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Catalytic Nitrene Transfer from Chloramine-T

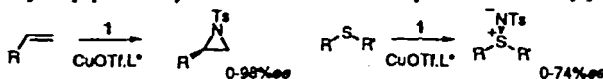
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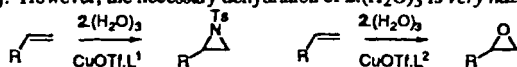
A copper catalyst for aziridination and amination with chloramine-T hydrate is reported.

Keywords: aziridine; copper; chloramine-T

The first synthetically useful aziridination of alkenes was reported by Evans in 1991 [1]. Copper-catalysed asymmetric aziridination was described by Evans and by Jacobsen [2]. The nitrene transfer reagent in these reactions was TsN=IPh **1**. Although imidation of sulfides by chloramine-T (TsNClNa **2**), via an ionic mechanism, was known, it was not until 1996 that Uemura reported an asymmetric nitrene-transfer imidation of sulfides using **1** [3]. Our joint paper on "asymmetric sulfimination" was published in 1997 [4].

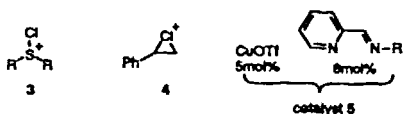


The synthesis of TsN=IPh **1** is notoriously difficult and its reactions have an undesirable by-product, PhI. Chloramine-T **2**, on the other hand, is a cheap, commercially available solid which leads only to sodium chloride as by-product of imidation. While it is routinely used for sulfimination, only very recently has an aziridination with chloramine-T been published [5]. However, the necessary dehydration of **2**·(H₂O)₃ is very hazardous.



In our earlier work on sulfimidation [6] we noted that copper-catalysed imidation with chloramine-T appeared to have two possible mechanisms, Lewis acid or nitrene-transfer. The former is similar to the mechanism assumed for reaction of chloramine-T hydrate with sulfides, with the copper catalyst accelerating at least one of the steps. In the absence of molecular sieves, the proposed sulfonium intermediates **3** are intercepted by water to produce sulfoxides. This was observed in reactions where no other nitrogen ligand was present. When ligands such as pyridine or bipy were added, no sulfoxide was observed even in the absence of sieves. This is consistent with the operation of a nitrene-transfer mechanism, which can not obviously lead to sulfoxide.

We thus carried out a similar study with styrene as substrate. Interestingly, the copper (I) triflate - bipy catalyst appeared to act as a Lewis acid in this case, giving mixtures of aziridine and epoxide. We believe these two products arise from a common chloronium intermediate **4**. Clearly a better ligand for copper was needed and we chose to replace one half of the bipy with an imine. With the new catalysts **5** no epoxide was observed, even with no sieves and we therefore believe a nitrene-transfer mechanism to be operating.



Pleasingly, catalysts **5** induce (i) aziridination of aryl alkenes, (ii) allylic amination of cyclohexene and (iii) benzylic amination of tetralin, as published elsewhere [7].

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