SYNLETT
Spotlight 382

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

Diphenylvinylsulfonium Triflate

Compiled by Sven P. Fritz

Sven P. Fritz was born in Aachen, Germany. After participating in an Erasmus stay at the University of Leeds, UK, he received his B.Sc. degree from the University of Regensburg, Germany. He then completed a dual bachelor degree within the EU Atlantis fellowship programme, working with Prof. Jeffrey Aubé, at the University of Kansas, USA. He is currently focusing on the synthesis of small heterocycles with vinylsulfonium salts, in the group of Prof. Varinder K. Aggarwal, at the University of Bristol, UK.

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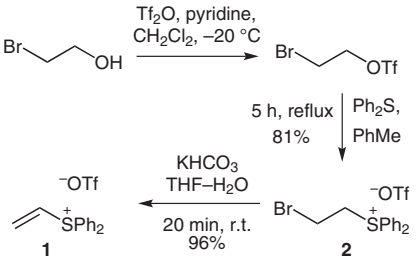
Introduction

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.

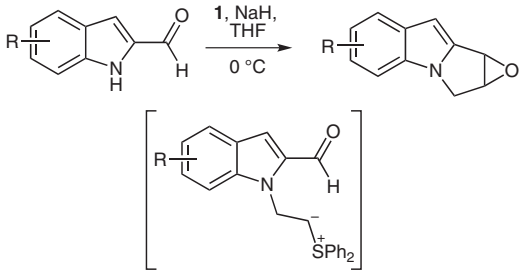
Extensive use in epoxidation, aziridination and other annulation reactions has shown the wide applicability of vinylsulfonium salts as two-carbon bridges.



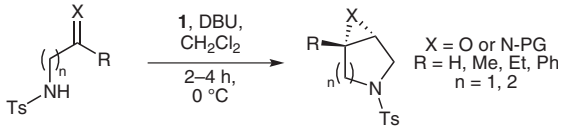
Scheme 1 Preparation of diphenylvinylsulfonium triflate (**1**).

Abstracts

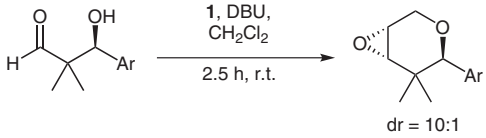
(A) *Synthesis of Mitomycin K:*
One of the first applications was the use of diphenylvinylsulfonium triflate (**1**) in the epoxy-annulation reaction towards mitomycin K, by Kim and Jimenez.[1] In this case, a substituted indole aldehyde was treated with **1**, using sodium hydride as base, to afford 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 heterocyles.[2] An enantioselective variant, using a chiral vinylsulfonium salt, was also reported.



(C) *Synthesis of 4,5-Epoxytetrahydropyrans:*
Ley and co-workers[3] 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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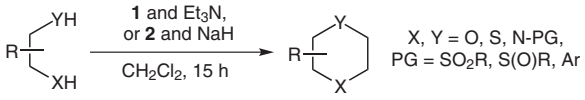
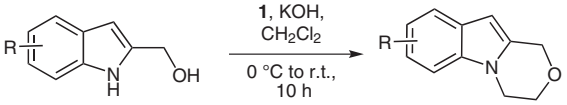
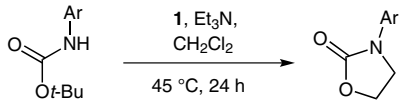
(D) *Synthesis of Six-Membered Heterocycles:*
In 2008 Aggarwal and co-workers[4] discovered that reactions of vinyl sulfonium salt **1**, with 1,2-aminoalcohols/thiols or 1,2-diamines, in the presence of base led to morpholines, thiomorpholines and piperazines. This methodology was later expanded to the in situ generation of **1** from **2**[5] and the use of easier-to-cleave sulfinamide protecting groups[6], instead of sulfonamides.



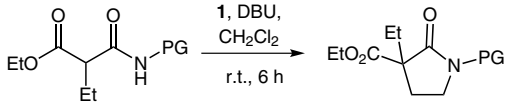
(E) *Synthesis of Oxazino[4,3-a]indoles:*
Chen et al.[7] later expanded this methodology to the synthesis of biologically important oxazino[4,3-a]indoles using KOH as base.



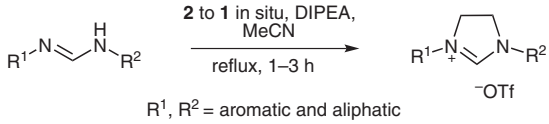
(F) *Synthesis of N-Aryloxazolidin-2-ones:*
Xie and co-workers[8] developed a novel tandem reaction with vinyl sulfonium triflate **1** to transform *tert*-butyl carbamates into *N*-aryloxazolidin-2-ones.



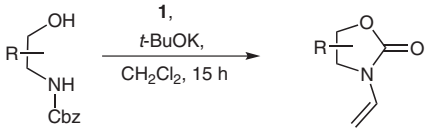
(G) *Synthesis of Pyrrolidin-2-ones:*
Xie et al.[9] later expanded their method to the synthesis of pharmacologically important five-membered pyrrolidin-2-ones, using the acidic β-C–H bond for nucleophilic attack of vinyl sulfonium salt **1**. They were able to expand this method to a large variety of 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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