

Synthesis of aziridines using new catalytic systems with bromamine-T as the nitrene source

Bhanu M. Chanda*, Renu Vyas, Sudhir S. Landge

Organic Chemistry Technology, National Chemical Laboratory, Pune 411008, India

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Abstract

Two new polymer based catalysts, one manganese derived and the other iron derived have been prepared and characterised and successfully applied in the aziridination reaction. For the first time aziridination with $H\beta$ in the absence of any metal catalyst has been carried out. The latter reaction is shown to give selectively the *trans* product in the case of substituted olefins. The results from preliminary studies on asymmetric aziridination with several naturally occurring alkaloids are also discussed.

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1. Introduction

Aziridines are important heterocyclic compounds as they form part of several natural products [1], mostly with biological activity. The shortest route to the aziridines is its direct preparation from olefins, which involves transition metal catalysed transfer of nitrogen atom [2]. We have recently developed [3] an improved process for aziridination of olefins with Bromamine-T. However, heterogeneous aziridination is not well studied. In this paper, we present our results of heterogeneous aziridination of alkenes with new catalytic systems as well as with zeolite $H\beta$. Three pioneering developments in catalytic asymmetric aziridination include that of Evans et al. who used bis(oxazoline)–copper complex as chiral catalyst for the enantioselective aziridination of olefins [4]. Asymmetric aziridination of styrene with (diimine) copper (I) Schiff bases as catalysts was performed by Jacobsen et al. [5] and Masamune and Lowenthal [6] achieved enantioselective aziridination with modified bisoxazoline ligand. Herein, we present our results of asymmetric aziridination with naturally occurring alkaloids.

2. Experimental

The solvents were purified and dried as per standard procedures. The polymeric material used for the preparation of the catalysts was obtained from Ion Exchange (India) and the natural alkaloids were purchased from Aldrich. Bromamine-T was prepared as per literature method [3]. All the spectral data were recorded on standard instruments.

2.1. Polymer supported catalysts

In the present investigations a new chelated manganese metal complex on a polymer support [7] as well as a new iron complex on a polymer support have been well characterised and successfully applied in the aziridination of alkenes with Bromamine-T [8,11].

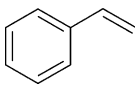
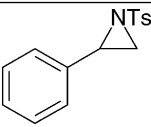
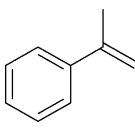
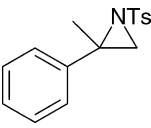
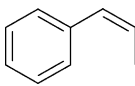
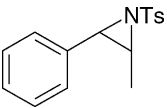



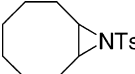
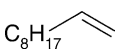
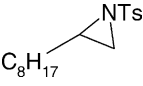
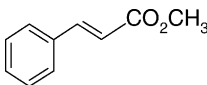
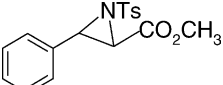
2.2. Synthesis and characterization of the two new catalysts

Preparation and properties of the new iron catalyst is described in detail elsewhere [11]. The route followed for the manganese catalyst is as shown. (Scheme 1). The polymer supported iron complex was synthesised in non-aqueous

* Corresponding author. Fax: +91 20 589 3614.

E-mail address: bhanu@dalton.ncl.res.in (B.M. Chanda).

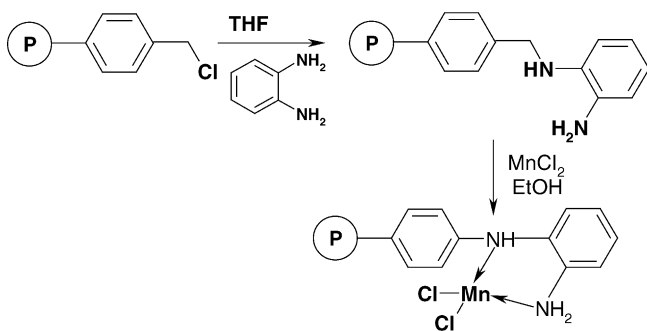
Table 1
Catalytic aziridination of olefins with Mn and Fe polymer catalysts

Entry	Substrate	Product	Yield (%) ^a	
			With Mn catalyst	With Fe catalyst
1			42	57
2			73	66
3			–	75
4			28	46
5			70	60
6	C_8H_{17} 		60	20
7			–	NR (RT), 30 (MW)

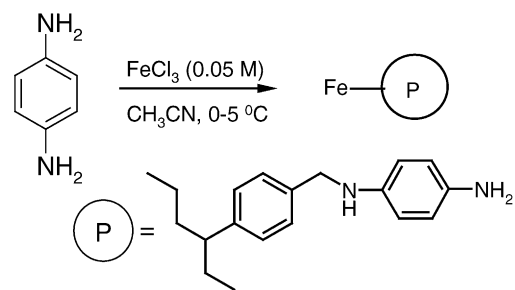
^a Isolated yield; NR: no reaction; MW: microwave.

medium starting from *p*-phenylene diamine (Scheme 2). Styrene was converted to the corresponding aziridine in high yield. The results obtained from both these catalysts are given in Table 1.

Zeolite beta is high silica, large-pore crystalline aluminosilicate material [9]. A single report [10] of heterogeneous aziridination using Cu exchanged HY zeolite with $PhI = NTs$ as the source of nitrogen is available. In the present work, aziridination of styrene using $H\beta$ (500 mg, 10% (w/w)) in the absence of any metal catalyst (Scheme 3) gave the product in good yield. Several olefins were subjected to aziridination in a similar fashion (Table 2).



