

SYNLETT Spotlight 215

Sodium Hypochlorite (NaOCl)

Compiled by Hojat Veisi



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

Hojat Veisi was born in Ilam/Hollilan-Kahreh, Iran, in 1982. He received his B.Sc. in chemistry from Razi University, Kermanshah, Iran in 2003, and his M.Sc. in organic chemistry from Bu-Ali Sina University, Hamadan, under the guidance of Dr. Ahmad Khoramabadi Zad in 2005. Presently he is a Ph.D. student at Bu-Ali Sina University, Hamadan, under the supervision of Dr. Ramin Ghorbani-Vaghei. His research field is the synthesis and application of *N*-halo reagents in organic reactions. The purpose of this research is according to green chemistry.

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Introduction

Sodium hypochlorite (NaOCl), commonly known as bleach, is a strong oxidizing and bleaching agent. This reagent is one of the most important oxidants in organic synthesis and is a source of oxygen for olefin epoxidation.¹ NaOCl has found wide application in organic synthesis, such as chlorination of benzene derivatives,² epoxidation of olefins without metal catalysts,³ enantioselective epoxidation of alkenes with catalyst,⁴ selective oxidation of benzylic hydrocarbons,⁵ oxidation of alcohols,⁶ synthesis of 3-oxazolins,⁷ dihydroxylation of olefins,⁸ oxidation of aliphatic ethers to esters under ruthenium catalysis,⁹ etc. NaOCl has also been found useful for H₂S-odor control via oxidation of H₂S (Scheme 1).



Scheme 1

Commercially, NaOCl is available in solutions of various concentrations, with 12.5% (w/w) being the most common for bulk usage. This product contains 0.15 kg of available chlorine per liter.¹⁰ It is a liquid ($\rho = 1.206 \text{ g/ml}$ at 25 °C) which boils at 111 °C

Sodium hypochlorite is a solution made from the reaction of chlorine with a sodium hydroxide solution (Scheme 2).

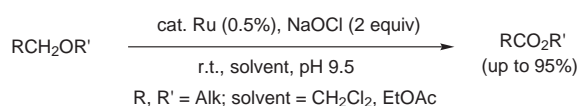


Scheme 2

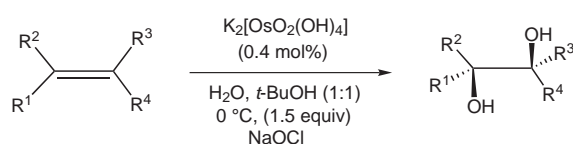
NaOCl is corrosive and oxidising, it has a variety of uses, and is an excellent disinfectant/antimicrobial agent. The advantages of using NaOCl include operational simplicity, availability, selectivity, and low cost, and it is a green medium for organic reactions.

Abstracts

(A) Luka Gonsalvi and co-workers reported a highly efficient use of NaOCl in the Ru-catalysed oxidation of aliphatic ethers to esters. The selectivity of α -oxidation of ethers to esters via Ru-NaOCl can be dramatically improved by pH control, at high substrate/catalyst ratios using a stoichiometric amount of hypochlorite in biphasic media at room temperature.⁹



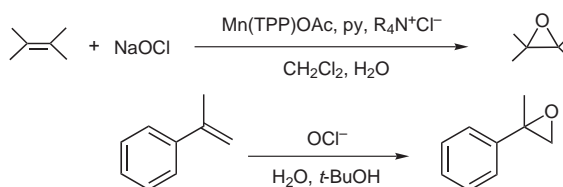
(B) A new practical method for the osmium-catalyzed dihydroxylation of olefins using bleach as the terminal oxidant is reported for the first time. Aromatic and aliphatic olefins yield the corresponding *cis*-1,2-diols in the presence of dihydroquinidine derivatives (Sharpless ligand) with good to excellent chemo- and enantioselectivities under optimized pH conditions. In the presence of a small excess of NaOCl as reoxidant fast dihydroxylation takes place even at 0 °C. Under optimum reaction conditions it is possible to dihydroxylate terminal aliphatic and aromatic olefins as well as internal olefins. The low price of the oxidant and the simple handling of bleach make this dihydroxylation variant attractive for further applications.⁸



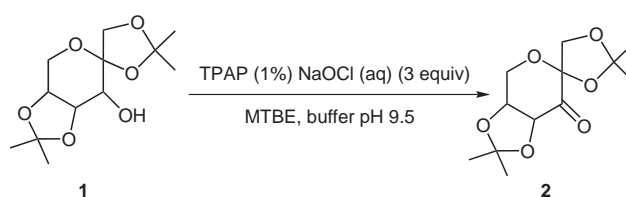
(C) Hopkins and Chisholm reported a useful method for the chlorination of benzene derivatives with cold aqueous NaOCl. The reaction gives good yields of monochloro derivatives when the orientation is favourable. Products chlorinated at the aromatic nucleus have been prepared in the present work from various substituted benzoic acids, arylacetic acids, aryloxyacetic acids and arylaldehydes, using sodium hypochlorite as the reagent. The results indicated that this method of halogenation is more widely applicable than previously supposed.²

| Substrate | Product | Yield (%) |
|---------------|----------|-----------|
| vanillin | 5-chloro | 0% |
| anisic acid | 3-chloro | 80% |
| vanillic acid | 5-chloro | 85% |

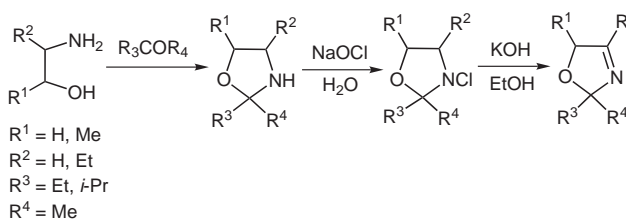
(D) A new catalytic route is reported for the epoxidation of simple olefins with NaOCl as oxygen source and manganese porphyrin complexes as catalyst. Among all the oxidants that are potentially donors of one oxygen atom, NaOCl has been shown to be a good reagent for efficient catalytic oxygenation reactions.¹ Also, an easy method reported for epoxidation of olefins using bleach and either a stoichiometric or a catalytic amount of bromide has been developed. Without any transition-metal catalyst a variety of non-activated olefins gives epoxides in high yields and good selectivity at ambient conditions.³



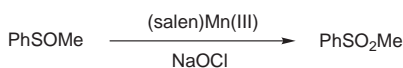
(E) Selective ruthenium-catalyzed oxidation of 1,2:4,5-di-*O*-isopropylidene- β -D-fructopyranose and other alcohols was reported by Luca Gonsalvi et al. The asymmetric epoxidation catalyst 1,2:4,5-di-*O*-isopropylidene- β -D-erythro-2,3-hexadiol-2,3-pyranose **2** was obtained in high yield from 1,2:4,5-di-*O*-isopropylidene- β -D-fructopyranose **1** via a recyclable ruthenium-catalyzed hypochlorite oxidation protocol under biphasic conditions (MTBE/water) in the presence of an alkaline buffer (pH 9.5). Other secondary alcohols were also oxidized selectively to the corresponding ketones.¹¹



(F) A series of new aliphatic 3-oxazolines was obtained in moderate to good yields via oxidation of the corresponding 1,3-oxazolidines by N-chlorination with sodium hypochlorite followed by elimination in basic medium. Some of the 3-oxazolines obtained present interesting properties in the field of fragrance chemistry.⁷



(G) Oxidation of aryl methyl sulfoxides with sodium hypochlorite catalyzed by (salen)Mn(III) complexes was reported by Chellamani and Harikengaram.¹²



References

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