

SYNLETT Spotlight 181

Synthetic Applications of Oxone®

Compiled by Wei He



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

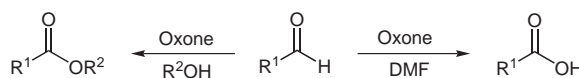
Oxone® consists of $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$; its active component is potassium peroxymonosulfate (KHSO_5), a powerful oxidizing agent in synthetic organic chemistry which has proved to be a versatile reagent for various organic transformations. Oxone® is commercially available and can be used immediately. Apart from its well-known applications as oxidizing agent in some transformations reviewed by Narsaiah,¹ it has found a number of other

applications in synthetic chemistry in recent years, such as deprotection of functional groups, functional-group transformations, and cleavage of linker molecules from solid support. It has also shown wide potential in chiral ketone-catalysed asymmetric epoxidation of alkenes² leading to a variety of natural product skeletons, where its unique regioselective properties gave excellent results for the preparation of key intermediates.

Abstracts

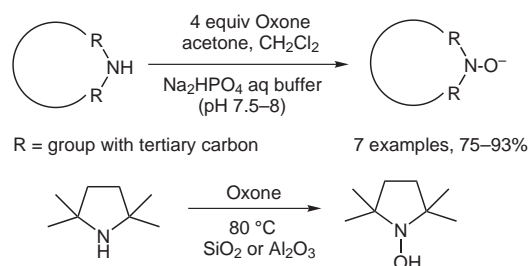
(A) Oxidation of aldehydes to acids and esters:

B. Borhan and coworkers³ reported a highly efficient, mild and simple protocol for the oxidation of aldehydes to carboxylic acids using Oxone® as the sole oxidant. Direct conversion of aldehydes to their corresponding esters in alcoholic solvents was also reported, which was proved to be a valuable alternative to traditional metal-mediated oxidations.



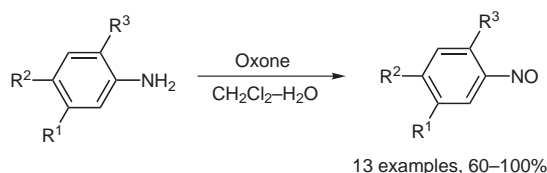
(B) Oxidation of alkyl amines to nitroxides and hydroxylamines:

Secondary amines were oxidized to the corresponding nitroxides with Oxone® in aqueous buffered solution at 0 °C and yields of 75–93% can be obtained for different substrates.⁴ When Oxone® is supported on silica or alumina, primary and secondary amines can also be oxidized selectively to hydroxylamines in either the presence or absence of a solvent.⁵



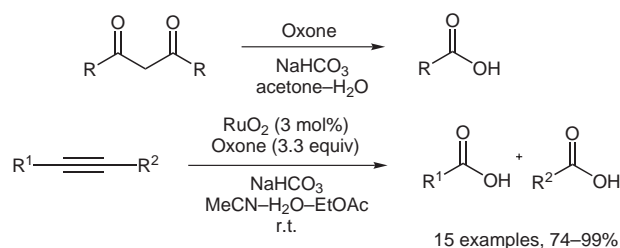
(C) Oxidation of aromatic amines to nitro- or nitrosoarenes:

Apart from oxidation to nitro compounds with Oxone® in 5–20% aqueous acetone and buffered sodium bicarbonate,⁶ aromatic amines can also be oxidized to nitrosoarenes in CH_2Cl_2 – H_2O in good to excellent yields.⁷

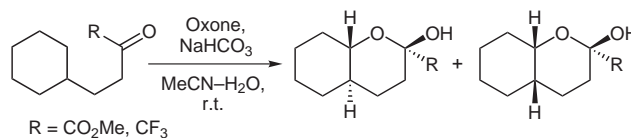


(D) *Oxidative cleavage of 1,3-dicarbonyls and alkynes to carboxylic acids:*

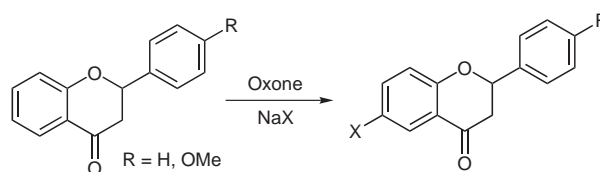
Using Oxone® as oxidizing agent, 1,3-dicarbonyls were transformed to carboxylic acids in good yield.⁸ Also alkynes were transformed to carboxylic acids with ruthenium-catalyzed Oxone® oxidative cleavage.⁹

(E) *Oxidation of unactivated C–H bonds:*

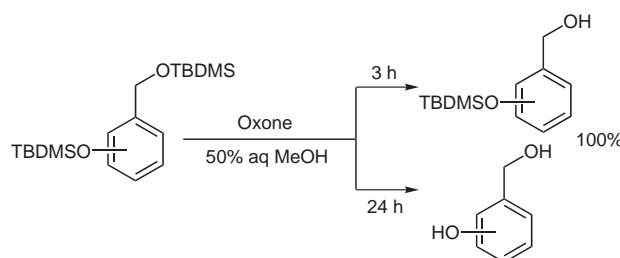
D. Yang and coworkers¹⁰ have reported the intramolecular oxidation of unactivated C–H bonds by dioxiranes generated in situ. This method has been applied successfully for the construction of novel tetrahydropyran derivatives.

(F) *Selective halogenation reaction:*

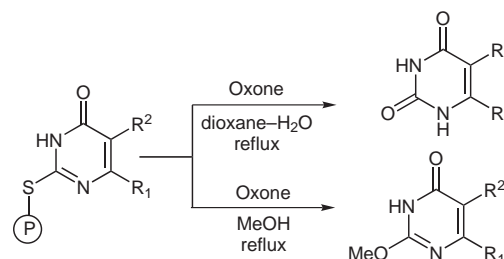
When using NaX combined with Oxone®, selective halogenation could be carried out effectively in some flavanones.¹¹

(G) *Deprotection of tert-butyldimethylsilyl ethers:*

G. Sabitha et al.¹² have reported an approach for the cleavage of *tert*-butyldimethylsilyl ethers by Oxone® in 50% aqueous methanol at room temperature. This method enables one to deprotect *tert*-butyldimethylsilyl ethers to yield primary alcohols in the presence of *tert*-butyldimethylsilyl ethers of secondary and tertiary alcohols and phenols, which could tolerate a wide variety of other functional groups. The silyl ethers of phenols were also deprotected after longer reaction times.

(H) *Cleavage methodology for solid-phase synthesis:*

E. Petricci¹³ et al. have developed an original and highly efficient Oxone® cleavage methodology for the solid-phase synthesis of substituted uracils.



References

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