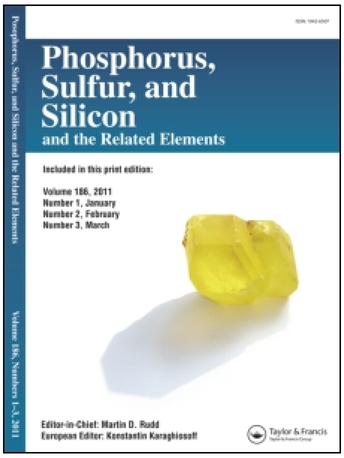

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Catalytic Nitrene Transfer from Chloramine-T

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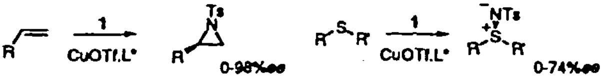
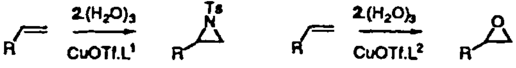
A copper catalyst for aziridination and amination with chloramine-T hydrate is reported.

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 sulfimidation" 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 sulfimidation, only very recently has an aziridination with chloramine-T been published [5]. However, the necessary dehydration of $2.(H_2O)_3$ is *very hazardous*.

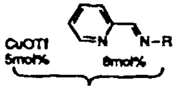


In our earlier work on sulfimidation [6] we noted that copper-catalysed imidation with chloramine-T appeared to have two possible mechanisms, Lewis acid or nitrene-transfer. The former is similar to the mechanism assumed for reaction of chloramine-T hydrate with sulfides, with the copper catalyst accelerating 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.

3

4



catalyst 5

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

Acknowledgements

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