CHEMICAL REVIEWS

Review

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Journey Describing Applications of Oxone in Synthetic Chemistry

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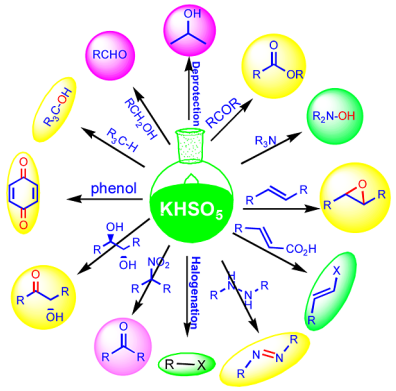

CONTENTS

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1. INTRODUCTION

The existence of a peroxygen acid of sulfur was recognized nearly one and half centuries ago,[1,2] but it was not until 1898 that Caro[3] demonstrated the existence of two such acids. It was known to Caro at the time that salts of persulfuric acid (peroxydisulfuric acid, $H_2S_2O_8$) converted aniline into an insoluble dye (aniline black). When Caro treated aniline with a solution of ammonium persulfate in concentrated sulfuric acid, he obtained nitrobenzene but no aniline black. Three years later, Baeyer and Villiger[4] published conclusive evidence that Caro's acid was peroxymonosulfuric acid (H_2SO_5). Peroxysulfuric acid (H_2SO_5), commonly called Caro's acid because it was first described by the German chemist Heinrich Caro,[3] and its potassium salt are both oxidizing agents and have been known for this property for some time. However, they were not used in organic synthesis to any degree, which is not that surprising due to their explosive character.[5] Today a potentially explosive substance that once proved difficult to isolate, purify, and identify now exists as a stable triple salt ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$). Potassium peroxymonosulfate is marketed by Evonik (formerly Degussa) under the trade name Caroat and DuPont under the trade name Oxone. Martin prepared Oxone by reacting a H_2O_2 solution containing 70 wt % H_2O_2 with oleum and an alkali potassium compound.[6] Similarly, Wolfgang and Siegfried prepared Oxone from sulfuric acid, hydrogen peroxide, and potassium hydroxide.[7]

Oxone is a white Crystallin solid, easy to handle, not toxic, soluble in water, and, above all, cheap and stable. The commercial triple salt contains only about 50% of active oxidant per mole, and in 2002 a new procedure was developed to prepare pure potassium monoperoxysulfate.[8] The active oxidant within the mixture, the anion peroxymonosulfate (HSO_5^-), has been the subject of a great deal of study in various fields.[8] Generally, reaction with Oxone is performed in water, methanol, acetone, DMF, or a miscible mixture including one of the above-mentioned solvents. To overcome the need for aqueous conditions, Chrobok[9] used ionic liquid as solvent for Baeyer–Villiger reaction, and also several tetraalkylammonium salts of Oxone have been reported.

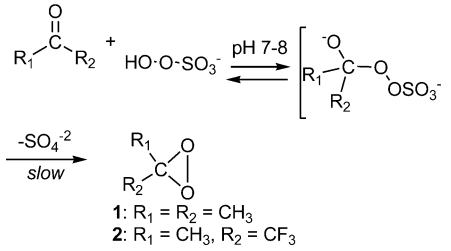
These tetraalkylammonium salts of Oxone include ammonium peroxymonosulfate, tetra-*n*-butylammonium peroxymonosulfate (TBA-OX), tetra-*n*-pentylammonium peroxymonosulfate, and tetra-*n*-hexylammonium peroxymonosulfate.[8,10,11] In 1985, Dehmlow et al. reported a methodology to prepare TBA-OX and other tetraalkylammonium salts of peroxymonosulfate by cationic exchange from Oxone.[10] However, it was only in 1988 that Trost and co-workers popularized TBA-OX as an organic soluble form of Oxone that was capable of oxidizing sulfides to sulfones under anhydrous conditions.[11] This reagent was prepared from cationic exchange of the bulk potassium ions and thus yielded a soluble version of the triple salt, i.e., tetra-*n*-butylammonium salts of sulfate and bisulfate were also formed. The oxidative activity of nBu_4NHSO_5 was 37.5% of the actual weight. A second type of soluble peroxymonosulfate has been described recently by Hajipour and co-workers.[12] The reported benzyltriphenylphosphonium peroxymonosulfate salt has the ability to perform some of the oxidative reactions that have been well developed for Oxone.[8] One minireview was previously published in 2003 with 83 references.[5]

2. GENERAL REACTIVITY

2.1. Reaction with Ketones

Edwards et al.[13] perfomed reactions between Oxone and simple ketones first in 1979 at a pH close to neutrality (7.5–8.0) and generated dioxiranes. Later syntheses of different chiral dixoranes (**1** and **2**) were reported by reaction of Oxone with chiral ketones. Dioxiranes are three-membered rings and essentially represent strained peroxides that might be considered as paradigm reagents of electrophilic O transfer. Stringent kinetic, stereochemical, and ^{18}O-labeling data allowed establishment of a likely mechanism for dioxirane formation to be proposed (Scheme 1).[13,14]

Scheme 1. Synthesis of Dioxiranes



The dioxirane generated in solution can accept attack by further caroate ions, yielding sulfate ion and molecular oxygen. However, in a competitive process, it can then also be attacked by a variety of electron-rich substrates, viz., "S", yielding the oxidation product "SO" (Scheme 2). In both reactions, the parent ketone is regenerated, so it returns to the catalytic cycle.[13,15]

2.2. Reaction with Halides

Oxone reacts with metals and ammonium halides, and the reaction proceeds through formation of hypohalous acid (HOX).[16] Hypohalous acid has a higher degree of instability due to its pronounced ionic nature, and it is thus more reactive

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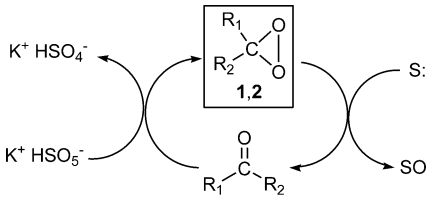
Scheme 2. Mechanism for the Generation of Dioxiranes from Oxone and Ketones



toward the aromatic nucleus. Scheme 3 presents the overall stoichiometry of the reaction. Generation of hypohalous acid

Scheme 3. Mechanism for Generation of HOX from Oxone and Halides

$$ArH + MX + 2KHSO_4\text{-}KHSO_5\text{.}K_2SO_4 \longrightarrow ArX + MOH + K_2S_2O_8\text{-}KHSO_4\text{.}K_2SO_4 + H_2O \quad (1)$$

$$2KHSO_5\text{-}KHSO_4\text{.}K_2SO_4 + MX \longrightarrow HOX + MOH + K_2S_2O_8\text{-}KHSO_4\text{.}K_2SO_4 \quad (2)$$

$$2HOOSO_3K \longrightarrow 2(\dot{O}H) + 2(\dot{O}SO_3K) \quad (3)$$

$$MX + 2(\dot{O}H) + 2(\dot{O}SO_3K) \longrightarrow MOH + HO\text{-}X^+ + K_2S_2O_8 \quad (4)$$

M = Metal, NH_4

(HOX) is shown by eq 2 in Scheme 3; eq 3 in Scheme 3 represents dissociation of the active component (from Oxone) into radicals. Then the resultant OH radical oxidizes the MX to produce HOX and MOH as shown by eq 4 (Scheme 3). Finally, the HOX delivers an X^+ for further reaction.[16] Interestingly, HOX is used for halgenation of organic compounds[16] (see section 7) as well for oxidation of benzylic alcohols.[17]

3. OXIDATION OF C−H BONDS

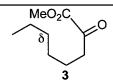
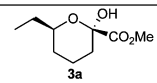
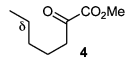
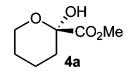
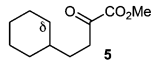
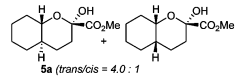
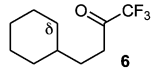
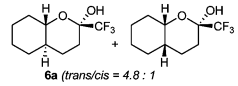
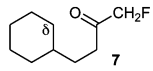
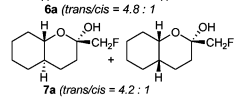
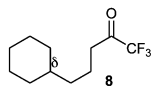
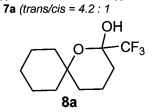
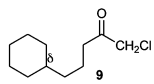
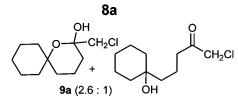
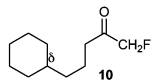
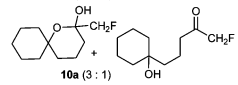
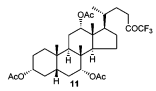
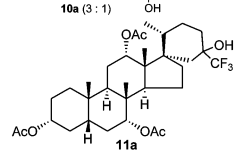
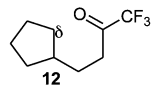
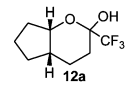
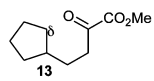
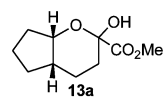
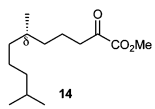
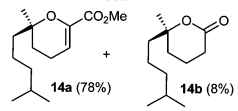
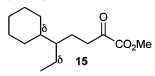
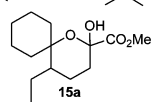
3.1. Oxidation of Unactivated C−H Bonds

Selective functionalization of saturated hydrocarbons is of significant importance for both basic research and practical applications in synthetic organic chemistry. Development of efficient methods for regio- and stereoselective C−H bond activation has attracted considerable attention over the past decades.[18−32] Owing to geometric constraints, intramolecular reactions represent an effective approach for regioselective functionalization of C−H bonds.[33−55] Yang et al.[56] reported a preliminary study of a novel reaction for oxidation of unactivated C−H bonds at the δ site of aliphatic ketones to synthesize tetrahydropyrans.[57] Dioxiranes, which are generated from a ketone and Oxone in these reactions (Schemes 1 and 2), have excellent reactivity toward unactivated C−H bonds under mild and neutral conditions. The oxidation reaction is both stereospecific and has a more selective preference for tertiary C−H bonds over secondary ones. Initially oxidation of linear α-keto esters **3** and **4** was found to give hemiketals **3a** (70% yield) and **4a** (86% yield), respectively, as the major oxidation products (Table 1).

