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Asymmetric catalysis as a method for the synthesis of chiral organophosphorus compounds

Oleg I. Kolodiazhnyi *, Valery P. Kukhar, Anastasy O. Kolodiazhna

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Murmanska Str., 1, Kiev, Ukraine

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ABSTRACT

This review discusses methods for the metallo-, organo- and biocatalytic asymmetric synthesis of chiral organophosphorus compounds with many applications in stereoselective synthesis with references to updated literature reports as well as the author's original research. Asymmetric catalytic hydrogenation and reduction with chiral organometallic complexes, together with actively used asymmetric organocatalytic versions of various reactions enable us to synthesize chiral organophosphonates and phosphinates with high enantioselectivity and purity. Asymmetric catalysis is also an effective tool to realize some classic reactions of phosphorus chemistry in a stereospecific manner.

Contents

Abbreviations: Ac, acetyl; An, anisyl; Ar, aryl; BINOL, 1,10-bi-2-naphthol; Bn, benzyl; Boc, *tert*-butoxycarbonyl; Bu, butyl; Bz, benzoyl; cat, catalyst; Cbz, benzyloxycarbonyl; COD, cyclooctadiene; conv, conversion; Cy, cyclohexyl; DABCO, 1,4-diazabicyclo[2.2.2]octane; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; de, diastereomeric excess; DKR, dynamic kinetic resolution; DMF, *N*,*N*-dimethylformamide; dmpe, 1,2-bis(dimethylphosphino)ethane; DMSO, dimethylsulfoxide; ee, enantiomeric excess; Et, ethyl; Fmoc, 9-fluorenylmethoxycarbonyl; Fu, furanyl; Hex, hexyl; L, Lig, ligand; MBD, 4-methoxybenzoic acid; Me, methyl; Mes, mesyl; Mnt, (1*R*,2*S*,5*R*)-menthyl; MTBE, methyl *tert*-butyl ether; nphth, naphthyl; Oct, octyl; Pent, pentyl; Ph, phenyl; Piv, pivaloyl; PMHS, polymethylhydrosiloxane; PMP, *p*-methoxyphenyl; PNBA, *p*-nitrobenzoic acid; Pr, propyl; py, pyridyl; SP, sparteine; Q, quinine; QN, quinidine; HQN, hydroquinidine; TADDOL, α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol; TBAB, tetra-*n*-butylammonium bromide; TBDPS, *tert*-butyldiphenylsilyl; TBS, *tert*-butyldimethylsilyl; THF, tetrahydrofuran; Tf, trifluoromethanesulfonyl; TFA, trifluoroacetic acid; TMS, trimethylsilyl; Tl, tolyl; TPP, tetraphenylporphyrin; Ts, 4-toluenesulfonyl (tosyl).

* Corresponding author. Tel.: +380 44 573 2555; fax: +380 44 5732552.
E-mail address: olegkol321@rambler.ru (O.I. Kolodiazhnyi).

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1. Introduction

Chiral phosphorus compounds play an important role in many areas of science including biologically active pharmaceuticals, agrochemicals, and ligands for transition metal complexes. Recent years have seen a steady growth in the use of chiral organophosphorus catalysts in asymmetric synthesis. Complexes with transition metals containing PAMP, DIPAMP, DIOP, CHIRAPHOS ligands are widely used for the asymmetric formation of C–H and C–C bonds. Many methods can be used to prepare enantiomerically pure organophosphorus compounds including classical resolution via diastereoisomers, chemical kinetic resolution, enzymatic resolution, chromatographic resolution, and asymmetric catalysis. Asymmetric synthesis and asymmetric catalysis have been, and remain, a primary research field of chemistry. Therefore, methods for the asymmetric synthesis of organophosphorus compounds have been studied extensively in many academic and industrial research laboratories.[2–4] Over the last few years, great success has been achieved in the asymmetric synthesis of organophosphorus compounds, primarily with phosphine ligands for catalyzed asymmetric hydrogenation reactions, and many articles devoted to the synthesis of chiral organophosphorus compounds have been published.[1–4]

