

SYNLETT Spotlight 112

Oxaziridines

Compiled by Jitendra Kumar Mishra



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

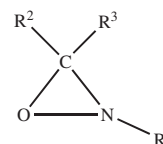
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Introduction

Oxaziridines were first discovered in 1956¹ and have been widely investigated, principally for two reasons. The presence of an inherently weak N–O bond in a strained ring promised a group of compounds of unusually high reactivity. In addition, this system possesses the structural elements that seem to be required in order to observe stereochemical isomerism at nitrogen: ring strain and an atom with unshared electron pairs attached to the nitrogen.

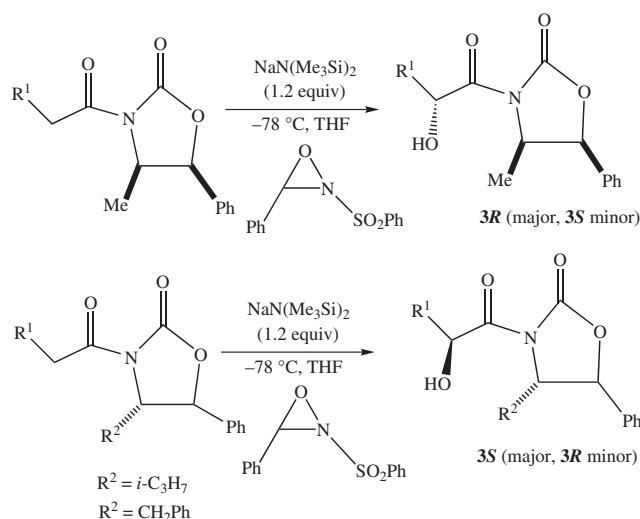


Oxaziridines can be used as both oxygenating and aminating agents in their reactions with a wide variety of nucleophiles. Oxaziridines with small groups on N, for example hydrogen or methyl, act as aminating agents, whereas those with bulky or electron withdrawing groups on N preferentially transfer the oxygen atom. Oxaziridine-mediated processes are of interest due to the easy accessibility of the reagents and their potential for asymmetric induction.

Abstracts

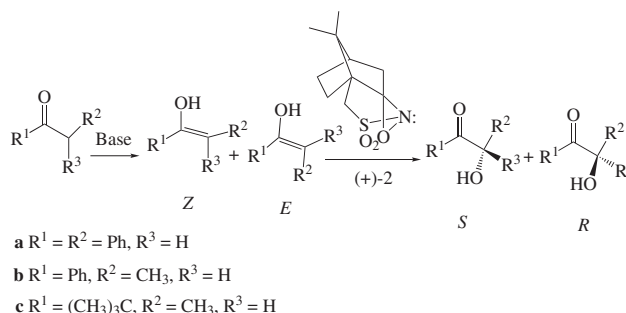
(A) For asymmetric oxygenation of chiral imide enolates:

Evans and coworkers have found that the α -hydroxylation reactions of chiral enolates derived from oxazolidinone carboximide proceed with exceptional facility with the oxidant 2-(phenylsulfonyl)-3-phenyl oxaziridine. The following carboximides were transformed into their respective Z-sodium enolates (1.2 equiv of $\text{NaN}(\text{Me}_3\text{Si})_2$, THF, -78°C) with slight excess of oxaziridine.²



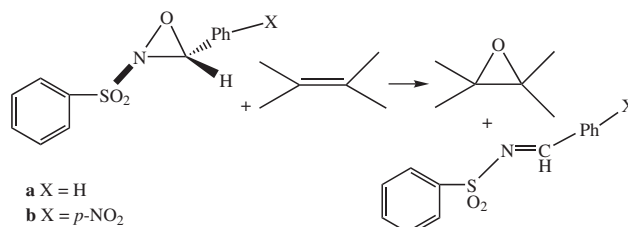
(B) For asymmetric oxidation of ketone enolates:

The reagent-controlled asymmetric oxidation of trisubstituted enolate anions can be done by enantiomerically pure camphorsulfonyl oxaziridine.³

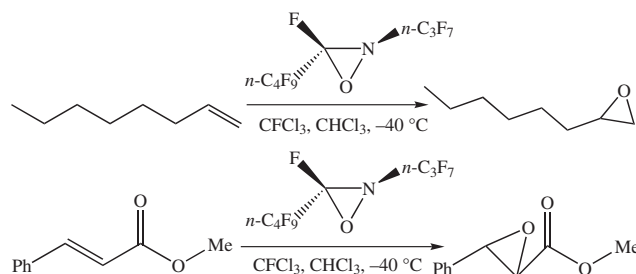


(C) For epoxidation of alkenes:

Epoxidation of alkenes are also possible by using oxaziridine.⁴

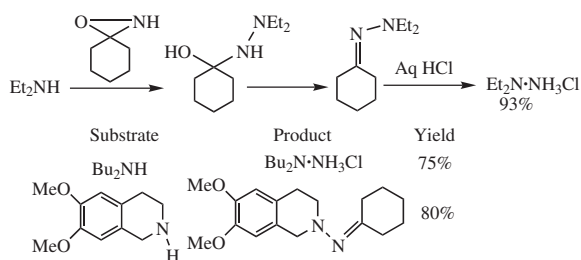


(D) For epoxidation of alkenes (with perfluorinated oxaziridines): Alkyl-substituted olefins are epoxidized by perfluoro-*cis*-2,3-dialkyl oxaziridines under mild conditions. Similarly electron deficient substrates (e.g. α,β -enones) can also be epoxidized.⁵



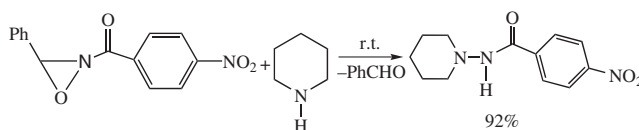
(E) For amination of N-nucleophiles:

Oxaziridines can be used as an aminating reagent for N-amination of 2° amines.⁶



(F) For N-acylamidation:

Direct N-acyl transfer as a method for protected hydrazine synthesis has also been shown to proceed in good yield with a wide variety of substrates.⁷



References

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