SYNLETT Spotlight 382

Diphenylvinylsulfonium Triflate

Compiled by Sven P. Fritz

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

Diphenylvinylsulfonium triflate (**1**) is a pale, yellow, stable and free-flowing oil. It can easily be prepared from its commercially available precursor diphenylbromoethylsulfonium 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.

Extensive use in epoxidation, aziridination and other annulation reactions has shown the wide applicability of vinylsulfonium salts as two-carbon bridges.

Scheme 1 Preparation of diphenylvinylsulfonium triflate (**1**).

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.

(D) *Synthesis of Six-Membered Heterocycles:*

In 2008 Aggarwal and co-workers⁴ 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**⁵ and the use of easier-to-cleave sulfinamide protecting groups⁶, instead of sulfonamides.

(E) *Synthesis of Oxazino[4,3-a]indoles:*

Chen et al.⁷ 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-workers⁸ developed a novel tandem reaction with vinyl sulfonium triflate **1** to transform *tert*-butyl carbamates into *N*-aryl-oxazolidin-2-ones.

(G) *Synthesis of Pyrrolidin-2-ones:*

Xie et al.⁹ later expanded their method to the synthesis of pharmacologically 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.¹⁰ applied in situ generated **1** towards the synthesis of imidazolinium salts, an important class of NHC-precursors. This was also possible as a one-pot procedure from easily available starting materials.

(I) *Synthesis of N-Vinyloxazolidinones:*

Yar et al.¹¹ later demonstrated the synthesis of *N*-vinyloxazolidinones 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.

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