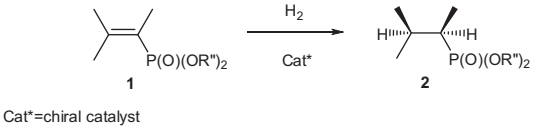
Various asymmetric metallocomplexes, organo- and biocatalysis, have been devoted to the synthesis of separate classes of organophosphorus bonds. The present review discusses all types of asymmetric catalysis of organophosphorus compounds and compares their advantages.[1–7] The review describes the asymmetric catalytic hydrogenation, reduction of unsaturated compounds, oxidation, electrophilic and nucleophilic substitution at the phosphorus atom, the addition of phosphorous nucleophiles, cycloaddition reactions, and others. Currently, asymmetric catalysis is one of the most convenient methods for the synthesis of chiral organophosphorus compounds. Therefore, it is interesting to analyze the data dedicated to the asymmetric synthesis of chiral organophosphorus compounds published over the last 15 years.[5]

2. Asymmetric hydrogenation

Homogeneous asymmetric hydrogenation with chiral complexes of transition metals is one of the most important industrial methods for the preparation of enantiomerically pure organic molecules. Asymmetric hydrogenation of prochiral aminophosphonates, ketophosphonates, and ketoiminophosphonates is one of the most effective, practical, and economic synthetic methods for the preparation of chiral organophosphorus compounds.[2] Various chiral complexes of transition metals, bearing chiral phosphine ligands, have been used as catalysts for the asymmetric hydrogenation of unsaturated phosphorus compounds. The asymmetric catalytic hydrogenation of phosphonates containing C=C, C=O, or C=N bonds, has used rhodium, ruthenium, and iridium complexes with chiral bis-phosphine ligands.[8,9] Nojori first published the application of BINAP-Ru catalysts for the asymmetric hydrogenation of ketophosphonates.[9–11]

2.1. Asymmetric hydrogenation of alkene phosphonates

Asymmetric catalytic hydrogenation of unsaturated phosphonates is widely used in the synthesis of aminophosphonates and aminophosphonic acids of biological interest (Scheme 1).[12–33] Some examples of the most often used ligands for hydrogenation of unsaturated phosphonates are shown in Scheme 2.



Scheme 1. Asymmetric catalytic hydrogenation of unsaturated phosphonates.

The first work devoted to the asymmetric synthesis of aminophosphonates by catalytic hydrogenation of unsaturated phosphonates, was published approximately thirty years ago. Schollkopf et al.[12] in 1985 reported asymmetric hydrogenation of *N*-[1-(dimethoxyphosphoryl)-ethenyl]formamide, using a rhodium catalyst with (+)-DIOP **10** chiral ligand to afford the (1-aminoethyl)phosphonate L-**19** in good yields and 76% ee enantioselectivity. The initially formed formamide L-**19** was hydrolyzed with conc. hydrochloric acid to give the aminophosphonic acid L-**20**. Crystallization from water/methanol increased the enantiomeric purity of L-**20** up to 93% ee (Scheme 3).

The hydrogenation of α-enamidophosphonates has attracted the interest of several groups as a method for the synthesis of chiral aminophosphonates and a number of articles have been published on this subject. Oehme et al.[13] reported that chiral Rh(I) complexes with BPPM ligands **6** or PROPRAPHOS **7** are active catalysts for the asymmetric hydrogenation of (*E*)-phenylenamidophosphonates displaying high reaction rates and relatively high stereoselectivities. For example, the hydrogenation of amidovinylphosphonates **21a**,**b** catalyzed by the BPPM(**6**)/Rh complex, afforded α-aminophosphonates **22a**,**b** with 96% ee, and since PROPRAPHOS **7** is available in both configurations, (*R*)- and (*S*)-α-aminophosphonic acid esters **22c** could be obtained with enantioselectivities of 88–96% ee (Scheme 4).

Burk et al.[14] proposed cationic rhodium complexes of C_2 symmetric DuPHOS **4a**,**b** and BPE **5a**,**b** ligands as effective catalysts for the asymmetric hydrogenation of *N*-aryl and *N*-benzyloxycarbonyl-enamido phosphonates **23** (Scheme 4). The catalyst Et-DuPHOS/Rh(COD) provided good enantioselectivity for both types of