

SYNLETT Spotlight 141

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

Compiled by Geetanjali Agnihotri



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

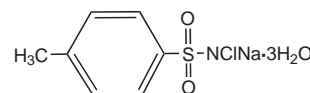
Geetanjali Agnihotri was born in 1978 in Etawah, India. She received her B.Sc. (Chemistry) and M.Sc. (Chemistry) in 1997 and 1999, respectively, from S.S.J.M. University, Kanpur, India. She is currently pursuing her Ph.D. under the supervision of Dr Anup Kumar Misra, Medicinal and Process Chemistry Division, Central Drug Research Institute, Lucknow. Her research interest is mainly focused on the synthesis of complex oligosaccharides and transformation of carbohydrates into bioactive molecules of medicinal interest.

Medicinal and Process Chemistry Division, Central Drug Research Institute, Chattar Manzil Palace, Lucknow 226001, UP, India.
E-mail: geetagni@yahoo.co.in

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

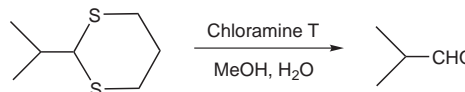
a source of both 'halonium' ion as well as a 'nitrogen anion'. As a result, these reagents react with a surprising range of functional groups, leading to an array of molecular transformations. The synthetic applications of Chloramine-T have been well-documented for amino-hydroxylation, amino-chalcogenation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



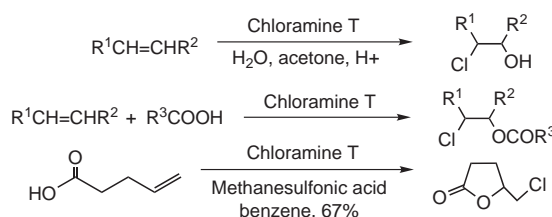
Sodium *N*-Chloro *p*-toluenesulfonamide trihydrate or TsNCl·Na·3H₂O

Abstracts

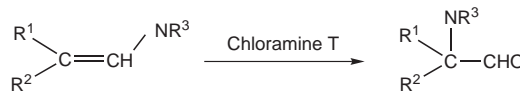
(A) Chloramine-T reacts with a variety of sulfur-containing compounds to form sulfur–nitrogen bonds.^{1a} A partial listing includes thiols, sulfides, disulfides, sulfimides, xanthates, thioketones, sulfonyl chlorides and sulfinyl chlorides. The reaction of Chloramine-T with sulfides forms the basis 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.



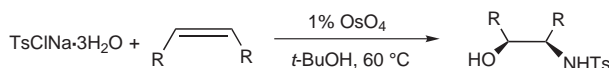
(B) Chloramine-T reacts with olefins in acetone–water acidified with non-nucleophilic acid to give chlorohydrins.^{2a} In acetic acid medium, it affords 1,2-chloroacetoxy derivatives.^{2b} On reaction with unsaturated organic acid like allylacetic acid in the presence of methanesulfonic acid, it yields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



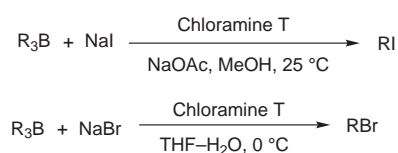
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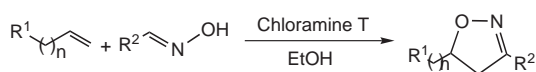
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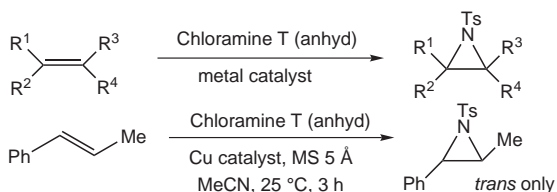
(E) Chloramine-T reacts with NaBr and NaI to provide a convenient method of generating BrCl and ICl, respectively. Trialkylboranes react with sodium iodide in the presence of Chloramine-T to form the alkyl iodides.^{5a} Similarly, with sodium bromide, they afford alkyl bromides.^{5b} Under analogous 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}



