SYNLETT Spotlight

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

Diphenylvinylsulfonium Triflate

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Introduction

Diphenylvinylsulfonium triflate (1) is a pale, yellow, stable and free-flowing oil. It can easily be prepared from its commercially available precursor diphenylbromomethylsulfonium triflate (2, Scheme 1). Alternatively, it is also possible to generate vinylsulfonium salt 1 in situ from bromide 2.

Nucleophiles readily undergo conjugate addition to vinylsulfonium salts to form sulfur ylide intermediates, which can undergo a range of further transformations.

Abstracts

(A) Synthesis of Mitomycin K:
One of the first applications was the use of diphenylvinylsulfonium triflate (1) in the epoxy-annulation reaction towards mitomycin K, by Kim and Jimenez.1 In this case, a substituted indole aldehyde was treated with 1, using sodium hydride as base, to afford an intermediate ylide, which underwent epoxide formation.

(B) Epoxy-Annulation Reactions:
This methodology was further extended to the synthesis of five- and six-membered epoxides or aziridine fused heterocycles.2 An enantioselective variant, using a chiral vinylsulfonium salt, was also reported.

(C) Synthesis of 4,5-Epoxytetrahydropyrans:
Ley and co-workers3 applied the same method to the synthesis of 4,5-epoxytetrahydropyrans, achieving high diastereoselectivity. Additionally, their work compared the difference in reactivity of 1 to the equivalent vinylphosphonium salt, which could be used to form the corresponding olefin in high yield.

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(D) **Synthesis of Six-Membered Heterocycles:**
In 2008 Aggarwal and co-workers discovered that reactions of vinyl sulfonium salt 1, with 1,2-aminoalcohols/thiols or 1,2-diamines, in the presence of base led to morpholines, thiomorpholines and piperazines. This methodology was later expanded to the in situ generation of 1 from 2 and the use of easier-to-cleave sulfonamide protecting groups, instead of sulfonamides.

(E) **Synthesis of Oxazino[4,3-a]indoles:**
Chen et al. later expanded this methodology to the synthesis of biologically important oxazino[4,3-a]indoles using KOH as base.

(F) **Synthesis of N-Aryloxazolidin-2-ones:**
Xie and co-workers developed a novel tandem reaction with vinyl sulfonium salt biologically important oxazino[4,3-a]indoles using KOH as base.

(G) **Synthesis of Pyrrolidin-2-ones:**
Xie et al. later expanded their method to the synthesis of pharmaco-logically important five-membered pyrrolidin-2-ones, using the acidic β-C–H bond for nucleophilic attack of vinyl sulfonium salt 1. They were able to expand this method to a large variety of N-protecting groups and electron-withdrawing substituents. They also discovered that reaction of an amide with 1 leads to formation of aminoethanol esters.

(H) **Synthesis of Imidazolinium Salts:**
McGarrigle et al. applied in situ generated protecting groups, instead of sulfonamides.

(I) **Synthesis of N-Vinylxazolidinones:**
Yar et al. later demonstrated the synthesis of N-vinylxazolidinones from N-Cbz protected aminoalcohols. Tandem mass spectrometry was used to investigate the mechanism of this reaction, in which an intermediate alkoxide acts as a base to effect an intramolecular E2 elimination prior to attack at the Cbz protecting group.

References

8. (a) Xie, C. S.; Han, D. Y.; Liu, J. H.; Xie, T. *Synlett* 2009, 3155.