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LETTERS

Bromamine-T: A Superior Source of Nitrene for Aziridination of Olefins.

Renu Vyas, Bhanu. M. Chanda* and Ashutosh V. Bedekar*

Division of Organic Chemistry: Technology
National Chemical Laboratory, Pune 411 008, India.

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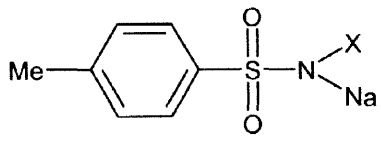
Abstract:

Bromamine-T as a superior source of nitrene compared to Chloramine-T in the Cu-catalyzed aziridination of olefins is reported in this communication.

Keywords: Aziridines; Bromamine-T; Copper catalyzed.

In recent years metal catalyzed nitrene transfer to olefins has gained interest as this provides an easy access to aziridines, an important class of compounds [1]. Copper [2], Manganese [3] and Iron [3a, 3b] catalyzed nitrene transfer reaction to olefins using [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrene source has been widely investigated lately.

A team of Japanese researchers led by Komatsu [4] has recently reported copper catalyzed aziridination of alkenes using commercially available Chloramine-T, **1** as the source of nitrene. A range of olefins is subjected to this reaction with moderate yields in a few cases. Encouraged by their findings we have investigated Bromamine-T, **2** as the source for nitrene for the aziridination of olefins and our comparative results are presented in this communication. There are only a few reports of the use of **2** as a titrant in oximetric estimations [5] and for oxidation of dimethylsulphoxide [6].



*Chloramine-T; X=Cl, **1***
*Bromamine-T; X=Br, **2***

The reaction was performed with anhydrous Bromamine-T [5a, 7], excess of olefin in acetonitrile in the presence of freshly prepared CuCl as the catalyst and 5Å powdered molecular sieves under the conditions optimized for **1** [4]. The results of aziridination of several olefins with **2** are presented in Table-1. We have reported the isolated yields in all the cases and a marked improvement can be seen when compared to aziridination with **1**.

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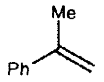
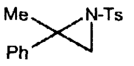
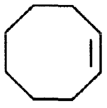
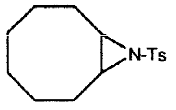
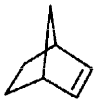
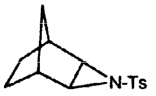
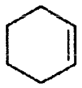
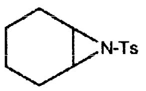
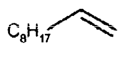
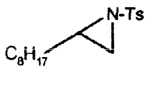
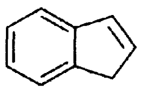
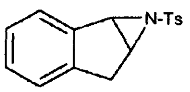
Table-1

Comparison of Cu-catalyzed aziridination of olefins[a] with Bromamine-T, **2** and Chloramine-T, **1**.

Entry	Olefin	Aziridine	Yield (%)[b] with the source of nitrene as,	
			Chloramine-T, **1**[ref. 4]	Bromamine-T, **2**
1			31	48
2			75	81
3			38	70 72[c]
4			45	73
5			5[d]	55
6			12[d]	20
7			30[d]	45

[a]with CuCl (10 mol% for entries 1, 5-7) or CuCl (5 mol% for entries 2-4) and 5 eq. substrate in CH_3CN at room temperature (3 h); [b]isolated yield and characterised by spectroscopic analysis; [c]with $CuCl_2$ (5 mol%); [d]present work.

It is assumed that the enhanced reactivity of Bromamine-T could be due to weaker nitrogen-bromine bond in **2** facilitating the formation of copper nitrenoid complex. It is also observed that $CuCl_2$ catalyzes aziridination of cyclooctene (entry-3) with same efficiency as CuCl. We believe Bromamine-T acts as an oxidant and probably the catalytic species is Cu(II) in this reaction as also reported by Evans [2b].

In conclusion, it is demonstrated that Bromamine-T is a superior source of nitrene in the Cu-catalyzed aziridination of olefins compared to Chloramine-T as recently reported.

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7. Preparation of Bromamine-T: An aqueous solution of chloramine-T trihydrate was treated with bromine (3 eq.) at room temperature. Precipitated dibromamine-T was added portion wise to aqueous NaOH (3.3 eq.) over an hour. The pale yellow crystals of Bromamine-T were filtered, washed with water and vacuum dried at 80 °C.