SYNLETT
Spotlight 181

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

Synthetic Applications of Oxone®

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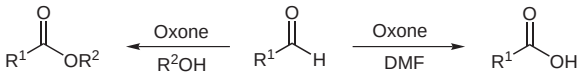
Introduction

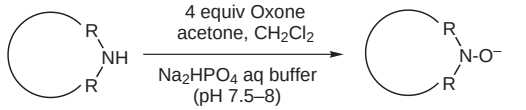
Oxone® consists of $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$; its active component is potassium peroxymonosulfate ($KHSO_5$), a powerful oxidizing agent in synthetic organic chemistry which has proved to be a versatile reagent for various organic transformations. Oxone® is commercially available and can be 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 alkenes[2] 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 coworkers[3] 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.

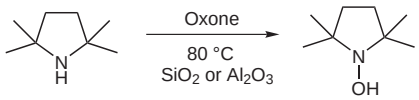


(B) *Oxidation of alkyl amines to nitroxides and hydroxylamines:*
Secondary amines were oxidized to the corresponding nitroxides with Oxone® in aqueous buffered solution at 0 °C and yields of 75–93% can be obtained for different substrates.[4] When Oxone® is supported on silica or alumina, primary and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

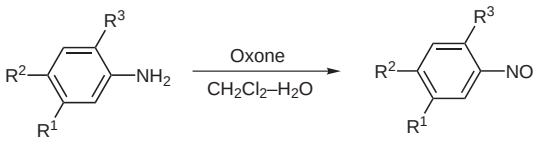


R = group with tertiary carbon

7 examples, 75–93%



(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]



13 examples, 60–100%

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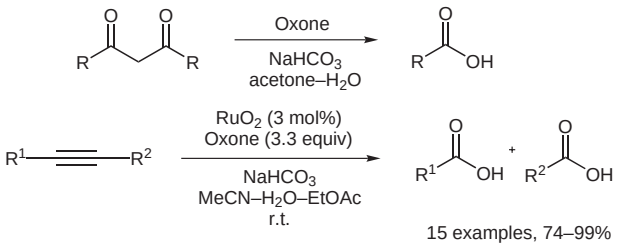
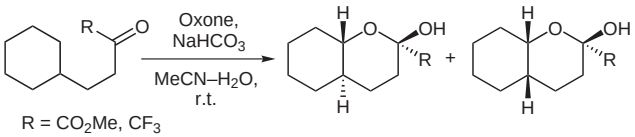
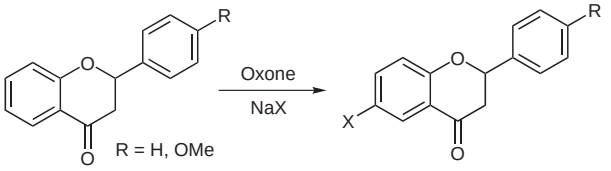
(D) *Oxidative cleavage of 1,3-dicarbonyls and alkynes to carboxylic acids:*
Using Oxone® as oxidizing agent, 1,3-dicarbonyls were transformed to carboxylic acids in good yield.[8] Also alkynes were transformed to carboxylic acids with ruthenium-catalyzed Oxone® oxidative cleavage.[9]



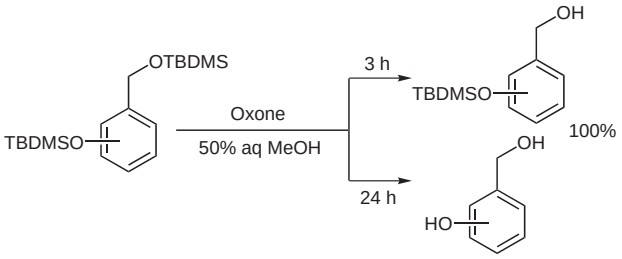
(E) *Oxidation of unactivated C–H bonds:*
D. Yang and coworkers[10] have reported the intramolecular oxidation of unactivated C–H bonds by dioxiranes generated in situ. This method has been applied successfully for the construction of novel tetrahydropyran derivatives.



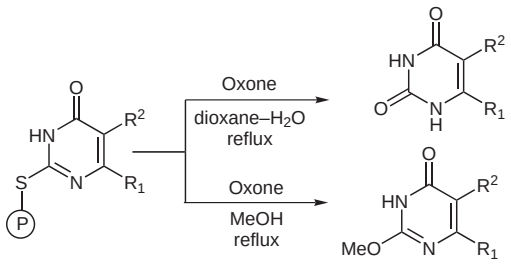
(F) *Selective halogenation reaction:*
When using NaX combined with Oxone®, selective halogenation could be carried out effectively in some flavanones.[11]



(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. Petricci[13] et al. have developed an original and highly efficient Oxone® cleavage methodology for the solid-phase synthesis of substituted uracils.



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