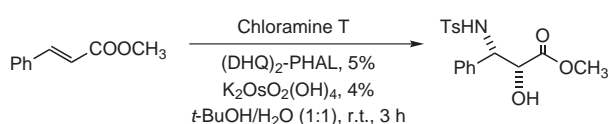
(F) Chloramine-T was used to mediate the cycloaddition of aldoximes to alkenes, resulting in various isoxazolines. Aldoximes react with Chloramine-T, leading to the formation of nitrile oxides, which further react in situ intra- or intermolecularly with olefinic compounds to produce different isoxazolines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



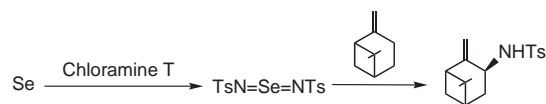
(G) As a nitrogen source, Chloramine-T has been used for the aziridination of alkenes. When Chloramine-T was added to an alkene in the presence of CuCl catalyst and molecular sieves 5Å, the corresponding aziridine was obtained in moderate to good yield.^{7a} In the absence of metal catalyst, olefins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



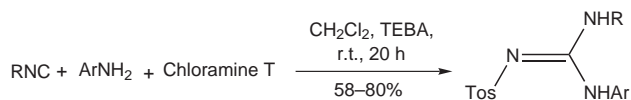
(H) Olefins, on treatment with Chloramine-T in the presence of water, a chiral alkaloid ligand and catalytic osmium tetroxide, undergo enantioselective vicinal addition of a sulfonamide and a hydroxyl group.⁸



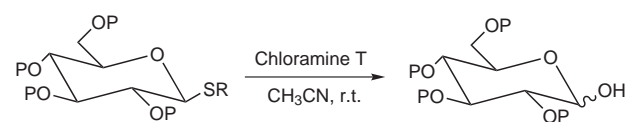
(I) Chloramine-T is also used in allylic amination reactions. Two molar equivalents of anhydrous Chloramine-T reacted with Se metal in CH₂Cl₂ to give an imidoselenium compound, which further reacted with mono-, di-, tri- or tetra-substituted olefins affording allylic amination products in good yield.^{9a}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



References

- (1) (a) Brenner, D. H. In *Synthetic Reagents*, Vol.6; Pizey, J. S., Ed.; Wiley: New York, **1985**, 9. (b) Emerson, D. W.; Wynberg, H. *Tetrahedron Lett.* **1971**, 3445.
- (2) (a) Damin, B.; Grapon, J.; Sillion, B. *Synthesis* **1981**, 362. (b) Damin, B.; Grapon, J.; Sillion, B. *Tetrahedron Lett.* **1980**, 21, 1709. (c) Damin, B.; Forestiere, A.; Grapon, J.; Sillion, B. *J. Org. Chem.* **1981**, 46, 3552.
- (3) Dyong, I.; Chi, Q. L. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 933.
- (4) Sharpless, K. B.; Chong, A. O.; O'Shima, K. *J. Org. Chem.* **1976**, 41, 177.
- (5) (a) Kabalka, G. W.; Gooch, E. E. *J. Org. Chem.* **1981**, 46, 2582. (b) Kabalka, G. W.; Sastry, A. R. K.; Hylarides, M. D. *J. Org. Chem.* **1981**, 46, 3113. (c) Kabalka, G. W.; Mereddy, A. R. *Tetrahedron Lett.* **2004**, 45, 1417.
- (6) Hassner, A.; Rai, K. M. L. *Synthesis* **1989**, 57.
- (7) (a) Ando, T.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **1998**, 39, 309. (b) Thakur, V.; Sudalai, A. *Tetrahedron Lett.* **2003**, 44, 989. (c) Ando, T.; Kano, D.; Minakata, S. R. I.; Komatsu, M. *Tetrahedron* **1998**, 54, 13485. (d) Simkhovich, L.; Gross, S. *Tetrahedron Lett.* **2001**, 42, 8089.
- (8) Li, G.; Chang, H.-T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 451.
- (9) (a) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, 98, 269. (b) Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1981**, 447.
- (10) Bossio, R.; Marcaccini, S.; Pepino, R. *Tetrahedron Lett.* **1995**, 36, 2325.
- (11) Misra, A. K.; Agnihotri, G. *Carbohydr. Res.* **2004**, 339, 885.