Scheme 1.

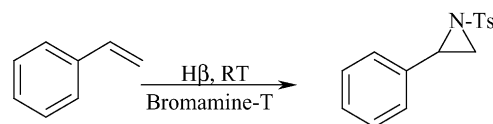


Scheme 2.

2.3. Aziridination of olefins

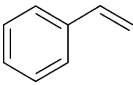
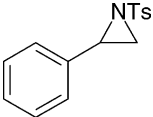
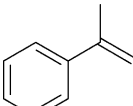
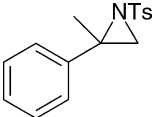

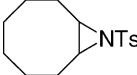

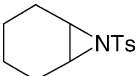
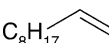
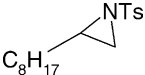
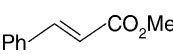
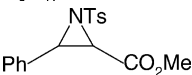
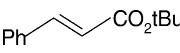
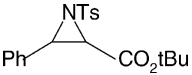
2.3.1. A typical procedure for the aziridination of olefins

Styrene (0.10 ml; 2.0 mmol), bromamine-T (0.10 g; 0.4 mmol), and the catalyst (0.10 g) along with activated powdered molecular sieves (0.05 g) in dry acetonitrile (5 ml)

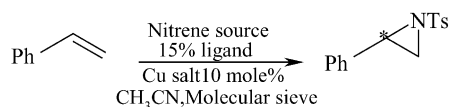


Scheme 3.

Table 2
H β catalysed aziridination of olefins

Entry	Substrate	Product	Yield (%) ^a	Temperature (°C)
1			54	RT
2			52	RT
3			43	RT
4			60	45
5			26	RT
6			28	RT
7			35	RT
			44	45

^a Isolated yield.



was stirred for 15 h at ambient temperature to afford *N*-*p*-toluenesulfonyl-2-phenylaziridine (6.0 mg; 42%).

2.3.2. A typical procedure for asymmetric aziridination of styrene

A suspension of anhydrous copper(II) chloride, alkaloid (12 mol%) in dry acetonitrile at 60 °C for 2 h. was stirred with Bromamine-T or PhI = NTs (1 mol) and the olefin (5 mol) for 5 h at room temperature (Scheme 4). The results are summarised in Table 3.

Table 3
Enantioselective aziridination of olefins using copper alkaloids complexes

Entry	Substrate	Nitrene Source	Solvent	Metal Salt	Ligand	Yield %	ee (%) ^a
1	Styrene	PhI = NTs	EDC	Cu(acac) ₂	Quinine	50	28
2	Styrene	PhI = NTs	CH ₃ CN	CuCl ₂	Quinine	43	17
3	Styrene	Chloramine-T	CH ₃ CN	CuCl	Quinine	32	7
4	Styrene	Bromamine-T	CH ₃ CN	CuCl ₂	Dihydro-quinine	39	43
5	Styrene	Bromamine-T	CH ₃ CN	CuCl ₂	Cinchonine	10	20
6	Styrene	Bromamine-T	CH ₃ CN	CuCl ₂	<i>N</i> -benzyl ephedrine	60	10
7	DHN	Bromamine-T	CH ₃ CN	CuCl ₂	Sparteine	38	12

^a The ee's were measured by comparison with known optical rotations. Aziridination of quinine is not observed in the experiments carried out with quinine as the ligand.

3. Result and discussion

The polymer anchored Mn-complex was found to be a good heterogeneous catalyst for the aziridination of olefins with bromamine-T. Equally effective was the new iron-catalyst in the aziridination reaction (Table 1). With the latter, even less reactive methacrylamate underwent aziridination under microwave conditions. Recyclability and reusability of the catalysts without loss of activity could be effected. Our Mn-based catalyst's performance is better than Mn-based homogeneous counterpart investigated for PhI = NTs. H β catalysed aziridination of olefins selectively gives the *trans* product, which can be attributed to the pore size of the zeolite. Extensive molecular modelling studies are underway to explain the mechanism.

For the first time, we have studied asymmetric aziridination of alkenes with Bromamine-T with cinchona alkaloids as well as sparteine and *N*-benzyl ephedrine as ligands. Highest enantioselectivity was realised with the cinchona alkaloid dihydroquinine (Table 3).

The aziridines were characterised by usual analytical techniques.

4. Conclusion

The manganese and the iron polymer based catalysts have been found to be efficient in aziridination reactions. H β catalyses aziridination under heterogeneous conditions in the absence of any metal catalyst giving selectively the *trans* product. Studies on asymmetric aziridination, have demonstrated the efficacy of cinchona alkaloids as ligands.

Acknowledgements

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- [11] Monomer (poly *p*-phenylene diamine) was first dissolved in acetonitrile and cooled to 0–5 °C. A cooled solution of 0.05 M FeCl₃ in CH₃CN was added to it dropwise with stirring over 12–15 h. The reddish black coloured precipitate obtained was dried at room temperature to give the product which was characterised using AAS, ESR, FT-IR, DTA-TGA analysis, surface area measurements and C, H, N analysis. The metal content of the catalyst was found to be 1.5 ppm. The surface area measurement of the catalyst was 55 mg². The DTA-TGA analysis showed that the catalyst is stable upto 220 °C. The ESR spectrum appeared as a typical pattern of octahedral iron present in +3 oxidation state. The FT-IR showed N-H stretching frequencies at 3120 cm⁻¹.