Tetrahedron 68 (2012) 1581–1589

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Phosphites and diamidophosphites based on mono-ethers of BINOL: a comparison of enantioselectivity in asymmetric catalytic reactions

Konstantin N. Gavrilov [a,*], Sergey V. Zheglov [a], Mariya N. Gavrilova [a], Ivan M. Novikov [a], Marina G. Maksimova [a], Nikolay N. Groshkin [a], Eugenie A. Rastorguev [b], Vadim A. Davankov [b]

[a] Department of Chemistry, Ryazan State University, 46 Svoboda Street, 390000 Ryazan, Russian Federation
[b] Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 27 September 2011
Received in revised form 8 November 2011
Accepted 28 November 2011
Available online 6 December 2011

Keywords:
Asymmetric allylic substitution
Palladium
Asymmetric addition
Rhodium
Phosphites
Diamidophosphites

ABSTRACT

Novel *P*-monodentate phosphite-type ligands have been synthesized in one step from BINOL monotosylate and BINOL mono-(−)-menthylcarbonate. The use of these ligands provides up to 96% ee in Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate and up to 99% ee in Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone. The influence of the structural modules such as the nature of phosphorus-containing ring or exocyclic substituent on the enantioselectivity is discussed.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Asymmetric metal complex catalysis is one of the most effective and environmentally safe methods for the synthesis of enantiopure organic and heteroorganic compounds, as reflected by the many publications in this field and the award of the Nobel Prize in 2001 to W. S. Knowles, R. Noyori, and K. B. Sharpless. In addition to the well-known application in pharmaceutical chemistry, this method is successfully used in the synthesis of enantiopure fragrance compounds, plant protection chemicals, polymers, and liquid crystals.[1] To achieve the highest levels of reactivity and selectivity in catalytic enantioselective reactions, several reaction parameters must be optimized, the most crucial of which is perhaps the design of appropriate chiral ligands, among which phosphorus-containing compounds are worth noting.[1f,2] Since the early 1970s, an impressive number of chiral phosphorus-based ligands have been applied in many asymmetric catalytic reactions.[1–3] Nevertheless, only a handful of them (so-called privileged ligands), rooted in a few core structures, can be regarded a truly successful in demonstrating proficiency in various mechanistically unrelated reactions.[4] Therefore, the tuning of existing ligands and/or the development of novel chiral ligands with improved performance continue to attract the interest of synthetic chemists.[1b,5]

From a practical point of view, air-stable, inexpensive, and easily accessible ligands are highly desirable.[6] Optically active phosphite-type compounds completely satisfy these criteria. Indeed, various P–O and/or P–N bond containing phosphorus ligands may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. Another advantage of phosphite-type ligands is that they are less sensitive to air and other oxidizing agents than phosphines. Hence, this makes it possible to develop protocols for the whole process, including the ligand synthesis, that do not necessitate the use of a glove box. Furthermore, they are amenable to parallel synthesis, even in solid phase synthesis. Such key advantages allow synthesis and screening of extensive libraries of chiral ligands aiming at high activities and selectivities for each particular reaction. In addition, phosphite-type ligands are characterized by pronounced π-acidity and low cost. It should be noted, that phosphites are rather prone to decomposition reactions such as hydrolysis or alcoholysis but, in many instances, these side reactions can be suppressed when bulky ligands (especially with aryl substituents) are used.[1f,2,7]

Herein, we report the synthesis of a small series of novel phosphite-type ligands containing dissymmetric monoprotected BINOL fragments and their evaluation in Pd-catalyzed asymmetric allylation and Rh-catalyzed asymmetric addition. Note, that

* Corresponding author. Tel.: +7 4912 280580; fax: +7 4912 281435; e-mail address: k.gavrilov@rsu.edu.ru (K.N. Gavrilov).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.11.092

enantioselective Pd-catalyzed allylic substitution has emerged as a powerful synthetic tool, which is tolerant of various functional groups in the substrate and operates with a wide range of *C*-, *N*-, *O*-, *S*- and *P*-nucleophiles. As consequence, Pd-catalyzed allylic substitution is a novel and highly efficient strategy in the total synthesis of enantiopure natural and unnatural products.[1c,8] The asymmetric conjugate addition of arylboronic acids to α,β-unsaturated carbonyl compounds constitutes nowadays a very efficient method for the stereoselective construction of C–C bonds.[9] On the other hand, both catalytic processes are a common benchmark tests for initial ligand screening. From a functional point of view, the reached ees are the simplest indexes for evaluating new chiral ligands.[6,8g,h]

The steric and electronic properties of the chiral ligands have a tremendous effect on the performance of asymmetric metal catalysts. A well-conceived stereoselector should possess one or more structural features that may be varied readily in a systematic fashion, in order to optimize the design for a given purpose. A design is informative to the extent that variations in the ligand features can be correlated to changes in the reactivity or selectivity of the catalyst. In particular, the nature of phosphocycle and the stereochemistry of coordinating atom are crucial features for obtaining satisfactory asymmetric induction.[1b,3,4,5c,d] Our novel phosphite-type ligands **4**, **5** give some new examples in this field.

