistry (Eds. G. Helmchen; R.W. Hoffmann; J. Mulzer; E. Schaumann); Thieme Stuttgart, 1995, Vol. E21a, p. 537.
3. W. de Graaf, J. Boersma, G. van Knoten, C. J. Elsevier, *J. Organomet. Chem.* **1989**, *378*, 115.
4. a) T. Kusumoto, T. Hiyama, *Chem. Lett.* **1985**, 1405; b) T. Kusumoto, K. Ando, T. Hiyama, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1280.
5. A. Tillack, S. Pulst, W. Baumann, H. Baudisch, K. Kortus, U. Rosenthal, *J. Organomet. Chem.* **1997**, *532*, 117.
6. H. Brunner, W. Zettlmeier, *Handbook of Enantioselective Catalysis*, VCH Weinheim, 1993,Vol. II and references cited therein.
7. J. Holz, M. Quirmbach, U. Schmidt, D. Heller, R. Stürmer, A. Börner, *J. Org. Chem.* **1998**, *63*, 8031.