In this work it is of note that despite the presence of several other secondary C−H bonds, it is specifically the δ C−H bonds that were selectively oxidized. In each of the branched substrates **5**−**10**, there is one tertiary C−H bond in addition to several secondary ones, and interestingly, only the δ site was oxidized (entries 3−8, Table 1). Here intermolecular C−H

Table 1. Selective Oxidation of the C−H Bond

Ketone (10 mM) —Oxone/$NaHCO_3$, CH_3CN/H_2O, rt, 24 h→ Product

entry	Ketone	Product	Yield (%)	Ref
1			70	56
2			86	56
3			83	56
4			87	56
5			70	56
6			78	56
7			77	56
8			73	56
9			58	56
10			74	58
11			67	58
12			86	58
13			73	58

bond oxidation by dioxiranes is unlikely as reactions of compounds **5**−**7** proceeded via selective oxidation of secondary C−H bonds and concomitant ring closure to form 6-membered rings despite the presence of tertiary C−H bonds. Similarly, Wong et al. reported on selective intramolecular oxidation of ketones **12**−**15**.[58] In contrast to the hydroxylation reactions of ketones **5** and **6** bearing a cyclohexane ring, hydroxylation reactions of trifluoromethyl ketone **12** and α-keto ester **13** bearing a cyclopentane ring provided exclusively the cis bicyclic products **12a** (74% yield) and **13a** (67% yield), respectively (Table 1, entries 10 and 11). Oxidation of ketone **14** afforded the dehydrated cyclic product **14a** in 78% yield together with lactone **14b** in 8% yield (Table 1, entry 12). Formation of lactone **14b** was probably due to the Baeyer−Villiger rearrangement. Oxidation of **15** took place exclusively at the tertiary C−H bond to give **15a** (73% yield), and no product

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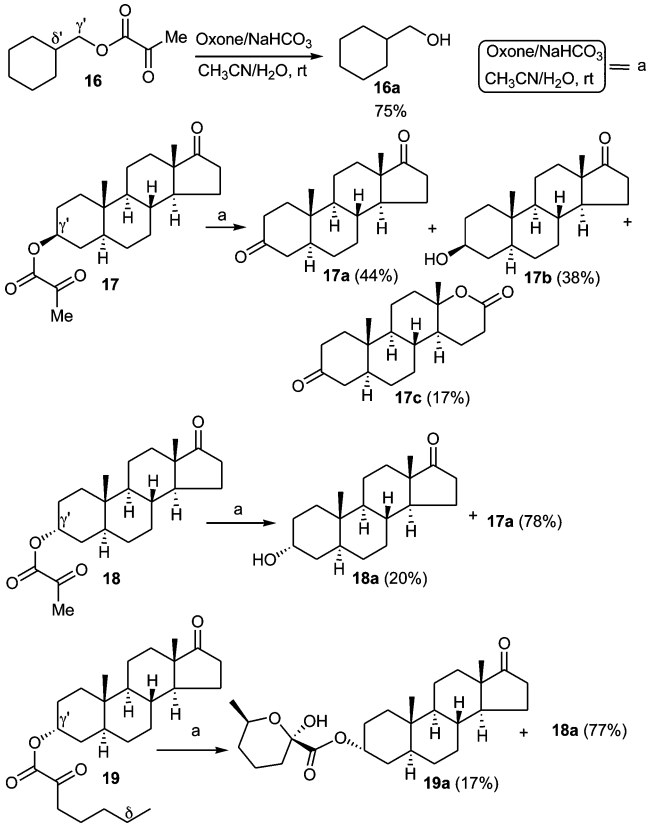
derived from oxidation of any secondary alternative C−H bond was found (Table 1, entry 13).

3.2. Oxidation of the C−H Bond of Ketones

Wong et al. also reported dioxirane-mediated oxidation of a C−H bond in ketones.[58] Ketone **16** has a tertiary δ' and a γ' C−H bond, and the secondary C−H bonds are adjacent to the oxygen atom of the ester moiety. Ketone **16** was subjected to the oxidation reaction conditions (10 mM), but no oxidized product and only hydrolyzed product cyclohexanemethanol **16a** was obtained (Scheme 4). In contrast, oxidation of the C3-

Scheme 4. Oxidation of the C−H Bond of Ketones



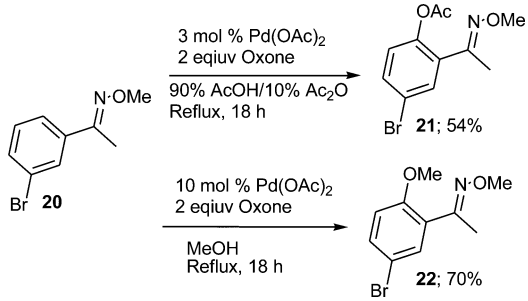
epimers **17** and **18**, both bearing a tertiary γ' C−H bond, afforded androstane-3,17-dione (**17a**) after 120 h as the major product along with the ester hydrolysis products **17b** and **18a**. In the oxidation of **17**, a further minor product **17c** was also isolated (17% yield), which presumably arose from the Baeyer−Villiger oxidation of **17a** by Oxone. Control experiments further indicated that **17a** could not be generated from intermolecular oxidation of androsterone **17b** and epiandrosterone **18a** by methyl pyruvate and Oxone at the same substrate concentration (1.5 mM). It was thus proposed that **17a** is formed through a regioselective intramolecular oxidation of the axial and equatorial tertiary γ' C−H bonds of **17** and **18**, respectively. The dioxirane generated from the ketone moieties of **17** and **18** could contort back to oxidize the C−H bonds under a spiro transition state to afford hemiketals, which were then hydrolyzed to give **17a**. Overall, oxidation of **17** and **18** to **17a** by Oxone constitutes an alternative to the known photolysis reaction reported by Binkley.[59,60]

To investigate the relative reactivity of the intramolecular δ C−H bond and the γ' C−H bond in the oxidation reactions, ketone **19** was subjected to oxidation. Interestingly, ketone **19** has the activated ketone group and also there are two secondary δ C−H bonds connected to a tether of three sp^3 carbons. On the other side, there is an equatorial tertiary γ' C−H bond linked to a tether of an ester group (sp^2 hybridized). Under both reaction conditions (at 10 and 1.5 mM), hemiketal **19a** and epiandrosterone **18a** were obtained, resulting from oxidation of the δ C−H bond of the ketone side chain and ester hydrolysis, respectively. These results indicated that oxidation of the δ C−H bond in saturated hydrocarbon chains was much more favorable than that of the γ' C−H bond.

3.3. Oxidation of Aromatic C−H Bonds

Carbon−hydrogen bond oxygenation reactions with Oxone are particularly attractive because they can be easily, safely, and inexpensively scaled upward. For example, acetoxylation of **20** proceeds cleanly and efficiently when carried out on a scale of 15 g of substrate. An approximately 100-fold increase in scale is also possible, provided the initially optimized reaction conditions are employed. Product **21** was readily isolated via Kugelrohr distillation in 54% yield (Scheme 5). Notably, the

Scheme 5. Oxidation of Aromatic C−H Bonds Using Oxone



large-scale reaction was conducted using just 3 mol % of $Pd(OAc)_2$, and the catalyst loading could potentially be reduced even further, albeit with longer reaction times. Changing the solvent from acetic acid to methanol resulted in the methoxy analogue **22** being produced in a 70% isolated yield.[61] Oxone could be utilized as terminal oxidants for these transformations but not the source of the oxygen atom incorporated into products **21** and **22**. Furthermore, a wide variety of functional groups, including aryl halides, nitriles, ethers, enolizable oxime ethers, amides, and benzylic C−H bonds, were tolerated under oxidizing reaction conditions. In fact, in some cases, Oxone showed substantially improved functional group tolerance.

3.4. Oxidation of Hydrocarbon Unactivated C−H Bonds

Besides the numerous methods used for synthesis of dioxiranes in situ, a major breakthrough resulted from the finding that a few representatives of this family of peroxides, chiefly dimethyldioxirane DDO (**1**)[62,63] and its trifluoro analogue TFDO (**2**),[64] could actually be isolated (in solution together with the parent ketone) by a simple process amounting to codistillation from buffered ketone−caroate mixtures. A few representative cases might serve to illustrate the key feature of dioxirane reactivity, that is, its efficiency to give selective O-atom insertions into alkane and cycloalkane C−H bonds under extremely mild conditions so that even simple "unactivated" hydrocarbons can be oxyfunctionalized (Scheme 6). Inspection of Scheme 6 suggests that these oxidations may generally require reaction times of hours and excess oxidant when employing DDO.[15,65,66] Also, over long reaction times or

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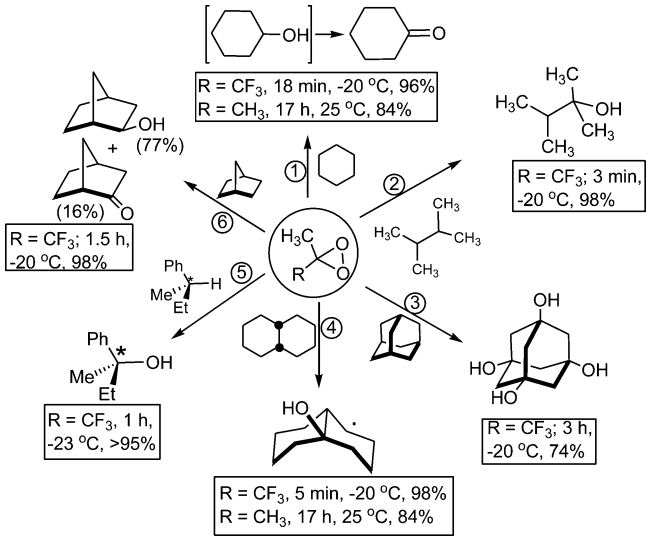
Scheme 6. Dioxirane-Mediated Oxidation of Hydrocarbon C−H Bonds



abnormal reaction conditions (depletion of dissolved air O_2 and nitroxide initiators), DDO free radical reactivity might be triggered.[67,68] By way of contrast however, the more powerful TFDO is capable of effecting these transformations often in a matter of minutes and with unchanged selectivity.[65] In this respect, quite noticeable is the practically complete conversion of cyclohexane into cyclohexanone by TFDO (transformation 1) in over 95% yield at −20 °C during ca. 18 min that is quite noteworthy. Furthermore, it was discovered that both DDO and TFDO are most effective and useful in the transformation of alcohols into carbonyl compounds.[69]

