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TRIMETHYLSILYL TETRAFLUOROBORATE
A CONVENIENT REAGENT FOR SOLVOLYSIS REACTIONS

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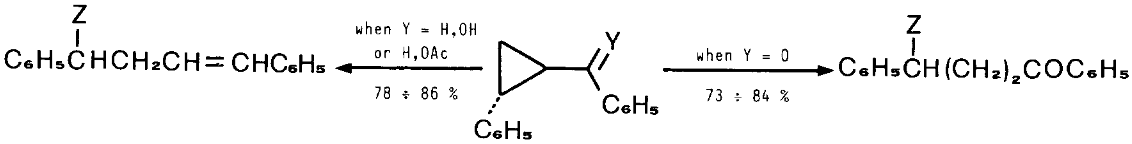
Abstract: *Conversions of cyclopropyl carbinols (or their acetates) and ketones into homoallyl and γ-substituted ketone derivatives, respectively, are accomplished by trimethylsilyl tetrafluoroborate efficiently and under mild conditions.*

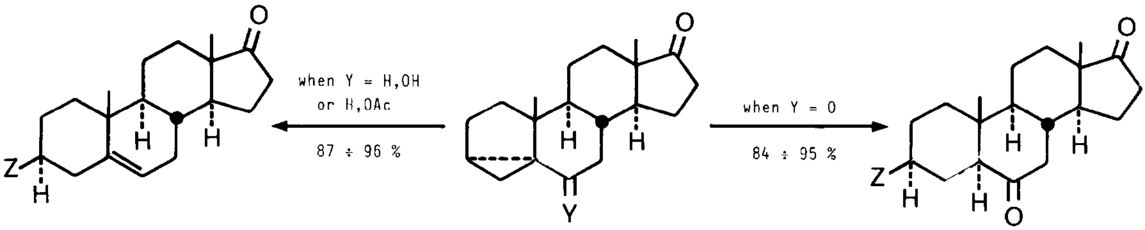
Solvolyses are initiated often by the interaction of substrates with protic acids. Thus, for example, the transformation of cyclopropyl carbinols and ketones into homoallyl and γ-substituted ketone derivatives, respectively, has been carried out frequently in this manner.[1]

Recently trimethylsilyl iodide has replaced the proton source in such reactions, causing them, however, to yield exclusively iodo products.[2]

In connection with a study of cyclopropane ring scission by solvolytic means there was developed a silicon-containing reagent which permits the use of a variety of nucleophiles for termination of the reaction.

A stoichiometric combination of trimethylsilyl chloride and silver tetrafluoroborate in acetonitrile or acetone solution yields a mild, but highly efficient reagent (presumably $Me_3SiN{=}C^+Me,BF_4^-$ and $Me_3SiOC^+Me_2,BF_4^-$, respectively[3]) for the following, nearly instantaneous conversions:





The presence of sodium chloride, bromide or iodide in the solutions results in the formation of halides (Z=Cl, Br or I, respectively). The use of moist solutions yields alcohols (Z=OH) and, finally, the use of totally anhydrous solutions in the absence of any additives, followed by aqueous work-up, leads to acetamides (Z=NHAc).

The reagent is prepared in ca. 0.1M concentration by the dissolution of 1.1 equivalents of Me_3SiCl and $AgBF_4$ each in acetonitrile or acetone and the filtration of the resultant AgCl precipitate (the filtration being avoided in small-scale reactions). A 0.5M solution of 1.0 equivalents of the cyclopropane in the same solvent is added with stirring under nitrogen at 0°C and the reaction worked-up within a few minutes.

The trimethylsilyl tetrafluoroborate (TST) offers the advantages of mild fast reactions, excellent solvolysis yields, flexibility of nucleophile use and avoidance of acid catalysts.

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