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An efficient transition metal-free aziridination of alkenes with Chloramine-T using aqueous H_2O_2/HBr

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Abstract—The combination of aqueous H_2O_2 and HBr was found to be an efficient transition metal-free green catalytic system for the aziridination of a variety of alkenes under very mild reaction conditions.

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Aziridination of alkenes is an important transformation as aziridines are very important synthetic building blocks, extensively used as electrophiles[1] and synthetic intermediates in the preparation of a wide range of nitrogen-containing compounds.[2] Among the various methods reported in the literature, the metal catalyzed reaction of nitrenes, generated in situ, with olefins is an efficient method for the preparation of aziridines. In this context [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs)[3] has been shown to be a very convenient nitrene precursor for aziridination in the presence of several transition metal-based catalysts.[4] However, there are drawbacks with the use of PhI=NTs, it is expensive, yields iodobenzene in equimolar amounts, and oxygenated hydrocarbons are dominant by-products.[5] *N*-Chloronium salts of sulfonamides such as Chloramine-T together with several metal catalysts have been used as a cheap, convenient, and practical nitrogen source for aziridination,[6] but the methods suffer from certain drawbacks such as the use of transition metals as catalysts and lower yields of the products due to competing hydrogen abstraction and insertion reactions. In recent years much attention has been paid to the development of transition metal-free catalyst systems in order to obtain more efficient processes. For example, bromine-based catalysts such as phenyltrimethylammonium tribromide,[7] pyridiniumbromide perbromide,[8] and *N*-bromamides[9] are very efficient catalysts for the aziridination of olefins using Chloramine-T as the nitrogen source, but these systems are not easily accessible. A recent report by Neumann and co-workers [10] on the use of a combination of hydrogen peroxide and hydrohalic acid as a green halogenating agent for arenes inspired us to explore the potential of such a transition metal-free system for aziridination of alkenes. In this letter we describe, for the first time, a very simple and highly efficient aziridination of alkenes with Chloramine-T using aqueous H_2O_2 and HBr.

The aziridination of a variety of alkenes was carried out to test the generality of this method and the results are summarized in Table 1. All the alkenes used were efficiently converted to their corresponding aziridines in excellent yields with Chloramine-T using aqueous H_2O_2/HBr as catalyst (20 mol%) in acetonitrile at room temperature, in the presence of $MgSO_4$ as a water-trapping agent under a nitrogen atmosphere (Scheme 1). Among the various alkenes studied, aromatic substituted alkenes bearing electron-donating groups on the

Table 1. H_2O_2/HBr catalyzed aziridination of olefins with Chloramine-T[11]

Entry	Olefin	Reaction time (h)	Yield[a] (%)
1	Styrene	5.0	75
2	4-Methylstyrene	3.5	86
3	3-Methylstyrene	4.0	80
4	α-Methylstyrene	2.5	92
5	Methyl methacrylate	6.5	72
6	Cyclohexene	5.0	75
7	Vinylcyclohexane	5.5	55
8	*trans*-Methyl cinnamate	10.0	45
9	4-Chlorostyrene	8.0	60
10	Cycloheptene	5.0	67

[a] Isolated yields.

Keywords: Aziridination; Olefins; H_2O_2; HBr; Nitrene.

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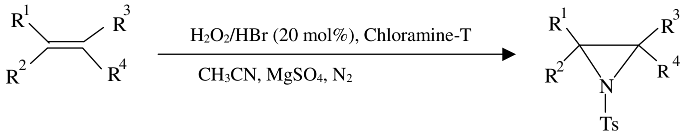
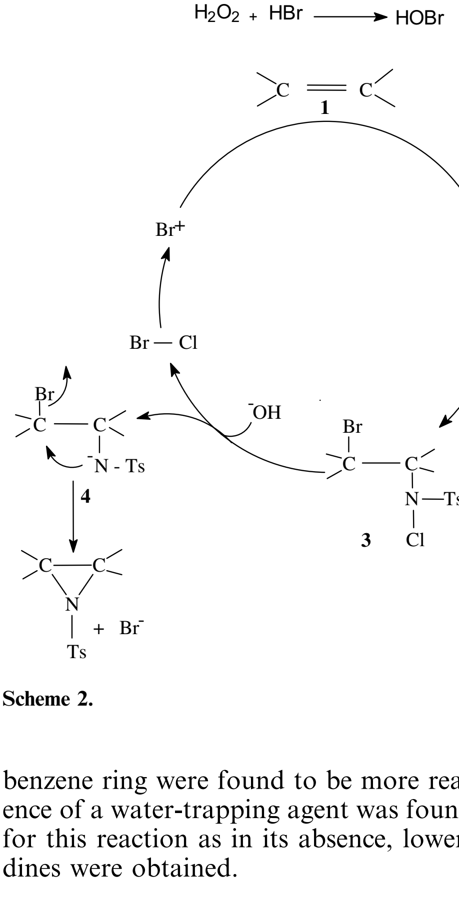


Scheme 1.



Scheme 2.

benzene ring were found to be more reactive. The presence of a water-trapping agent was found to be essential for this reaction as in its absence, lower yields of aziridines were obtained.

Although the mechanism of this reaction is not clear at this stage, the reaction probably involves the formation of hypobromous acid by the reaction of aq hydrogen peroxide with hydrobromic acid, which acts as a source of bromonium ions. The bromonium ion reacts with olefin **1** to afford intermediate **2**, which undergoes ring opening by Ts(Cl)N^- to give β-bromo-*N*-chloro-*p*-toluenesulfonamide **3**. Attack of OH^- on the N–Cl group of presumed intermediate **3** generates the anion **4** subsequent cyclization of which yields the aziridine (Scheme 2).[7]

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11. *Typical experimental procedure:* To a stirred solution of hydrogen peroxide (aq 30%, 0.023 ml, 20 mol%) in acetonitrile (5 ml) was added hydrobromic acid (48%, 0.033 ml, 20 mol%), 4-methylstyrene (118 mg, 1 mmol), Chloramine-T trihydrate (337 mg, 1.2 mmol) and $MgSO_4$ (100 mg) under a nitrogen atmosphere at 25 °C. Stirring was continued for 3.5 h and the reaction progress was monitored by TLC (SiO_2) using ethyl acetate/hexane (4:6) as eluent. After completion, the solvent was evaporated under reduced pressure. The residue obtained was purified through a short silica gel column using hexane/ethyl acetate (4:1) as eluent. Evaporation of the solvent yielded *N*-(*p*-tolylsulfonyl)-2-(*p*-methylphenyl)aziridine (yield 247 mg, 80%). Similarly, other aziridines were prepared via this procedure.