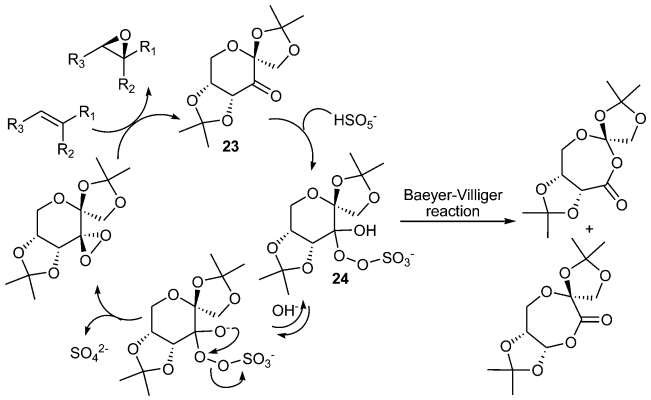
With the notable exception of norbornane (transformation 6, Scheme 6), in general TFDO oxygenations of alkanes are typified by preferential tertiary C−H bond oxidations vs secondary selectivities. Indicative of this finding is the selective bridgehead hydroxylation of adamantane by TFDO to yield tetrahydroxy adamantane (transformation 3), accompanied only by its trihydroxy analogue. In this reaction, kinetic data demonstrated that TFDO is more reactive than DDO by a factor of ca. 10^3. However, bearing the reactivity−selectivity principle (RSP) in mind,[15] the experimentally found selectivity for tertiary bridgehead C−H hydroxylation remains unchanged despite the much higher TFDO reactivity. As exemplified by the stereospecific bridgehead hydroxylation of *cis*-decalin (transformation 4), the high regio- and stereoselectivities recorded with DDO are maintained (and even enhanced) using TFDO. Also, optically active (−)-2-phenylbutane can be cleanly converted by TFDO into 2-phenyl-2-butanol in over 90% yield and with complete retention of configuration (transformation 5). It is now well established that oxygen-atom transfer from dioxiranes to nucleophilic two-electron or charge donors (e.g.,S = sulfide, phosphine, alkene) involves an S_N2-type displacement at the peroxide O−O bond with concerted bond breaking of the O−O bond and formation of a S−O bond.[15,70] It is thus unlikely that dioxirane O insertion into a C−H bond would proceed via the conventional S_N2 pathway since it involves C−H bond cleavage in the hydrocarbon fragment in addition to breaking of the peroxide O−O bond and of course would involve an inversion of configuration. A series of carefully developed mechanistic studies has discounted the possibility that these reactions proceed via a free-radical pathway. For instance, the kinetic isotope effect (KIE) for oxygen insertion into a tertiary C−H bond (k_H/k_D ca. 2.2 with TFDO and ca. 5 with DDO) and the mentioned selective hydroxylation of (−)-2-phenylbutane with complete retention of configuration strongly militates against a radical pathway and rather supports a mechanism involving concerted electrophilic O insertion.[15]

4. OLEFIN FUNCTIONALIZATION

4.1. Asymmetric Epoxidation of Olefins

Optically active epoxides are highly desirable and versatile intermediates since they can be converted into a wide variety of enantiomerically enriched molecules. Various useful methods have been developed for preparation of chiral epoxides, and thus, asymmetric epoxidation of olefins provides an excellent approach to the synthesis of such optically active epoxides.[13,70−87] Asymmetric epoxidation can be performed using dioxiranes which are usually generated from Oxone and chiral ketones (Scheme 7).[88] Oxone is effective for generation of

Scheme 7. Dioxiranes-Mediated Asymmetric Epoxidation Generated from Oxone and Chiral Ketones



dioxiranes and used as the oxidant for ketone-mediated epoxidations (Scheme 7). These epoxidations proceed via in-situ-generated dioxiranes and often require a range of pH 7−8.[13,88,89] However, higher pHs often lead to the rapid autodecomposition of Oxone.[90−92] Control of pH for expoxidation suppresses the decomposition of ketone **23**, and Baeyer−Villiger oxidation of the intermediate **24** could be one of the possible decomposition pathways for ketone **23**.

Dioxiranes, generated from Oxone and ketones, are remarkably versatile oxidizing agents that have demonstrated encouraging potential for asymmetric epoxidation of unfunctionalized olefins (Figure 1)[86,88,93−128] Interestingly, all types of olefins are able to be epoxidized with high ee.[86,88,93−128] Different chiral ketones,[86,88,93−128] chiral iminium salts, and chiral amines[86,88,129−135] were used in combination with Oxone for asymmetric epoxidation of olefins. High enantioselectivities were obtained for a variety of trans and trisubstituted olefins (Figure 1).

In order to rationalize the mechanism for asymmetric epoxidation of olefins, two transition state geometries, viz., spiro and planar, have been suggested for epoxidation with dioxiranes (Figure 2).[15,83,86,88,110,111,113,136−140] Some authors observed that epoxidation of cis hexenes with dimethyldioxirane was 7−9 times faster than that for the corresponding trans hexenes. These data suggested a spiro transition state was

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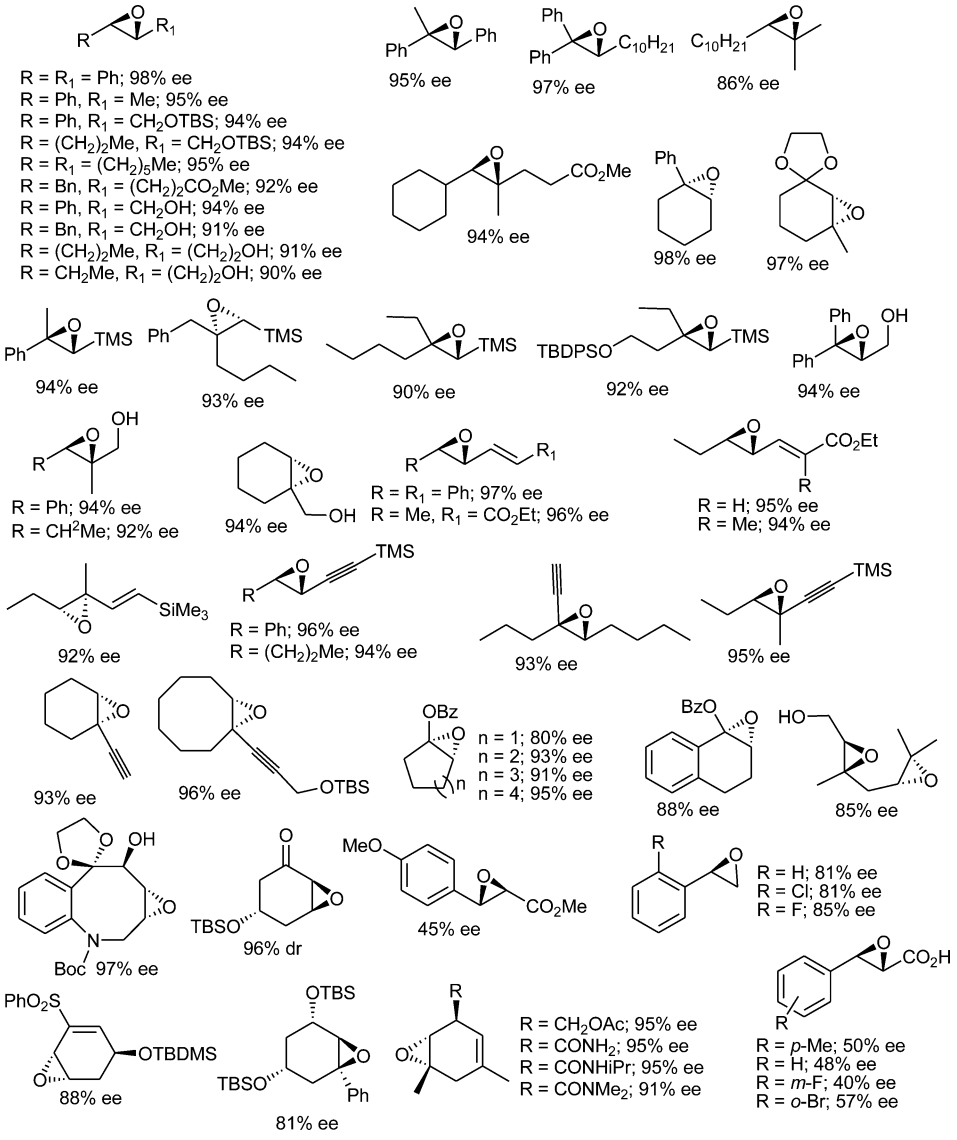

Figure 1. Asymmetric epoxidation of olefins using Oxone and chiral ketones.

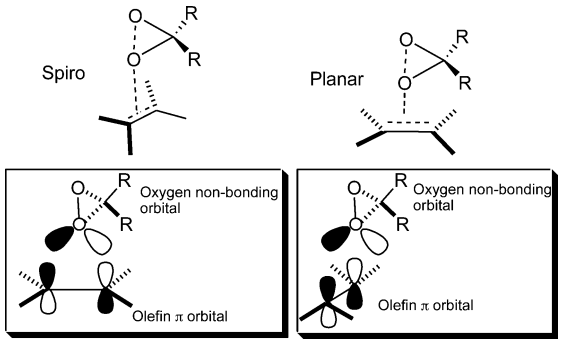

Figure 2. Spiro and planar transition states suggested for epoxidation with dioxiranes.

mostly the more favored one.[80] This was also confirmed by computational studies which showed that the spiro transition state is favored and presumably due to the stabilizing interaction of an oxygen lone pair with the π^* orbital of the alkene in the spiro transition state (Figure 2).[86,88,137,138]

4.2. Hydroxybromination and Dibromination of Olefins

Bromohydrins are usually prepared by ring opening of epoxides[141−147] using either hydrogen bromide or metal bromides. These procedures are generally associated with formation of byproducts such as vicinal dibromides and 1,2-diols, and additionally, these methods require prior synthesis of the epoxides. Apart from this, there are two general approaches for heterolytic addition of water and bromine to an olefinic bond. One involves use of molecular bromine or *N*-bromoimides,[148−156] and the other uses metal bromide or HBr along with an oxidizing agent.[153−160] Recently, Macharla et al.[141] reported a very simple, mild, and efficient method for direct synthesis of bromohydrins and dibromides from olefins using Oxone (as an oxidant) and NH_4Br (as a bromine source) without any catalyst in a highly regio- and stereoselective fashion and in a short reaction time. Aromatic olefins as well as cyclic and linear olefins also provided the corresponding hydroxybrominated products in moderate to high yields. Disubstituted olefins exclusively yielded the Markovnikov products, while with monosubstituted linear olefins, a limited amount of anti-Markovnikov product was also observed.[141] For

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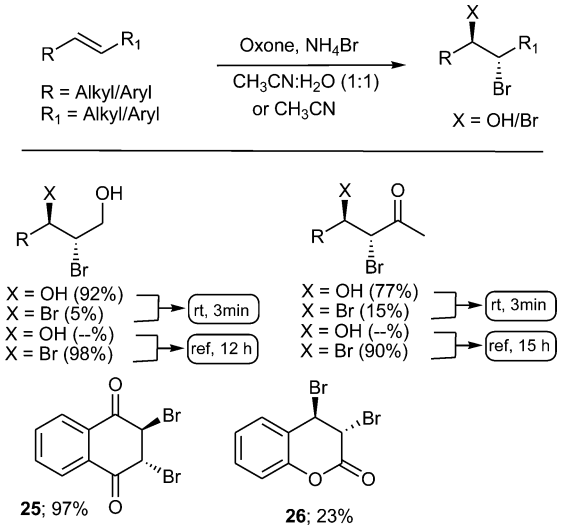
example, 1-dodecene provided the Markovnikov product (1-bromododecan-2-ol) as well as the anti-Markovnikov product (2-bromododecan-1-ol) in 47% and 14% yields, respectively (Scheme 8). Mixed regioselectivity was also observed with

