

SYNLETT Spotlight 347

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

Sodium Chlorite

Compiled by Marcelle Lima de Ferreira

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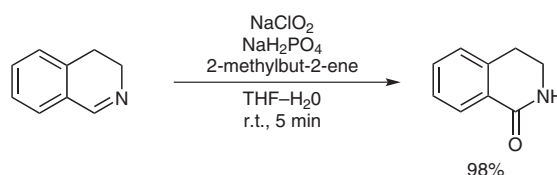
Introduction

Sodium chlorite (NaClO_2) is a highly efficient bleaching agent and oxidative disinfectant, widely applied in bleaching of textile, fiber, pulp and paper. In addition, this substance is employed to whiten sugar, starch, grease, ointment and wax.¹

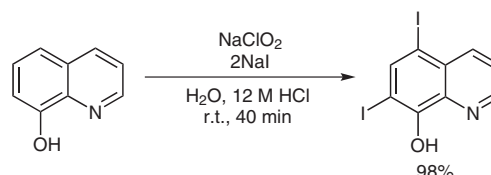
In organic synthesis, NaClO_2 is an inexpensive and versatile reagent, which has been explored for preparations of carboxylic acids from aldehydes² or primary alcohols³, amides from imines,⁴ enones from allylic and benzylic substrates,⁵ epoxides from olefins⁶ and γ -hydroxybutenolides from furans.⁷ Moreover, this reagent has also been employed in the oxidative deprotection of 1,3-dithiane groups,⁸ as oxidant and hydroxyl ion pump in osmium-catalyzed asymmetric dihydroxylation⁹ as well as in the iodination of aromatic and heterocyclic compounds.¹⁰

Abstracts

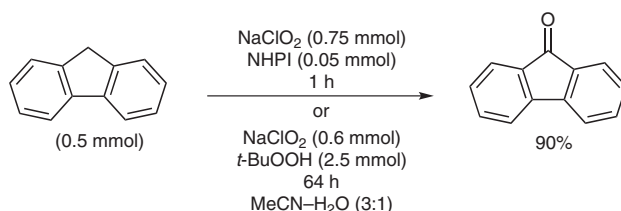
(A) Mohamed and co-workers reported a highly efficient oxidation of imines to the corresponding amides using sodium chlorite under buffered conditions. This method was applicable to linear as well as to cyclic imines in good to high yields. The good group tolerance, the mild buffered conditions and the use of cheap reagents are the main advantages of this protocol.⁴



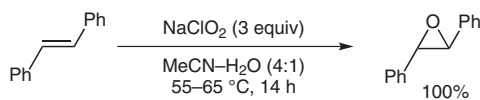
(B) Aromatic and heterocyclic compounds were efficiently iodinated using $\text{NaClO}_2/\text{NaI}$ system in presence of HCl . This protocol was applied for the iodination of phenols, aromatic amines and heterocyclic substrates, including nitrated derivatives, in good yields and with satisfactory purity by a simple extraction procedure and reductive washings with $\text{Na}_2\text{S}_2\text{O}_3$.¹⁰



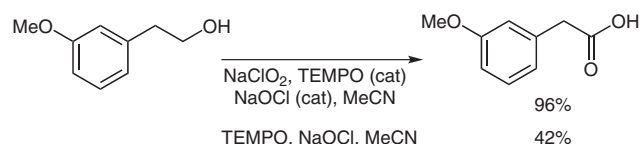
(C) Silvestre and Salvador reported the use of sodium chlorite either in combination with *tert*-butyl hydroperoxide, in stoichiometric conditions, or with *N*-hydroxyphthalimide as catalyst for mild, transition-metal-free and allylic or benzylic oxidations.⁵



