Trifluoromethanesulfonic (triflic) Anhydride

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Introduction

Trifluoromethanesulfonic (triflic) anhydride \((\text{CF}_3\text{SO}_2\text{O}; \text{Tf}_2\text{O})\) has proved to be a versatile reagent in organic synthesis over the last few decades.\(^1\) Due to the excellent leaving group properties of the triflate group, \(\text{Tf}_2\text{O}\) finds its use in the conversion of various compounds to triflates which can be transformed into other useful products. Detailed studies have established triflates to be some \(2 \times 10^3\) to \(2 \times 10^5\) times more reactive than the comparable tosylates.\(^1\)

The anhydride is best prepared by distillation of triflic acid from excess \(\text{P}_2\text{O}_5\).\(^5\) Stang found that yields can be considerably increased by using \(\text{P}_2\text{O}_5\) premixed with an equal volume of celite. The pure anhydride is a colourless liquid that is stable for long periods, insoluble in water, does not fume in air and hydrolyses slowly over several days at room temperature. The liquid boils at 81 °C at 760 torr pressure. The reagent is also commercially available.

Abstract

(A) The reaction of aliphatic esters with aliphatic and aromatic nitriles in presence of \(\text{Tf}_2\text{O}\) affords 4-alkoxyopyrimidines. This reaction proceeds through the intermediacy of alkoxy (trifloxy) carbenium ions\(^6\) and leads to isoquinolines in case of arylacetic acid esters.\(^7\) A similar reaction with ketones offers a broad scope for the preparation of functionalised pyrimidines.\(^8\)

(B) The iminium and iminotriflates derived from the treatment of secondary and tertiary amides has opened up broad avenues for transformations of the amide functionality. These salts are versatile reagents that can react with various N-, O- and S-nucleophiles, thereby transforming amide group into other functionalities.\(^9\)

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(C) Tf₂O has been utilised as a mild activation reagent in Vilsmeier–Haack formylation. Less nucleophilic aromatics can be formylated with DMF/Tf₂O.¹⁰

(D) α-Trifluoromethylsulfonamido furans, an important class of compounds, have recently been prepared by Tf₂O-mediated cyclisation of ketoamides and 5-hydroxy substituted pyrrolidinones.¹¹

(E) Tf₂O is used extensively in carbohydrate chemistry, frequently for glycosylation. Recently a novel sulfide- and sulfoxide-mediated dehydrative glycosylation technique employing Tf₂O has been developed.¹²

(F) In hypervalent iodine chemistry, PhIO–Tf₂O finds its use in the preparation of 1,4-disubstituted benzene derivatives. The extreme reactivity of the above complex even towards non-activated benzene derivatives affords (p-phenylene)bis(arylido)onium) ditriflates. This subsequently leads to the products.¹³

References

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