Scheme 8. Hydroxybromination and Dibromination of Olefins

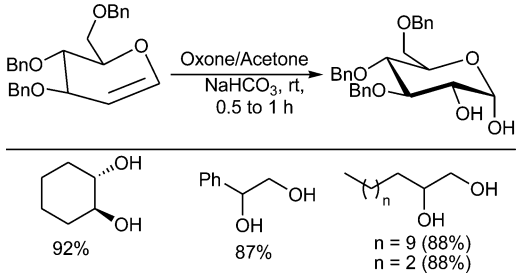


linear asymmetric *trans*-alkenes, viz., *trans*-2-octene afforded erythro-2-bromooctan-3-ol and erythro-3-bromooctan-2-ol in the ratio of 25:36. Bromohydroxylation of electron-deficient double bonds in 1,4-naphthoquinone and coumarin failed with only dibrominated products **25** and **26**, respectively, being isolated.[141]

4.3. Dihydroxylation of Olefins

A number of glycals and noncarbohydrate substrates have been converted into the respective 1,2-diols using a mixture of Oxone and acetone in good yields.[161] Various examples of differently protected glycals were investigated and provided moderate to good yields of the respective diols (almost a 1:1 anomeric mixture of the diols) (Scheme 9). The stereo-

Scheme 9. Synthesis of 1,2-Diols from Olefins Using Oxone and Acetone

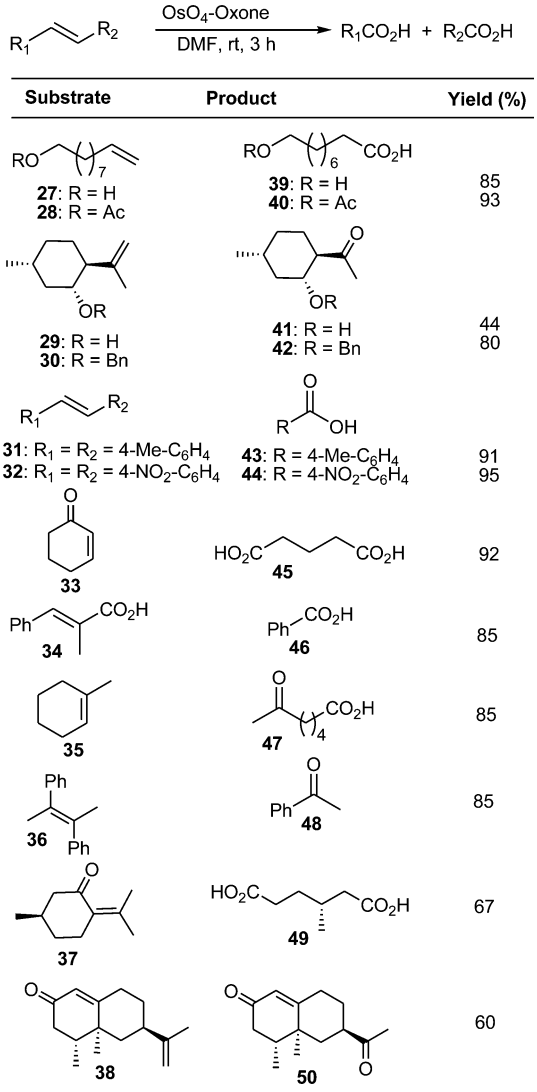


chemistry at C-2 was equatorial in every case. Interestingly, among the noncarbohydrate substrates, cyclohexene gave a good yield of the diol, but stilbene provided an epoxide, and in some cases the reaction was incomplete. It is known that formation of epoxides and their subsequent ring opening occurs better with glycals as substrates. This is why glycals are more nucleophilic than simple olefins, and the corresponding epoxides are thus more reactive toward ring opening.[161]

4.4. Oxidative Cleavage of Olefins

Selective oxidative cleavage of various olefins provided carboxylic acids or ketones using catalytic amounts of OsO_4 and Oxone in DMF as solvent (Scheme 10).[162,163] Initial

Scheme 10. Oxidative Cleavage of Olefins with the OsO_4–Oxone System



investigation of the oxidative cleavage of *trans*-stilbene cleanly provided benzoic acid in 95% yield. Similarly *trans*-cinnamic acid, styrene, and methyl cinnamate were also easily transformed to benzoic acid in 97%, 94%, and 96% yields, respectively. Cyclohexene and cyclooctene afforded the corresponding adipic acid and suberic acid in good yields. Additionally, simple alkyl olefins such as 1-decene, 1-nonene, and trans-2-nonene all afforded the appropriate alkyl carboxylic acids in excellent yields. The ester, methyl oleate afforded clean conversion to nonanoic acid and nonanedioic acid monomethyl ester.[164] A number of monosubstituted, 1,1-disubstituted, 1,2-disubstituted, trisubstituted, and tetrasubstituted olefins containing a variety of functional groups were also subjected to oxidative cleavage, and in all cases the yields of products were 80% or greater of the desired ketone or carboxylic acid. Alkenes **27**–**38** were also cleanly oxidized in high yields to the respective carboxylic acids or ketones **39**–**50**. Interestingly, *α*-

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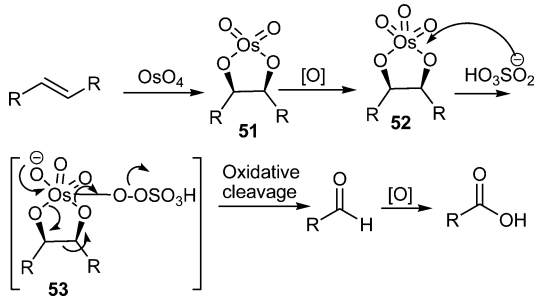
methyl cinammic acid (**34**) and 1-methyl cyclohexene (**35**) (examples of trisubstituted olefins) in the initial oxidation protocol did not deliver the desired product in high yield under standard conditions. Hydrolysis of the osmate intermediate was suggested to lead to formation of the observed diol side product, presumably as a result of the acidity of Oxone. However, addition of solid $NaHCO_3$ to the reaction substantially improved the oxidation of **34** and **35**, leading once again to high yields of the oxidatively cleaved products. α,β-Unsaturated systems pose an interesting case since their cleavage would initially yield an α-dicarbonyl functionality. Oxidation of 2-cyclohexenone **33** provided pentanedioic acid **45**, most probably via the α-dicarbonyl intermediate, which decarboxylates under the oxidative conditions. Baeyer–Villiger-like oxidative cleavage of α-dicarbonyls has been reported previously with peroxy compounds and is likely to be the operative route in the latter oxidation.[164,165] In a similar fashion, (+)-pulegone (**37**) and nootkatone (**38**) gave oxidative products in reasonable yields.[162,163]

Oxone can thus be used to oxidize olefins to carboxylic acids, and it is believed that in this process Oxone functions in three distinctive oxidizing roles: (1) it oxidizes the initially formed osmate back to Os(VIII), (2) it promotes oxidative cleavage to form an intermediate aldehyde, and (3) it independently oxidizes the aldehyde to the carboxylic acid. There is as yet still a certain amount of debate as to the exact mechanism about the oxidative cleavage proposals that have been made as to the intermediacy of an osmate ester which undergoes the oxidative cleavage.[162,163] Scheme 11 depicts the proposed mechanism, in

Scheme 11. Proposed Mechanism for Oxidation of Olefins to Carboxylic Acids

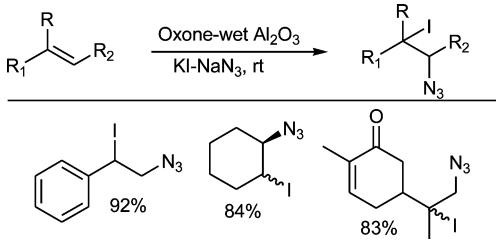


which the initially formed osmate **51** is oxidized by Oxone to furnish **52**, which is subsequently attacked by the same reagent written differently to yield intermediate **53**. Fragmentation of **53** regenerates OsO_4 and produces two aldehydes, which can undergo further oxidation to yield carboxylic acids (Scheme 11). Most authors believe that the nucleophilicity of Oxone and the fact that it contains an excellent leaving group (i.e., bisulfate) drives the reaction forward. On the other hand, as compared to other routinely used co-oxidants such as $NaIO_4$ and Cr oxides, Oxone does not oxidize alcohols or diols independently.[162,163]

4.5. Azidoiodination of Alkenes

β-Azido iodo compounds enjoy many applications in organic synthesis,[166−169] and a large number of different methods[170−175] have been developed for their preparation. It has been reported that Oxone in the presence of KI and NaN_3 can be used for selective conversion of alkenes into azido iodo derivatives (Scheme 12) in good yield and under relatively mild

Scheme 12. Azidoiodination of Alkenes Using the Oxone/KI/NaN_3 System

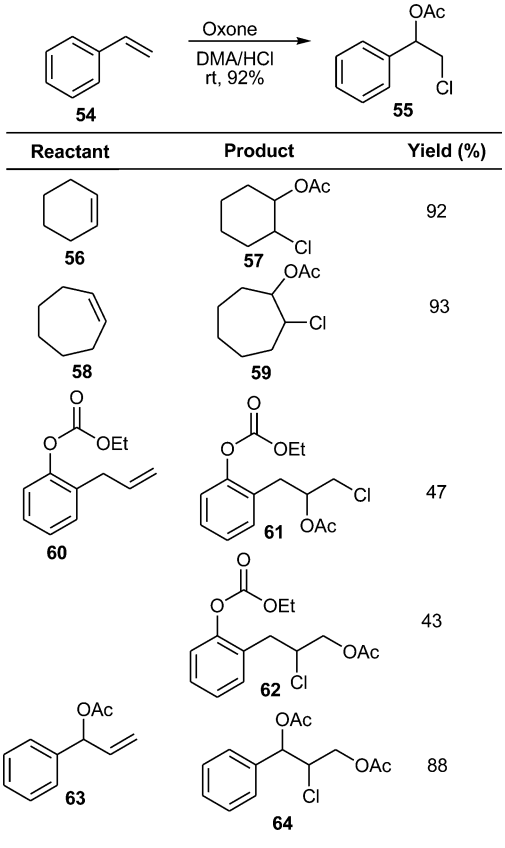


reaction conditions.[176] Surprisingly, the reaction did not work without Al_2O_3, and the authors hypothesized that Al_2O_3 may act both as a support and as a basic reagent to avoid azide decomposition. Reactions proceeded via an anti-Markovnikov addition and via a radical mechanism which may be favored by the low polarity of the solvent.[176,177] Another possibility for the observed regioselectivity is that the reaction may proceed via an ionic mechanism involving nucleophilic attack at the less substituted end of an iodonium ion.

