**SYNLETT Spotlight**

**Spotlight 347**

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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**Sodium Chlorite**

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**Introduction**

Sodium chlorite (NaClO₂) 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, NaClO₂ is an inexpensive and versatile reagent, which has been explored for preparations of carboxylic acids from aldehydes² or primary alcohols¹, amides from imines,³ enones from allylic and benzylic substrates,⁴ epoxides from olefins⁵ and γ-hydroxybutenolides from furans.⁶ Moreover, this reagent has also been employed in the oxidative deprotection of 1,3-dithiane groups,⁷ as oxidant and hydroxyl ion pump in osmium-catalyzed asymmetric dihydroxilation⁸ as well as in the iodination of aromatic and heterocyclic compounds.⁹

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**Preparation**

The production of NaClO₂ using a reducing agent is the most common methodology used to manufacture this substance. This process consists in the preparation of chlorine dioxide by reacting sodium chlorate in sulfuric acid (Scheme 1a) and, then the reaction of chlorine dioxide with a reducing agent in sodium hydroxide solution (Scheme 1b). The chlorine dioxide generation is generally based on the reduction of sodium chlorate by reducing agents, such as sulfur dioxide, hydrochloric acid, sodium chloride, methanol and hydrogen peroxide.¹

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**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 NaClO₂/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 Na₂S₂O₃.¹⁰

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**Scheme 1**

(A) 2NaClO₃ + H₂SO₄ + H₂O₂ → O₂ + 2ClO₂ + 2H₂O + Na₂SO₄

(b) 2ClO₂ + 2NaOH + 2H₂O₂ → 2NaClO₂ + O₂ + 2H₂O

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(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.

\[
\begin{align*}
\text{NaClO}_2 (0.75 \text{ mmol}) & \quad \text{NHPI (0.05 mmol)} \\
& \quad 1 \text{ h}
\end{align*}
\]

or

\[
\begin{align*}
\text{NaClO}_2 (0.6 \text{ mmol}) & \quad \text{t-BuOOH (2.5 mmol)} \\
& \quad 64 \text{ h} \\
\text{MeCN–H}_2\text{O (3:1)}
\end{align*}
\]

(D) A new valuable protocol for the racemic epoxidation of olefins that employs NaClO₂ as oxidant without the aid of catalyst in MeCN–H₂O 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.

\[
\begin{align*}
\text{Ph} & \quad \text{NaClO}_2 (3 \text{ equiv}) \\
& \quad \text{MeCN–H}_2\text{O (4:1)} \\
55–65 °C, 14 \text{ h}
\end{align*}
\]

(E) An efficient and environmentally benign method for oxidizing primary alcohols to carboxylic acids using stoichiometric NaClO₂, catalytic TEMPO and NaOCl was developed. In comparison with the TEMPO/NaOCl/CH₃Cl protocol, this new methodology gives significantly improved yields and purity of the desired product by reducing the chlorination of the aromatic groups.

\[
\begin{align*}
\text{NaClO}_2, \text{ TEMPO (cat)} & \quad \text{NaOCl (cat), MeCN} \\
& \quad \text{TEMPO, NaOCl, MeCN}
\end{align*}
\]

(F) Clive and co-workers reported that 3,4-disubstituted furans are converted into γ-hydroxy butenolides using NaClO₂ in aqueous EtOH containing NaH₂PO₄. The presence of two ester groups attached directly to furan ring prevents the oxidation.

\[
\begin{align*}
\text{NaClO}_2 & \quad \text{NaH₂PO₄} \\
\text{aq EtOH} & \quad \text{R = Alk, Ph, OAc, OBF₃, CO₂Me}
\end{align*}
\]

(G) Sodium chlorite can be used as the stoichiometric reoxidant in Sharpless asymmetric dihydroxilation. 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 NaClO₂ reaction is extremely fast compared with the corresponding unmodified and NaOH-modified K₃[Fe(CN)₆] processes.

\[
\begin{align*}
\text{NaCl} & \quad \text{[(DHQD)₂PHAL] (0.1 mmol)} \\
\text{K₂OsO₄⋅2H₂O (0.75 mmol)} & \quad \text{aq NaClO₂ 1 M (5 mmol)} \\
\text{H₂O–t-BuOH (1:1)} & \quad \text{OH}
\end{align*}
\]

(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 MeOH–H₂O (3:1) at room temperature in good yields.

\[
\begin{align*}
\text{NaClO₂ (6 mol amt)} & \quad \text{NaH₂PO₄ (2 mol amt)} \\
\text{MeOH–H₂O (3:1), r.t., 2 h}
\end{align*}
\]

References