Tetrahedron Letters 55 (2014) 713–715

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Bromamine-T as an efficient amine source for Sharpless asymmetric aminohydroxylation of olefins

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ARTICLE INFO

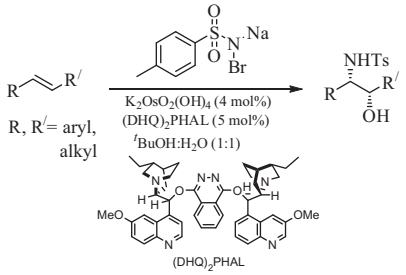
Article history:
Received 16 September 2013
Revised 29 November 2013
Accepted 2 December 2013
Available online 8 December 2013

Keywords:
Sharpless asymmetric aminohydroxylation
Bromamine-T
Potassium osmate
$(DHQ)_2PHAL$
Olefin

ABSTRACT

Asymmetric aminohydroxylation of various olefins was carried out using bromamine-T as nitrogen source in the presence of $(DHQ)_2PHAL$ ligand. The new nitrogen source has been found to be effective in terms of yield and reaction time. The optical purities of the products could be obtained with up to 99% ee.

Vicinal amino alcohols are very important structural motif in synthetic chemistry due to its occurrence in natural products, chiral reagents, and asymmetric catalysts. While there are a wide variety of synthetic routes to this functional group,[1] Sharpless asymmetric aminohydroxylation (AA) reaction remains the most powerful method for the stereospecific generation of vicinal amino alcohols from alkenes.[2] Since the discovery of the AA method by Sharpless and co-workers,[3] there have been a number of reports for improvement of the procedure,[2] The AA process has been successfully performed with a variety of nitrogen sources, including sulfonamides,[3,4] amides,[5] carbamates, [6] and aminoheterocycles.[7] Most N-halogenated oxidants used in the AA are prepared in situ by N-chlorination with *tert*-butyl hypochlorite in the presence of a base, however some of them are commercially unavailable. Recently Luxenburger and co-workers[8] and Castle group[9] had reported a base-free aminohydroxylation of substituted and functionalized alkene using benzoyloxycarbamates as the nitrogen source. Although it is possible to achieve excellent enantioselectivity in aminohydroxylation process by suitable choice of ligands, setting of a particular regioselectivity remains a challenging task, particularly for unsymmetrical alkene. The problem of regioselectivity is a complex one and many factors have been invoked to explain observed trends, such as alkene substitution, alkene polarization, ligand–substrate interactions, steric and electronic contributions of the ligand, and hydrophobic effects due to the solvent etc.[10] These are often mutually dependent on each other. Although development of tethered aminohydroxylation (TA)[11] gives secure regiochemistry, this reaction occurs without appreciable influence of chiral ligands and hence failed to give the same levels of enantioselectivity. Development of new nitrogen sources, new ligands, improved reaction conditions, and understanding of catalyst–substrate interactions have increased the scope and synthetic utility of the AA process. *N*-Bromo,*N*-sodio-*p*-toluenesulfonamide (bromamine-T) has been found to be superior to chloramines-T as nitrogen source for various organic transformations.[12] However, no study has been reported so far, on the use of bromamine-T for AA process. As a continuation of our work on asymmetric aminohydroxylation,[13] we report herein our experimental results on the use of bromamine-T as nitrogen source for the Sharpless's protocol (Scheme 1).



Scheme 1. Sharpless asymmetric aminohydroxylation using bromanine-T.

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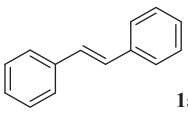
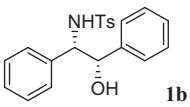
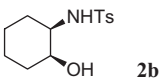
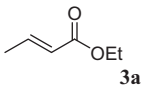
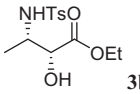
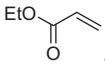
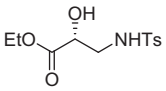
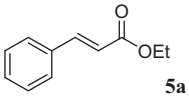
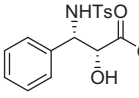
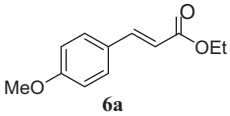
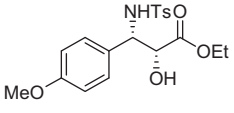
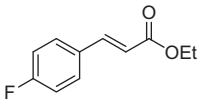
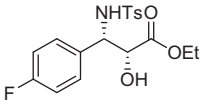
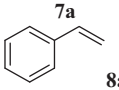
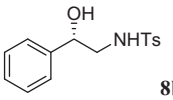
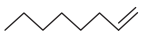
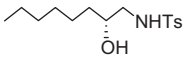
http://dx.doi.org/10.1016/j.tetlet.2013.12.002