4.6. 1,2-Acetoxychlorination of Olefins

1,2-Acetoxychlorination of an olefinic bond can be achieved starting from different olefins[178−190] and using different reagants.[187−190] It was interesting to note that the first 1,2-acetoxychlorinations of olefins that were successfully achieved using Oxone, DMA, and HCl are given in Scheme 13.[191] The authors reported that only one regioisomer was formed in each of the reactions, viz., styrene (**54**) and 3-acetoxy-3-phenyl-1-propene (**63**). Styrene (**54**) on one hand provided a Markovnikov adduct **55**, while 3-acetoxy-3-phenyl-1-propene

Scheme 13. 1,2-Acetoxychlorination of Olefins



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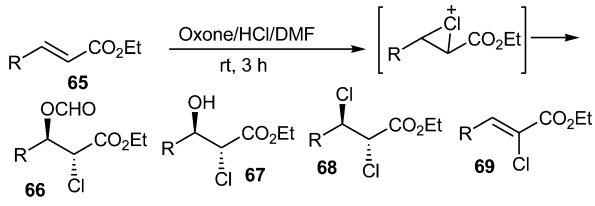
(63) provided an anti-Markovnikov adduct 64. It is interesting to note that cylohexene (56) and cycloheptene (58) provided their 1,2-acetoxychlorination products 57 and 59 in excellent yields. Reaction of 2-allylphenyl ethyl carbonate (60) provided a 1:l mixture of two regioisomers (61 and 62).

4.7. Reaction of Olefin with the Oxone/HCl/DMF System

The Oxone/HCl/DMF system has been studied for different synthetic conversions,[192−203] and reactions of α,β-unsaturated esters in which four different chlorinated products 66−69 were produced in variable yields (Scheme 14).[204] Besides the

Scheme 14. Reaction of α,β-Unsaturated Esters with the Oxone/HCl/DMF System



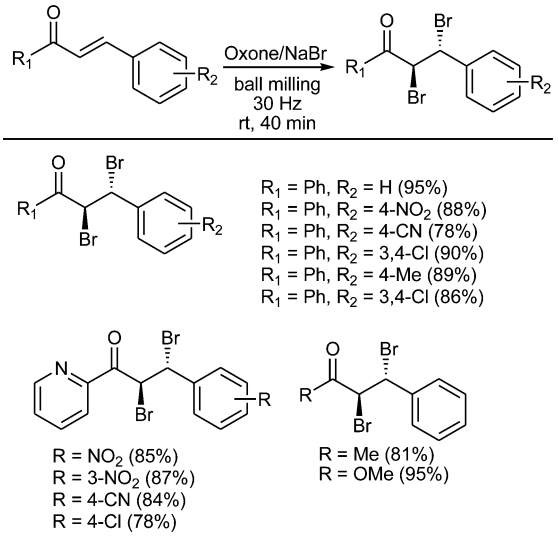
Reactant	Product (%)			
	66	67	68	69
$R_1 = R_2 = H, R_3 = Et$	66	9	2	-
$R_1 = R_2 = H, R_3 = Me$	41	31	6	14
$R_1 = Cl, R_2 = H, R_3 = Et$	51	18	12	12
$R_1 = H, R_2 = NO_2, R_3 = Et$	8	35	25	18
$R_1 = Me, R_2 = H, R_3 = Et$	65	17	5	-

expected compounds, viz., chlorohydrin 67 and dichlorinated ester 68, two additional compounds, the formyloxy chloroformate 66 and vinylic ester 69, were isolated. Of note in these results is that in most of the cases the formyloxy chloroformate-type derivative 66 was produced as the major product. However, it was equally interesting to note that changes in the molecular structure of the substrate or reaction conditions resulted in formation of the four different products. This may be due to unstability of the synthesized compounds under the reaction conditions or during the separation stage. This was made evident by the fact that α-chlorinated derivatives 69 were obtained from the corresponding compounds 66 by exposure to silica gel in DMF.[204]

4.8. Bromination of Olefins

Solvent-free organic reactions are more environmentally friendly protocols, and the mechanical ball-milling technique is also a powerful tool in promoting various solvent-free reactions.[205−215] New solvent-free brominations of various alkenes, including chalcones, azachalcones, 4-phenylbut-3-en-2-one, and methyl cinnamate, were efficiently achieved by employing sodium bromide and Oxone under mechanical milling conditions.[216] The reaction conditions and results for the solvent-free reaction of α,β-unsaturated carbonyl compounds with Oxone and NaBr under ball-milling conditions are summarized in Scheme 15. A great variety of chalcones and other α,β-unsaturated carbonyl compounds with either electron-withdrawing or electron-donating groups were successfully converted into their corresponding anti α,β-dibromo derivatives in excellent yields (Scheme 15). Interestingly

Scheme 15. Reaction of α,β-Unsaturated Carbonyl Compounds with Oxone and NaBr



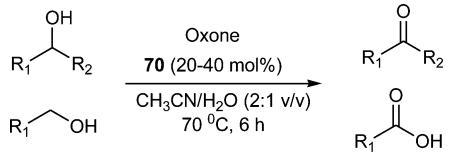
different aza-chalcones also reacted with the Oxone/NaBr system and provided the respective dibrominated products in excellent yields. Additionally, enone and cinnamate could also be transformed to anti α,β-dibromo derivatives in good yields.[216]

5. OXIDATION OF FUNCTIONAL GROUPS

5.1. Oxidation of Alcohols

5.1.1. IBX-Catalyzed Oxidations of Alcohols with Oxone. In 2005, Vinod and co-workers described the first catalytic use of 72 in the presence of Oxone as a co-oxidant for oxidation of primary and secondary alcohols in aqueous acetonitrile (Scheme 16).[217] Vinod and co-workers were

Scheme 16. IBX-Catalyzed Oxidations of Alcohols with Oxone



inspired by Santagostino's finding that 72 was obtained from 70 and Oxone in hot water.[218] Secondary alcohols were oxidized to the corresponding ketones, and fortunately no Bayer−Villiger oxidation products were observed. Primary alcohols were oxidized to the corresponding carboxylic acids, but unfortunately primary alcohols could not be selectively oxidized to the corresponding aldehydes.[217] In another study Borhan demonstrated that aldehydes easily reacted with water to give hemiacetals, which were oxidized to carboxylic acids in the presence of Oxone in wet DMF.[219] The proposed catalytic cycle is shown in Scheme 17.[220]

Inspiring from Vinod's report, Shulze and Giannis[221] described the in-situ-generated 72-catalyzed oxidation of alcohols in the presence of tetra-*n*-butylammonium sulfate (Bu_4NHSO_4) as a phase-transfer catalyst for generation of tetra-*n*-butylammonium Oxone in an ethyl acetate/water biphasic solvent system. Under Shulze and Giannis[221]

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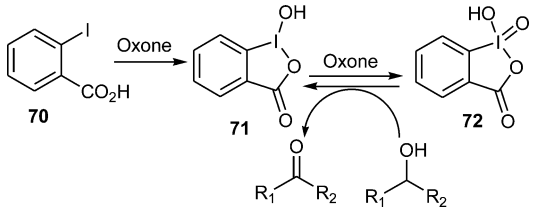
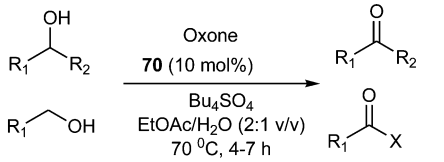
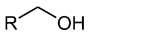
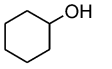
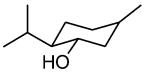
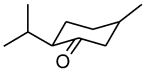
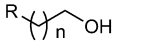
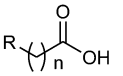
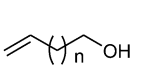
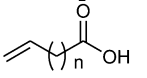
Scheme 17. In-Situ Generation of 72 from IBA 71 or 70 with Oxone and Catalytic Use of IBX (72) for Alcohol Oxidation



conditions, primary benzylic alcohols were oxidized to the corresponding aldehydes (Scheme 18). It is important to note

Scheme 18. IBX-Catalyzed Oxidations of Alcohols under Shulze and Giannis Condition



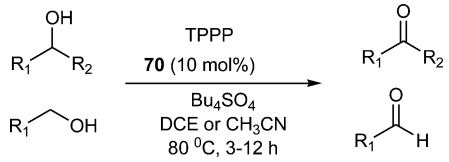
Sunstrate	Product	Yield (%)
		
R = Ph	R = Ph	72
R = 3-F-C_6H_4	R = 3-F-C_6H_4	91
R = 4-NO_2-C_6H_4	R = 4-NO_2-C_6H_4	93
		75
		82
		
R = Me, n = 6	R = Me, n = 6	77
R = CH_2Cl, n = 4	R = CH_2Cl, n = 4	82
		
n = 7	n = 7	74
n = 8	n = 8	83

that the above-described method also tolerates double bonds. For example, oxidation of 9-decen-1-ol to the corresponding acid and oxidation of 10-undecen-2-ol to the ketone took place in good yields. Surprisingly, benzylic alcohols were converted to aldehydes, and formation of the corresponding acids was not observed. Under Vinod's and Giannis' conditions, it was not possible to oxidize allylic and homoallylic alcohols and complex reaction mixtures were observed.[217,221]

Interestingly, oxidation of 5-nonanol was achieved in the presence of 1 mol % of **70** and gave 5-nonanone in good yield under Vinod's conditions.[217] However, oxidation of a sterically hindered alcohol such as (−)-menthol was problematic under the known conditions,[217,221] and Baeyer−Villiger products were also observed in aqueous acetonitrile. However, Baeyer−Villiger products were suppressed under Giannis' conditions,[221] and large amounts of acetic acid and ethanol were formed together with (−)-menthone. Various solvent systems were tested for the in-situ-generated **72**-catalyzed oxidation of (−)-menthol with Oxone. Oxidation preceded more cleanly and more rapidly in nonaqueous nitromethane than in organic solvents/water biphasic systems.

Page et al.[222] showed that the oxidant, tetraphenylphosphonium peroxmonoysulfate (TPPP), which was prepared from Oxone by counterion exchange with tetraphenylphosphonium chloride, could find use in oxidation reactions as an Oxone. The TPPP in the presence of a catalytic amount of **70** could oxidize several primary and secondary alcohols to their respective aldehydes and ketones under reflux conditions in acetonitrile or dichloroethane (Scheme 19).[223] Interestingly, TPPP and **70** used as an oxidizing system oxidized primary alcohols to their corresponding aldehydes without generation of carboxylic acid.

