SYNLETT Spotlight 141

Chloramine-T (Sodium *N*-Chloro-*p*-toluenesulfonamide)

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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

Sodium *N*-chloro-*p*-toluenesulfonamide, commonly known as Chloramine-T, has diverse chemical properties. Several other *N*-halogeno-*N*-metalloarylsulfonamides are also available, such as Chloramine B, Bromamine T, Bromamine B, and Iodamine-T. Chloramine-T in the hydrate form has been used in various types of chemical reactions more extensively than others in this group. It is commercially available, inexpensive, water-tolerant, non-toxic, easy to handle, and can be used without further purification. The usefulness of Chloramine-T is that it behaves as

a source of both 'halonium' ion as well as a 'nitrogen anion'. As a result, these reagents react with a surprising range of functional groups, leading to an array of molecular transformations. The synthetic applications of Chloramine-T have been well-documented for amino-hydroxylation, aminochalcogenation of alkenes, allylic aminations, and aziridinations.

Sodium *N*-Chloro *p*-toluenesulfonamide trihydrate or TsNCl·Na·3H₂O

Abstracts

(A) Chloramine-T reacts with a variety of sulfur-containing compounds to form sulfur–nitrogen bonds.^{1a} A partial listing includes thiols, sulfides, disulfides, sulfimides, xanthates, thioketones, sulfenyl chlorides and sulfinyl chlorides. The reaction of Chloramine-T with sulfides forms the basis for the deprotection of thio groups. Thus 1,3-dioxathiolanes,^{1b} 1,3-dithiolanes, and 1,3-dithianes are all cleaved by Chloramine-T to regenerate the carbonyl compounds.

(B) Chloramine-T reacts with olefins in acetone–water acidified with non-nucleophilic acid to give chlorohydrins.^{2a} In acetic acid medium, it affords 1,2-chloroacetoxy derivatives.^{2b} On reaction with unsaturated organic acid like allylacetic acid in the presence of methanesulfonic acid, it yields a chlorolactone.^{2c}

(C) Enamines in the presence of Chloramine-T afford almost quantitatively the *N,N*-dialkylated α -amino aldehydes.³

(D) Various olefins react with Chloramine-T in the presence of a catalytic amount of osmium tetroxide to afford vicinal hydroxy-*p*-toluenesulfonamides.⁴

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(E) Chloramine-T reacts with NaBr and NaI to provide a convenient method of generating BrCl and ICl, respectively. Trialkylboranes react with sodium iodide in the presence of Chloramine-T to form the alkyl iodides.^{5a} Similarly, with sodium bromide, they afford alkyl bromides.^{5b} Under analogous reaction conditions, potassium aryl trifluoroborates, vinyl trifluoroborates, and alkenyl trifluoroborates are converted to the respective iodide using NaI in the presence of Chloramine-T.^{5c}

(F) Chloramine-T was used to mediate the cycloaddition of aldoximes to alkenes, resulting in various isoxazolines. Aldoximes react with Chloramine-T, leading to the formation of nitrile oxides, which further react in situ intra- or intermolecularly with olefinic compounds to produce different isoxazolines in quantitative yield.⁶

(G) As a nitrogen source, Chloramine-T has been used for the aziridination of alkenes. When Chloramine-T was added to an alkene in the presence of CuCl catalyst and molecular sieves 5Å, the corresponding aziridine was obtained in moderate to good yield.^{7a} In the absence of metal catalyst, olefins can also be aziridinated using Chloramine-T upon treatment with *N*-bromosuccinimide,^{7b} iodine,^{7c} or iron corroles.^{7d}

(H) Olefins, on treatment with Chloramine-T in the presence of water, a chiral alkaloid ligand and catalytic osmium tetroxide, undergo enantioselective vicinal addition of a sulfonamide and a hydroxyl group.⁸

(I) Chloramine-T is also used in allylic amination reactions. Two molar equivalents of anhydrous Chloramine-T reacted with Se metal in CH₂Cl₂ to give an imidoselenium compound, which further reacted with mono-, di-, tri- or tetra-substituted olefins affording allylic amination products in good yield.^{9a} Tellurium behaves in a similar way.^{9b}

(J) The different alkyl isocyanides react with aromatic amines and Chloramine-T under phase-transfer catalysis to give sulfonyl guanidines in good yield.¹⁰

(K) Chloramine-T has been used as a neutral agent in the chemoselective hydrolysis of thioglycosides to their corresponding glycosyl hemiacetals in quantitative yield under very mild, metal-free conditions.¹¹

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