2. Results and discussion

The preparation of each ligand **4**, **5** was a convenient single-step operation (Scheme 1).

The appropriate enantiomer of monoacylated BINOL derivatives **1a** or **1b** reacted smoothly in toluene in the presence of Et_3N as a HCl scavenger and DMAP as catalyst with phosphorylating reagents **2** or **3**, whose syntheses have been described in the literature.[10,11] In turn, (S_a)- and (R_a)-2-hydroxy-2′-(−)-menthyl-1,1′-binaphthyl carbonate (S_a)-**1a** and (R_a)-**1a**, (S_a)- and (R_a)-2-hydroxy-2′-tosyloxy-1,1′-binaphthyl (S_a)-**1b** and (R_a)-**1b** were easily obtained by direct interaction between the corresponding enantiomer of BINOL and (−)-menthyl chloroformate or tosyl chloride.[12,13] Compounds **4** and **5** were obtained in moderate to good yields (66–82%), reflecting their stability during the workup and subsequent chromatographic purification. They also can be stored in the solid form under dry conditions at room temperature over several months without any degradation. Ligands **4** and **5** were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI TOF/TOF mass spectrometry as well as by elemental analysis.

All ligands are readily available and can be prepared on a gram scale. Indeed, the phosphorylating agent **2** can easily be synthesized in high yield from readily accessible (*S*)-glutamic acid anilide.[14] Furthermore, BINOL is commercially available in both enantiomeric forms and is one of the cheapest chiral auxiliaries currently on the market. As stated above, its transformation into derivatives **1a** and **1b** (as well as into phosphorylating agent **3**) requires only one step.

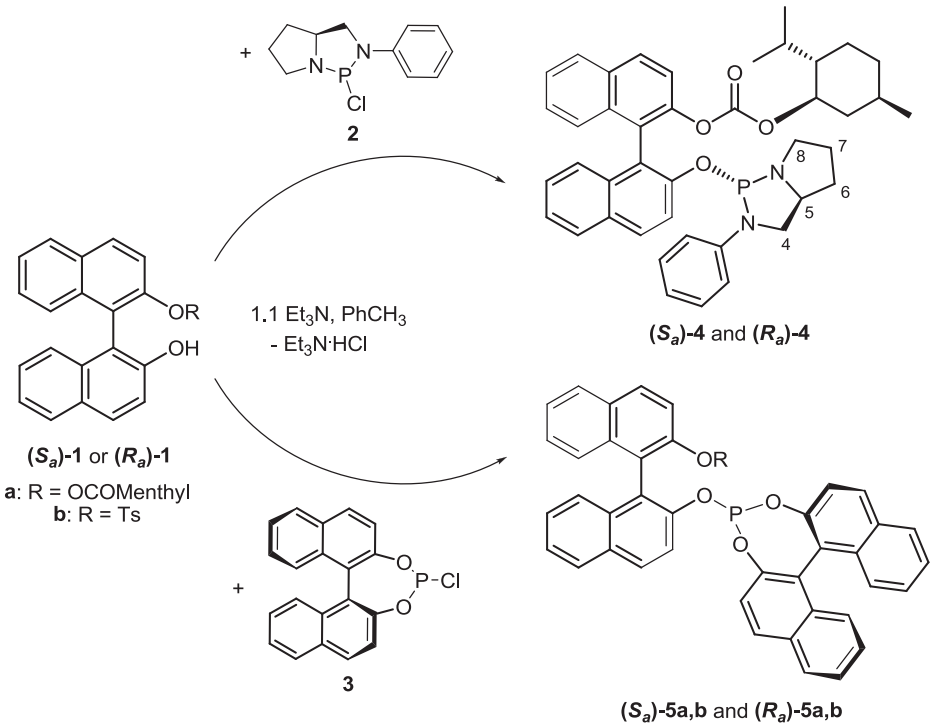
The ^{31}P NMR spectroscopic data for compounds **4** and **5** are summarized in Table 1.

Table 1
^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg.) of ligands (S_a)-**4**, (R_a)-**4**, (S_a)-**5a**,**b**, and (R_a)-**5a**,**b**

Ligand		δ_P	θ
(S_a)-**4**	(76%)[a]	127.1	153
	(24%)	118.9	
(R_a)-**4**	(78%)	125.1	165
	(22%)	118.2	
(S_a)-**5a**		143.6	152
(R_a)-**5a**		145.7	149
(S_a)-**5b**		146.3	171
(R_a)-**5b**		145.5	142

[a] Percentage of P*-epimers.

Diamidophosphites (S_a)-**4** and (R_a)-**4** are mixtures of epimers with respect to the phosphorus stereocentre and contain 76% and 78% of the major P*-epimers, respectively. The major epimers of (S_a)-**4** and (R_a)-**4** have the *P**-stereocentres with the (*R*) configuration. Indeed, the ^{13}C NMR spectra of these compounds are characterized



Scheme 1. Synthesis of diamidophosphites (S_a)-**4**, (R_a)-**4**, and phosphites (S_a)-**5a**,**b**; (R_a)-**5a**,**b**.

Download English Version:

https://daneshyari.com/en/article/5219039

Download Persian Version:

https://daneshyari.com/article/5219039

Daneshyari.com