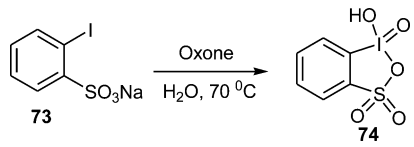
Scheme 19. TPPP and 70 System Oxidation of Alcohols



Page and co-workers demonstrated that TPPP could also promote oxidation of alcohols in the absence of **70**.[223] In another study Hajipour showed that benzyltriphenylphosphonium peroxymonosulfate in conjunction with a Lewis acid can be used for oxidation of alcohols.[12]

5.1.2. IBS-Catalyzed Oxidations of Alcohols with Oxone. Zhdankin's group demonstarted the preparation 2-iodoxybenzenesulfonic acid (IBS, **74**)[224] (Scheme 20), which additionally could be prepared by direct oxidation of sodium 2-iodobenzenesulfonic acid (**73**) with Oxone.[220]

Scheme 20. In-Situ Generation of 74 from 73 and Oxone



It has been reported previously[217−223,225−228] that it is difficult to selectively oxidize primary alcohols to the corresponding aldehydes or carboxylic acids with the same catalyst and reagents. Interestingly, method A (acetonitrile; no additive), method B (ethyl acetate, sodium sulfate), or method C (nitromethane, sodium sulfate) could selectively be used to oxidize primary α,β-unsaturated alcohols (allylic, propargylic, and benzylic alcohols) and aliphatic alcohols to their corresponding aldehydes and carboxylic acids in excellent yield by controlling the amount of Oxone added in the presence of precatalyst **73** (1−2 mol %) (Scheme 21)[229] In particular, methods B and C were effective for selective oxidation of acid-sensitive alcohols and selective and rapid oxidation of alcohols, respectively.[220]

In another study Ishihara and Uyanik[230] oxidized 4-bromobenzyl alcohol (6 g) to the corresponding aldehyde and carboxylic acid in excellent yield by controlling the amount of Oxone added in the presence of potasium 2-iodo-5-methylbenzenesulfonic acid (1 mol %): thus, 0.65 equiv was used for selective oxidation to the aldehyde, while 1.3 equiv was employed for oxidation to 4-bromobenzoic acid.

5.1.3. IBS-Catalyzed Cascade Oxidative Dehydrogenation of Cycloalkanols with Oxone. Although many

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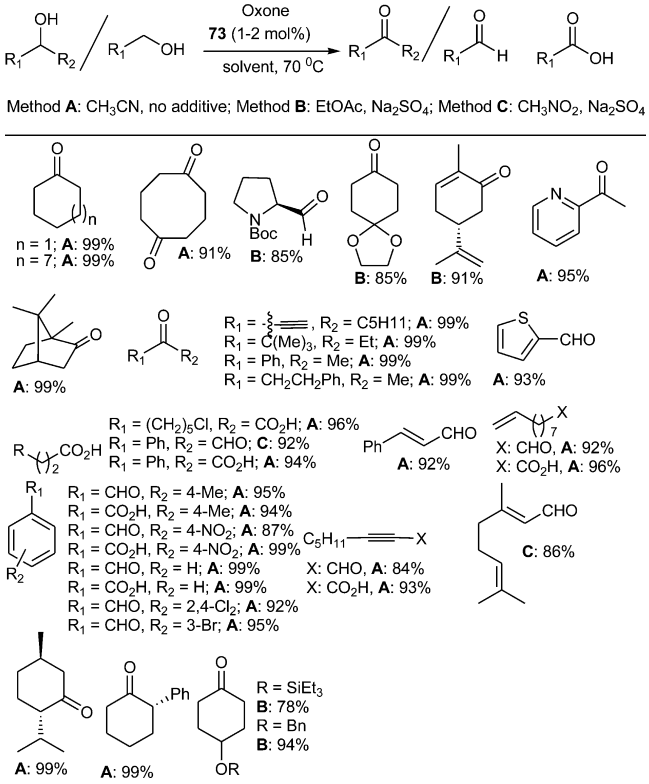
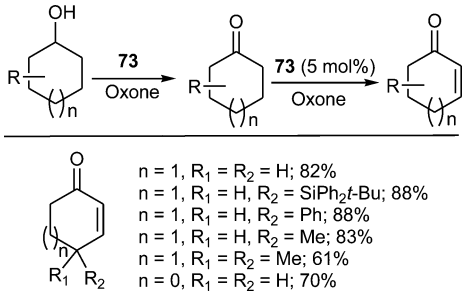
Scheme 21. In-Situ-Generated 74-Catalyzed Selective Oxidation of Primary and Secondary Alcohols to Their Corresponding Aldehydes or Carboxylic Acids and Ketones



methods have been reported for synthesis of α,β-unsaturated carbonyl compounds, it is quite difficult to catalytically dehydrogenate saturated carbonyl compounds to α,β-unsaturated carbonyl compounds.[229] Ishihara and Uyanik[229] showed that **74** catalyzed the cascade oxidative dehydrogenation of cycloalkanols to cycloalkenones. Oxidation of cyclohexanols to cyclohexanones and then oxidation of cyclohexanones to cyclohex-2-enones proceeded in excellent yields by controlling the amounts of **73** and Oxone (Scheme 22). Five- and six-

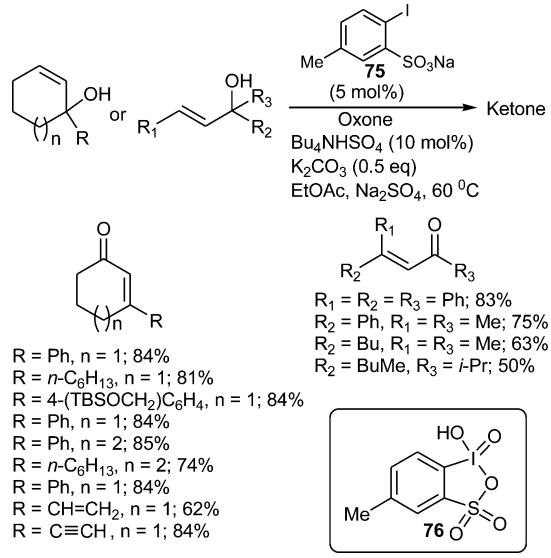
Scheme 22. 74-Catalyzed Cascade Oxidation of Cycloalkanols



membered cycloalkanols were transformed to the corresponding enones in good yield. Unfortunately, **74**-catalyzed oxidative dehydrogenation of linear carbonyl compounds to the linear α,β-unsaturated carbonyl compounds with Oxone was not successful under these conditions.

5.1.4. IBS-Catalyzed Oxidative Rearrangement of Tertiary Allylic Alcohols. Oxidative rearrangement of tertiary allylic alcohols to β-disubstituted α,β-unsaturated ketones or aldehydes using different reagents has been widely used in synthetic organic chemistry.[231] Ishihara et al.[231] used IBS/Oxone catalytic oxidation systems for oxidative rearrangement of tertiary allylic alcohols to enones with powdered Oxone promoted by catalytic quantities of sodium 2-iodo-5-methylbenzenesulfonic (**75**) (Scheme 23). 5-Me-IBS (**76**) is

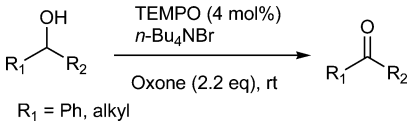
Scheme 23. IBS-Oxone-Catalyzed Oxidative Rearrangement of Tertiary Allylic Alcohols



generated in situ and serves as the actual catalyst for oxidation. Addition of inorganic bases, such as K_2CO_3, and a phase-transfer catalyst, such as tetra-*n*-butylammonium hydrogen sulfate [$(n\text{-Bu})_4NHSO_4$], extended the substrate scope for oxidative rearrangement reactions. Cyclic and acyclic substrates gave the corresponding enones in moderate to high yields.

5.1.5. Miscellaneous Alcohol Oxidation. Bolm et al.[232] demonstrated that the combination of TEMPO and Oxone is an efficient system for oxidation of alcohols to either aldehydes or ketones (Scheme 24). The performance of the catalyst is

Scheme 24. Oxidation of Alcohols with the TEMPO/Oxone System



largely influenced by the presence of quarternary ammonium salts, and thus, addition of tetrabutylammonium bromide proved useful for oxidation of most substrates. Furthermore, the reaction conditions of the TEMPO/Oxone system are much milder than those with previously reported stoichiometric oxidants, which results in an improved functional group tolerance avoiding overoxidation to the corresponding carboxylic acids. Interestingly, in some solvents such as toluene, secondary alcohols reacted even more efficiently than their primary counterparts, resulting in higher yields of the corresponding carbonyl compound. This observation was quite unexpected since it is known that TEMPO preferentially oxidizes primary alcohols.[233−241] Finally, it was found that primary alcohols were best oxidized in dichloromethane, while

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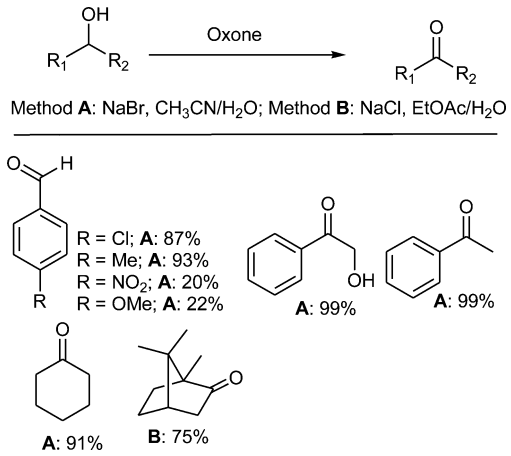
oxidation of secondary alcohols proceeds in toluene in excellent yield. Aliphatic substrates such as 1-nonanol and 2-nonanol showed the same trend but performed somewhat less efficiently, giving the products in up to 67% and 56% yields, respectively.[232]

Lee et al.[17] demonstrated the scope of the Oxone/NaBr combination reagent (method A) in the oxidation of benzylic alcohols to benzaldehydes satisfactorily (Scheme 25). In

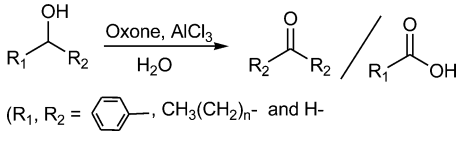
Scheme 25. Oxidation of Alcohols Using the Oxone/NaBr and Oxone/NaCl Systems



another study Wissinger et al.[242] used the Oxone/NaCl system (method B) for oxidation of secondary alcohols to ketones. In particular, method A could be applied to a reasonable range of benzylic alcohols and representative primary and secondary alcohols. However, in the absence of sodium bromide, the reaction did not proceed at all in 24 h at room temperature. The presence of electron-donating groups in the aromatic ring has little influence on the oxidation rates but these are markedly lowered by introducing a strong electron-acceptor group. Furthermore, the reaction was unsuccessful for electron-rich systems such as *p*-methoxybenzyl alcohol, which presumably suffered from additional complications due to competing bromodecarbonylation of the resulting *p*-anisaldehyde which was additionally accompanied by bromination on the phenyl ring to produce 4-bromoanisole (44%) and 2,4-dibromoanisole (14%). However, primary alcohols such as 1-pentanol were converted mainly into the dimeric esters, viz., pentyl valerate, presumably via a hemiacetal intermediate.[243]