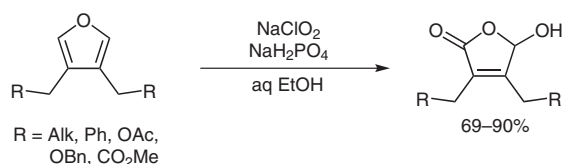
(D) A new valuable protocol for the racemic epoxidation of olefins that employs NaClO_2 as oxidant without the aid of catalyst in $\text{MeCN-H}_2\text{O}$ at 55–65 °C was reported for the first time by Geng and co-workers. The mechanistic studies show that chlorine dioxide is the key epoxidizing agent in this reaction.⁶



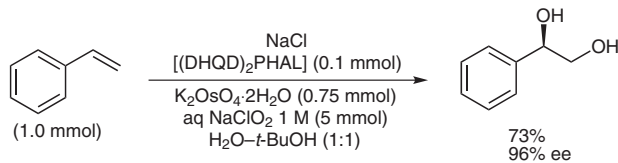
(E) An efficient and environmentally benign method for oxidizing primary alcohols to carboxylic acids using stoichiometric NaClO_2 , catalytic TEMPO and NaOCl was developed. In comparison with the TEMPO/NaOCl/ CH_2Cl_2 protocol,¹¹ this new methodology gives significantly improved yields and purity of the desired product by reducing the chlorination of the aromatic groups.³



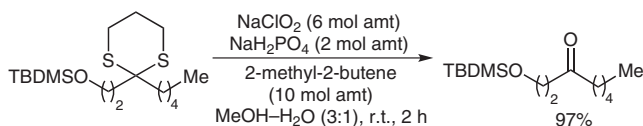
(F) Clive and co-workers reported that 3,4-disubstituted furans are converted into γ -hydroxy butenolides using NaClO_2 in aqueous EtOH containing NaH_2PO_4 . The presence of two ester groups attached directly to furan ring prevents the oxidation.⁷



(G) Sodium chlorite can be used as the stoichiometric reoxidant in Sharpless asymmetric dihydroxylation. One sodium chlorite provides the reaction with the stoichiometric number of electrons and hydroxide ions needed to dihydroxylate two olefins without the consumption of any additional base. The consumption of styrene in a NaClO_2 reaction is extremely fast compared with the corresponding unmodified and NaOH-modified $\text{K}_3[\text{Fe}(\text{CN})_6]$ processes.⁹



(H) A new facile and mild alternative for the deprotection of the 1,3-dithiane group was described by Ichige and co-workers. This protocol was developed using sodium chlorite, sodium dihydrogenphosphate, and 2-methyl-2-butene in $\text{MeOH-H}_2\text{O}$ (3:1) at room temperature in good yields.⁸



References

- Qian, Y.; Chen, Y.; Jiang, Y.; Zhang, L. *J. Cleaner Prod.* **2007**, *15*, 920.
- Dalcanale, E.; Montanari, F. *J. Org. Chem.* **1986**, *51*, 567.
- Zhao, M. M.; Li, J.; Mano, E.; Song, Z. J.; Tschaen, D. M. *Org. Synth.* **2005**, *81*, 195.
- Mohamed, M. A.; Yamada, K.; Tomioka, K. *Tetrahedron Lett.* **2009**, *50*, 3436.
- Sivestre, S. M.; Salvador, J. A. R. *Tetrahedron* **2007**, *63*, 2439.
- Geng, X.; Wang, Z.; Li, X.; Zhang, C. *J. Org. Chem.* **2005**, *70*, 9610.
- Clive, D. L. J.; Ou, L. *J. Org. Chem.* **2005**, *70*, 3318.
- Ichige, T.; Miyake, A.; Kanoh, N.; Nakata, M. *Synlett* **2004**, 1686.
- Junttila, M. H.; Hormi, O. E. O. *J. Org. Chem.* **2004**, *68*, 4816.
- Lista, L.; Pezzella, A.; Napolitano, A.; D'Ishia, M. *Tetrahedron* **2008**, *64*, 234.
- Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559.