Trifluoromethanesulfonic (triflic) Anhydride

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Introduction

Trifluoromethanesulfonic (triflic) anhydride [(CF3SO2)2O; Tf2O] has proved to be a versatile reagent in organic synthesis over the last few decades.1–3 Due to the excellent leaving group properties of the triflate group, Tf2O 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 × 104 to 2 × 105 times more reactive than the comparable tosylates.1

The anhydride is best prepared by distillation of triflic acid from excess P2O5.5 Stang found that yields can be considerably increased by using P2O5 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 Tf2O affords 4-alkoxypyrimidines. This reaction proceeds through the intermediacy of alkoxy (trifloxy) carbenium ions6 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
References

(3) Baraznekok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. Tetrahedron 2000, 56, 3077.