Recently Wu et al.[244] demonstrated that a combination of Oxone and the metalloid salt $AlCl_3$ is well able to oxidize the majority of alcohols into their corresponding carbonyl analogues in high yield in aqueous media (Scheme 26). In particular, oxidation of the benzylalcohols, phenylmethanol, 4-chlorophenylmethanol, and 4-nitrophenylmethanol were all oxidized to their corresponding acids with 100% conversion at room temperature. However, an increase in the number of carbon atoms in the chain influenced the outcome of the

Scheme 26. Reaction of Alcohols with Oxone and $AlCl_3$

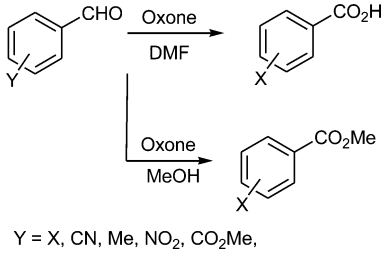


conversions by reducing them to 70% and even to 26% due to a reduction in the rate of reaction. It was further noted that the temperature of the reaction had to be increased to 60 °C (*n*-dodecanol, *n*-hexadecanol, and *n*-octadecanol).[244] In all cases conversion of primary alcohols by this protocol always lead to formation of the corresponding carboxylic acids.[245]

5.2. Oxidation of Aldehydes

A highly efficient, mild, and simple protocol has been established for oxidation of aryl aldehydes to carboxylic acids utilizing Oxone in DMF (Scheme 27).[219] Electron-with-

Scheme 27. Oxone Oxidations of Aromatic Aldehydes

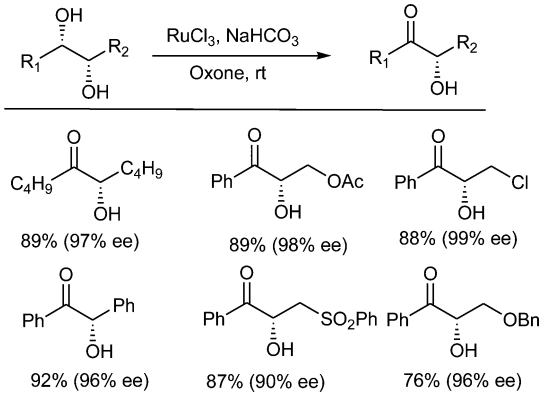


drawing, electron-neutral, and halogenated benzaldehydes were oxidized efficiently to their corresponding benzoic acids in good yields. However, electron-rich substrates such as 4-hydroxybenzaldehyde and *p*-anisaldehyde afforded their formate esters as the major products in 62% and 58% yields, respectively. It was suggested that for oxidation of electron-rich aromatic rings the molecules are presumed to undergo a Baeyer–Villiger reaction to afford the phenolic or Dakin products.[246] The potential scope of this method was evident since it was noted that oxidation of aliphatic aldehydes also occurs with high yields of greater than 90%. Interestingly, oxidation of aldehydes with Oxone in alcoholic solvents cleanly afforded high conversion to esters.[219] Thus, oxidation of benzaldehyde in alcohols such as methanol, ethanol, *n*-propanol, and 2-propanol afforded their corresponding esters in excellent yields.

5.3. Oxidation of Vicinal Diols

The versatility of oxygen-transfer processes is best exemplified by oxidation of vicinal diols. Plietker[247] reported the development of the first catalytic, regio- and chemoselective oxidation of vicinal diols to acyloins using $RuCl_3$ and Oxone (Scheme 28). This oxidation ($RuCl_3$ and Oxone) protocol proved to be useful for dehydrogenation of enantiomerically enriched

Scheme 28. Reaction of *vic*-Diols with $RuCl_3$ and Oxone



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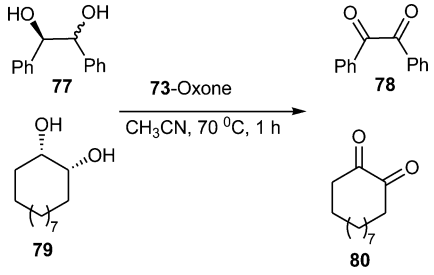
glycols. Interestingly, an acid-assisted epimerization of α-ketols was not observed in any case within the time frame of the monooxidation. Various α-hydroxy ketones (Scheme 28) were obtained with full retention of enantiopurity and a predictable absolute configuration. Interestingly, electron-rich diols are oxidized more slowly than electron-poor substrates.

In another study Ishihara et al.[229] reported that benzylic *sec,sec*-1,2-diol **77** and aliphatic *sec,sec*-1,2-diol **79** could be oxidized to diketones **78** and **80** in moderate to high yields using the IBS (**73**)/Oxone system. (Scheme 29). On the other hand, oxidation of aliphatic diols gave oxidative cleavage products. In the nonaqueous solvent system, the desired carbonyl products were obtained in nearly pure form by simple filtration of most wastes derived from Oxone and washing with water to remove catalyst derivatives.

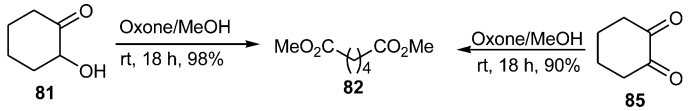
Scheme 29. Oxidation of *vic*-Diols with the IBS (73)/Oxone System

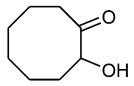
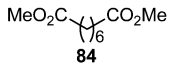
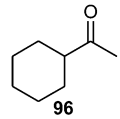
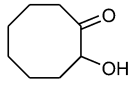
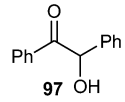
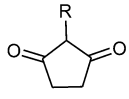
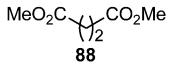
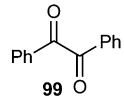
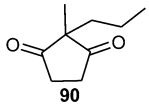
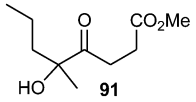
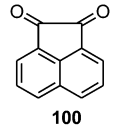
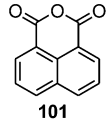
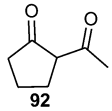
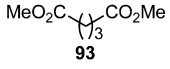
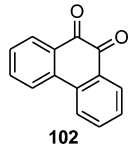
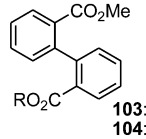
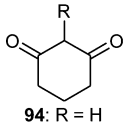
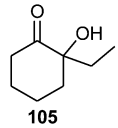
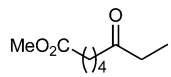


5.4. Oxidative Cleavage of Carbonyl Compounds

5.4.1. Oxidative Cleavage of Dicarbonyls and α-Hydroxyketones. Oxidative cleavage of α-hydroxyketones and α or any diones using Oxone was investigated where it was found that in many cases diesters were produced in one step.[248] Interestingly, oxidation of α-hydroxyketones and α or any diones in methanol as solvent afforded good to excellent yields of methyl diesters (Scheme 30). For example, α-hydroxyketones **81** and **83** afforded the corresponding products **82** and **84** in 98% and 69% yields, respectively. Cyclic α-diones, viz., **85** and **102**, were transformed efficiently to their respective dimethyl esters **82** and **103**, although in the latter case the yield was only 20%. Thus, cyclic and acyclic β-diones afforded the desired dimethyl esters in 78−99% yield. α-Branching did not affect the outcome of the reaction. However, bis α-branching viz., in the 1,3-dione **90**,[249] did hinder the reaction significantly, affording the tertiary hydroxyketone **91** with fair yield (65%). Interestingly, **91** did not undergo further oxidation unless heated, presumably due to steric constraints that hinder nucleophilic attack of the oxidant at the carbonyl carbon. Heating the reaction to 50 °C initiated oxidative cleavage but with relatively poor conversion, leading to only a 54% yield of the desired diester **88** with 22% of the starting material being recovered. The structurally related cyclic tertiary hydroxyketone **105**,[250] when exposed to the reaction protocol, reacted at room temperature, providing an inseparable 4:1 mixture of the dimethyl ester and the keto ester in a modest 50% yield. Additionally, the α-dione **100** did not yield the expected diester

Scheme 30. Oxidative Cleavage of Dicarbonyls and α-Hydroxyketones with Oxone



Substrate	Product	Yield (%)	Substrate	Product	Yield (%)
 **83**	 **84**	69	 **96**	**82**	78
 **86**	**86**	79	 **97**	PhCO2Me **98**	73
 **87**: R = Me **89**: R = H	 **88**	85 80	 **99**	**98**	77
 **90**	 **91**	65	 **100**	 **101**	98
 **92**	 **93**	86	 **102**	 **103**: R = Me (19) **104**: R = H (64)	
 **94**: R = H **95**: R = Me	**93**	99 86	 **105**	 **82**: 40 **106**: 10	

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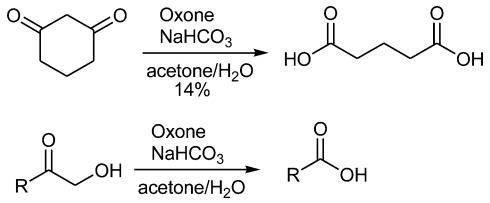
but provided the relatively stable intermediate anhydride **101** (98%). Ketone **102** did not afford the diester exclusively, providing both the dimethyl and the monomethyl esters in 19% and 64% yields, respectively. Conversion of **100** to the cyclic anhydride **101** and not the diester (and conversely oxidation of **102** to **103** and **104**) is probably related to the observations made by Blanc in the acetylation of 1,5- and 1,6-dicarboxylic acids and, in particular, the differences in the reaction of the latter two compounds.[251,252]

In another study, Ashford and Crega[253] reported the oxidative degradation of 1,3-dicarbonyl compounds and α-hydroxy ketones to carboxylic acids using Oxone (Scheme 31).

