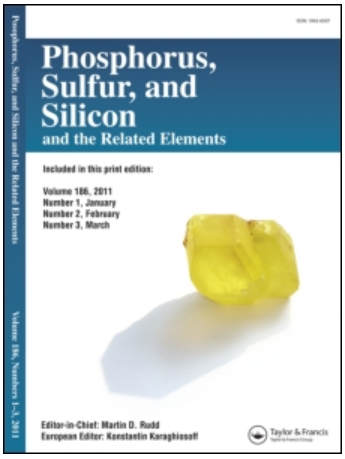

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Catalytic and Asymmetric Aziridination using Sulfur Ylides.

VARINDER K. AGGARWAL,[a*] ALISON THOMPSON,[a] RAY V.H. JONES[b] AND MIKE C.H. STANDEN.[b]

[a]*Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK.*
[b]*Zeneca Manufacturing Partnership, Process Technology Department, Earls Road, Grangemouth, Stirlingshire, FK3 8XG, UK.*

Abstract: This paper describes a new method for the preparation of aziridines from imines and diazocompounds which requires catalytic amounts of metal salts and sulfides and operates under neutral conditions. Using enantiomerically pure sulfides, high enantioselectivity has been achieved in the aziridination process.

KEYWORDS: Catalytic, asymmetric, aziridine, imine, diazo compound, sulfur ylide.

INTRODUCTION

Optically active aziridines constitute an extremely important class of organic compound, as they can be ring opened by a range of nucleophiles to yield products with useful functionality.[1]

One aziridination strategy involves the addition of sulfur ylides to imines,[2] but this reaction usually requires stoichiometric amounts of reagents and is currently racemic. We have previously shown[3] that in related epoxidation reactions such limitations can be overcome and epoxides can be generated using catalytic amounts of sulfide. In this paper we describe the application of our recently developed catalytic cycle for epoxidation to catalytic, asymmetric aziridination.

Results and Discussion

The proposed catalytic cycle for aziridination is shown in Scheme 1. The strategy involves generation of a sulfur ylide by nucleophilic attack of a sulfide on a metallocarbene which is itself formed by reaction of metal salt with a diazo compound. The ylide thus forms with regeneration of metal salt. Sulfur ylide attack on an activated imine species gives an intermediate betaine, which decomposes to yield aziridine and regenerate sulfide. Consequently, catalytic amounts of metal salt and sulfide are sufficient to obtain good yields of aziridine.

Typically, diazo compound (1.5 mmol) is added in 1 mL dichloromethane to a solution of sulfide (0.2 mmol), rhodium acetate (0.01 mmol) and imine (1.0 mmol) in 1 mL of dichloromethane over a period of three hours. The results are shown in Table 1.

Scheme 1

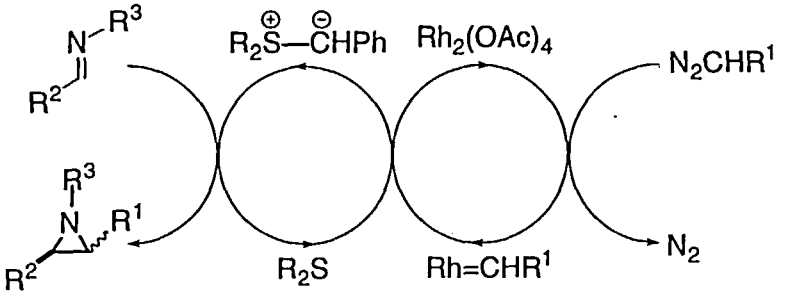


TABLE 1

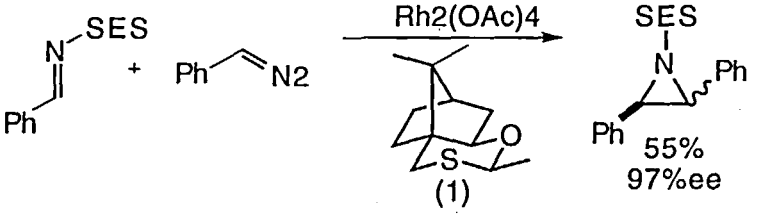
Preparation of aziridines using 20 mol% of sulfide.

Entry	R^1	R^2	R^3	R_2S	Yield/%	Ratio (*trans:cis*)
1	Ph	Ph	Ts	Me_2S	91	3:1
2	Ph	Ph	Dpp[a]	Me_2S	83	3:1
3	Ph	Ph	SES[b]	Me_2S	92	3:1
4	$C(O)NEt_2$	Ph	SES[b]	THT[c]	91[d]	2:1
5	CO_2Et	Ph	SES[b]	THT[c]	57[d]	1:3

(a) Diphenylphosphinyl (b) Trimethylsilylethanesulfonamide (c) Tetrahydrothiophene (d) Reactions conducted in THF at 60°C.

Table 1 shows that catalytic amounts of sulfide are sufficient to give good yields of aziridines. Variation of the electron withdrawing *N*-substituent allows the preparation of aziridines with readily cleavable groups (entries 2 and 3) and functionalised products may be prepared by using diazo esters and acetamides (entries 4 and 5). Additionally, the use of chiral sulfide (**1**) gives aziridines in good yield, with excellent enantioselectivity as shown in Scheme 2.

Scheme 2



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