Bromamine-T was prepared from chloramine-T following the literature procedure.[12a,14] We have evaluated the potential of the reagent using $(DHQ)_2PHAL$ ligand which is most widely used for AA process. Initially we have chosen *trans*-stilbene (Table 1, **1a**) as the model substrate to carry out the AA process following the experimental procedure identical to the original catalytic AA process.[3] When *trans*-stilbene was subjected to aminohydroxylation at room temperature,[15] occurrence of the reaction was indicated by a distinct color change from dark green to light yellow. The reaction was carried out by adding bromanine-T and $K_2OsO_2(OH)_4$ successively to a solution of $(DHQ)_2PHAL$ and *trans*-stilbene in a 1:1 mixture of ^tBuOH and H_2O at room temperature. After 2 h of reaction at room temperature, the reaction mixture was subjected to usual work-up procedure. Our preliminary analysis using TLC indicated the formation of single product. However, further analysis of the crude reaction mixture was not carried out using spectroscopy or HPLC. Finally, the crude product was purified using flash chromatography to get the pure amino alcohol. The reaction time (2 h) was found to be far better in comparison to that with chloramine-T (14 h).[3] Enantiomeric purity of the recrystallized product **1b** (Table 1) was found to be 62%, which was determined by HPLC method.

After gaining success in case of *trans*-stilbene, the process was extended to a variety of olefins which are summarized in Table 1. Cyclohexene (Table 1, **2a**) also responded very well under the reaction condition. α,β-Unsaturated esters such as cinnamates and acrylates underwent aminohydoxylation with excellent regioselectivity. These compounds produced β-amino regiomer predominantly with good yield and with high optical purity (up to 99% ee). However, ee of the aminohydroxylation product of ethyl-4-fluoro-cinnamate was found to be low (61%). Styrene (Table 1, **8a**) produced low optical yield (38% ee) under this reaction condition. Literature search revealed that aminohydroxylation of styrene using chloramine-T in the presence of cinchona alkaloid ligand has not been reported before. However, the use of *N*-sulfonyl-α,β-hydroxyamino acid based ligands and chloramine-T for aminohydroxylation of styrene resulted in poor yield as well as ee values.[4c] Later, Sharpless et al. found that the use of N-halo carbamates for similar substrates could produce aminoalcohols with high ee values.[6a] However yields were found to be low (≈60%) in this case.

We have further extended the process to 1-octene (Table 1, **9a**). Enantiomeric purity of the resulting product was found to be poor (40% ee) as determined by chiral HPLC analysis. The time requirement for the reaction in all cases was found to be better

Table 1
Catalytic asymmetric aminohydroxylation reaction with bromamine-T as the nitrogen source[a]

Entry	Substrate	Product	*T* (h)	Yield[b] (%)	ee[c]	$[\alpha]_D^{26}$[d]
1	 **1a**	 **1b**	2	60	62	−14.3
2	 **2a**	 **2b**	1	70	99	+ 2.1
3	 **3a**	 **3b**	2	60	99	−22.0
4	 **4a**	 **4b**	1.5	75	99	−3.1
5	 **5a**	 **5b**	2	70	99	−26.7
6	 **6a**	 **6b**	0.5	75	99	+28.5
7	 **7a**	 **7b**	1	72	61	+16.4
8	 **8a**	 **8b**	1	62	38	+28.6
9	 **9a**	 **9b**	1.5	72	40	+7.5

[a] Reactions were carried out in tBuOH/H_2O (1:1) using 4 mol % $K_2OsO_2(OH)_4$ and 5 mol % $(DHQ)_2PHAL$ ligand.
[b] Isolated yield.
[c] Enatiomeric excess of the recrystallized product was determined by HPLC.
[d] Specific rotation values with respect to recrystallized product except entry 9.

in comparison to the chloramine-T mediated aminohydroxylation process.[3] All the products were isolated with good yields (60–75%). All the products were recrystallized (except entry 9, Table 1) and enantiomeric purity was determined via HPLC analysis. Optical purities of corresponding aminoalcohols are comparable to those reported earlier.

In conclusion we have examined the suitability of bromamine-T for Sharpless asymmetric aminohydroxylation of olefins. The new nitrogen source is effective in terms of yield and reaction time of the process. The present method is highly regioselective and products are obtained with moderate to high optical purities. The present work had shown potentiality as new nitrogen source for the catalytic AA process.

Acknowledgments

Financial Support from DST (Grant No. SR/S1/OC-43/ 2011), India is gratefully acknowledged. A.J.B. thanks CSIR for senior research fellowship.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.12.002.

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15. *General experimental procedure for AA:* To a solution of $(DHQ)_2PHAL$ (0.039 g, 0.05 mmol, 5 mol %) in *t*BuOH (2 mL) and water (2 mL) in a round-bottomed flask were added alkene (1 mmol), bromamine-T (0.816 g, 3 mmol, 3 equiv), and $K_2OsO_2(OH)_4$ (0.014 g, 0.04 mmol, 4 mol %). Over the course of the reaction, the color changed from brown to deep green and then to yellow. After addition of aqueous sodium sulfite, the phases were separated and the aqueous phase was extracted with ethyl acetate. The extracts were washed with brine and dried over anhydrous sodium sulfate and concentrated to dryness to give the crude product. In some cases (entries 1, 2 and 6), the reaction became slurry, the products were isolated by filtration. Otherwise, the crude products were purified by flash column chromatography using petroleum ether and ethyl acetate as eluent.