Scheme 31. Reaction of 1,3-Dicarbonyls and α-Hydroxy Ketones with Oxone



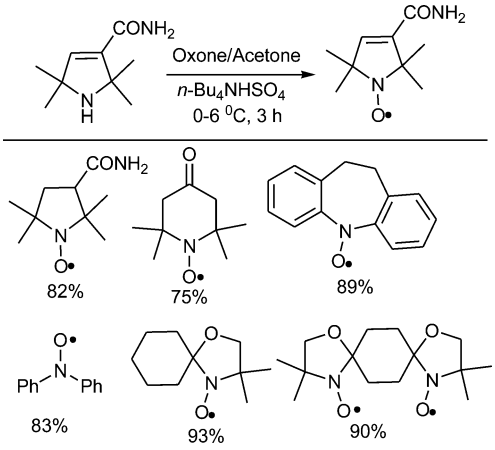
Preliminary results of the oxidative cleavage of 1,3-dicarbonyl compounds and α-hydroxy ketones showed that oxalate derivatives as well as simple malonic esters can be oxidized to carboxylic acids. It was also found that the reaction works equally well for aliphatic and aromatic 1,3-diketones. The simple symmetrical biaryl diketone undergoes clean conversion to benzoic acid. On the other hand, the cyclic alkyl diketones afforded the corresponding dicarboxylic acid. The most interesting comparative finding was that of 2-hydroxy-1-phenylethanone and acetophenone, where it was apparent that activation of the α-carbon by a simple hydroxyl group was sufficient for oxidative cleavage. Conjugated diketones and oxalates with alkyl substituents α to the carbonyl were not oxidatively cleaved.[253]

5.5. Oxidation of Amines

5.5.1. Oxidation of Amines to Nitroxides. Interest in the chemistry of nitroxides has been stimulated in recent years by their application as probes in materials,[254] spin labels in biochemistry,[255−257] and contrast agents in magnetic resonance imaging[258−260] or electron spin resonance imaging.[261] Secondary amines without α-hydrogens may be transformed to nitroxides under biphasic conditions (CH_2C1_2/H_2O) and with a phase-transfer catalyst $Bu_4NHSO_4^-$.[262] The process involves formation of dimethyloxirane by nucleophilic attack of Oxone on the carbonyl carbon with subsequent loss of potassium hydrogen sulfate (HSO_4^-).[89] Oxygen is transferred to the amine in a biphasic medium, affording the oxidized product (nitroxide) and regenerating the initial ketone (Scheme 32). However, little or no oxidation was observed in the absence of acetone. Different secondary amines were subjected to oxidation with Oxone and provided the corresponding nitrones in excellent yields.

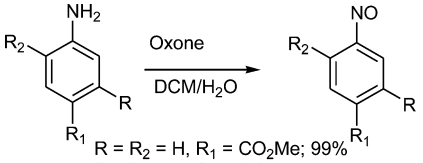
5.5.2. Oxidation of Aromatic Amines to Nitrosoarenes. Nitroso compounds undergo a variety of transformations which have great synthetic potential,[263−271] and they have additionally been studied as antiretroviral and antitumor agents.[272] Oxidation of the 4-aminobenzoic acid with Oxone in a mixture of water and CH_2Cl_2 demonstrated complete consumption of the starting material within 30 min, and 4-

Scheme 32. Amine Oxidation with Oxone



nitrosobenzoic acid was isolated quantitatively in 99% purity. This method was extended for oxidation of a great variety of substituted anilines with Oxone and provided nitrosoarenes in good to excellent yields (Scheme 33).[273] Functional groups

Scheme 33. Oxidation of Aromatic Amines to Nitrosoarenes with Oxone



R = R_2 = H, R_1 = CO_2Me; 99%
R = R_2 = H, R_1 = CO_2H; 99%
R_1 = R_2 = H, R = CO_2Me; 99%
R_1 = R_2 = H, R = CO_2H; 96%
R_1 = R_2 = H, R = CN; 96%
R = R_2 = H, R_1 = Br; 70%
R = R_2 = H, R_1 = Et; 65%
R = R_2 = H, R_1 = SO_3H; 85%
R = R_2 = H, R_1 = SO_3NBu_4; 97%
R = R_2 = H, R_1 = CH_2OH; 75%
R = R_2 = H, R_1 = CH_2CO_2H; 85%
R = R_2 = H, R_1 = CH_2NHBoc; 60%
R_1 = H, R_2 = Me, R = CO_2Me; 96%

such as carboxylic acids, esters, nitriles, and bromides and alkyl substituents were all well tolerated. However, nitroso compounds with functional groups having high water solubility or being unstable in the presence of the redox-active nitroso functionality led to somewhat inferior results. These substances may persist in the aqueous phase and thus were prone to further oxidation to the corresponding nitro compounds.[273]

5.5.3. Oxidation of Primary and Secondary Amines to Hydroxylamines. Hydroxylamines are useful synthetic intermediates which exhibit a wide range of pharmacological and physiological activities.[274] However, their direct preparation by oxidation of the corresponding amines is complicated by the ease of overoxidation to secondary products, especially for primary amine systems.[275] Fields and Kropp[276] reported the selective oxidation of primary and secondary amines to hydroxylamines using Oxone mediated by the contact surface of silica gel (Scheme 34). The secondary and primary amines were readily and selectively transformed to the corresponding hydroxylamines on treatment with Oxone/silica gel at 80 °C. Indeed, amines like dibutylamine and *N*-hydroxy-2,4,4-trimethylpentan-2-amine resisted oxidation beyond the hydroxylamine stage even on treatment with double the amount of

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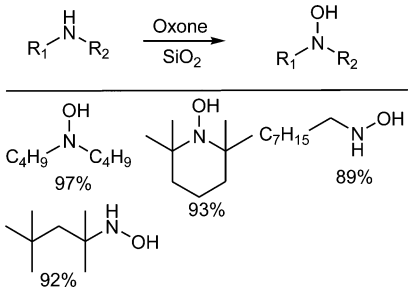
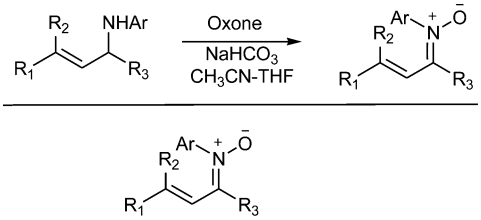
Scheme 34. Oxone Oxidation of Amines to Hydroxylamines



oxidant. Oxone/alumina was about equally effective with the secondary amines such as dibutylamine and 2,2,6,6-tetramethylpiperidine and the substituted primary amine *N*-hydroxy-2,4,4-trimethylpentan-2-amine but afforded substantial over-oxidation of the unsubstituted primary amine octan-1-amine to the oxime.[276]

5.5.4. Oxidation of Amine to Nitrone. Nitrones are widely recognized as important building blocks in organic synthesis. Much of this popularity can be ascribed to their facile [3 + 2] cycloadditions with alkene and alkyne dipolarophiles to form products such as isoxazolidines and 2,3-dihydroisoxazoles.[277−280] *N*-Allyl anilines were subjected to oxidation by Oxone under the conditions reported by Busqué and Figueredo[281] and afforded *α,β*-unsaturated *n*-aryl ketonitrones.[282] This modular approach facilitated the synthesis of *α,β*-unsaturated *n*-aryl ketonitrones with diverse substitution patterns (Scheme 35). These include substitution of the *n*-aryl

Scheme 35. Oxone Oxidation of Amine to Nitrone



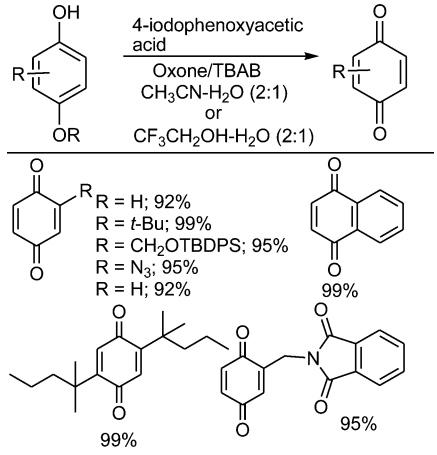
R_1 = Ar = Ph, R_2 = H, R_3 = Me; 80%
R_1 = Ph, Ar = 2'-tolyl, R_2 = H, R_3 = Me; 67%
R_1 = Ph, Ar = 4'-tolyl, R_2 = H, R_3 = Me; 62%
R_1 = Ph, Ar = 4'-Cl-Ph, R_2 = H, R_3 = Me; 34%
R_1 = Ar = Ph, R_2 = H, R_3 = *n*-Bu; 82%
R_1 = 4'-OMe-Ph, Ar = Ph, R_2 = H, R_3 = Me; 74%

groups by 2′-methyl, 4′-methyl, 4′-chloro, and 3′-methoxy groups and substitution of the ketonitrone by ethyl, *n*-butyl, and phenyl groups.[282]

5.6. Oxidation of Phenols to Quinones

5.6.1. Oxidation of Phenols to *p*-Quinones. *p*-Quinones are integral structural components of a large number of natural products and have proven to be the most useful synthetic intermediates.[283−293] Yakura et al.[289,290] demonstrated a novel catalytic hypervalent iodine oxidation of phenol derivatives using catalytic amounts of 4-iodophenoxyacetic acid and Oxone as a co-oxidant. *p*-Alkoxyphenols were oxidized to the corresponding *p*-quinones in aqueous acetonitrile in excellent yields (Scheme 36). Reactions of simple *p*-ethoxy- and *p*-butoxyphenols and hydroquinone afforded *p*-quinones in very high yield. This oxidation system was also effective for phenols bearing a bulky substituent at the ortho position and also for ester, *tert*-butyldiphenylsilyloxy, azide, and succinimide groups.

Scheme 36. Reaction of Phenols with 4-Iodophenoxyacetic Acid and Oxone



Unfortunately, oxidation of electron-poor phenols provided complex mixtures due to iodination of the aromatic ring, in contrast to the catalytic hypervalent iodine oxidations.[292−294] A substituent effect was observed in the oxidation for the iodobenzene ring; *p*-alkoxy is most effective, in the approximate order *p*-RO > *p*-Me, *o*-MeO, *m*-MeO > H > *o*-CO_2H.

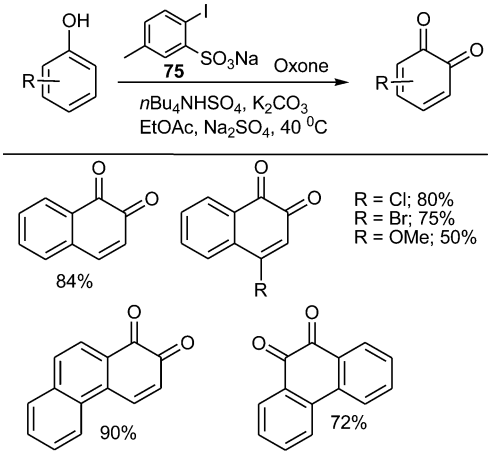
5.6.2. Oxidation of Phenols to *o*-Quinones. *o*-Quinones are also important synthetic intermediates for synthesis of medicinally and biologically important compounds.[295−305] Recently, Ishihara et al.[306] reported on the IBS-catalyzed regioselective oxidation of phenols to 1,2-quinones using Oxone. Different substituted phenols could be oxidized to the respective *o*-quinones using catalytic amounts of sodium salts of 2-iodobenzenesulfonic acids **75** and stoichiometric amounts of Oxone in the presence of the phase-transfer catalyst, tetrabutylammonium hydrogen sulfate (nBu_4NHSO_4). Different naphthols, phenanthrols, and phenols were subjected to IBS−Oxone oxidation and provided orthoquinones in high yields (Scheme 37).

6. NAMED REACTIONS

6.1. Nef Reaction

The Nef reaction[307] involves conversion of primary and secondary nitrocompounds into their respective carbonyl

Scheme 37. IBS−Oxone Oxidation of Phenols to *o*-Quinones



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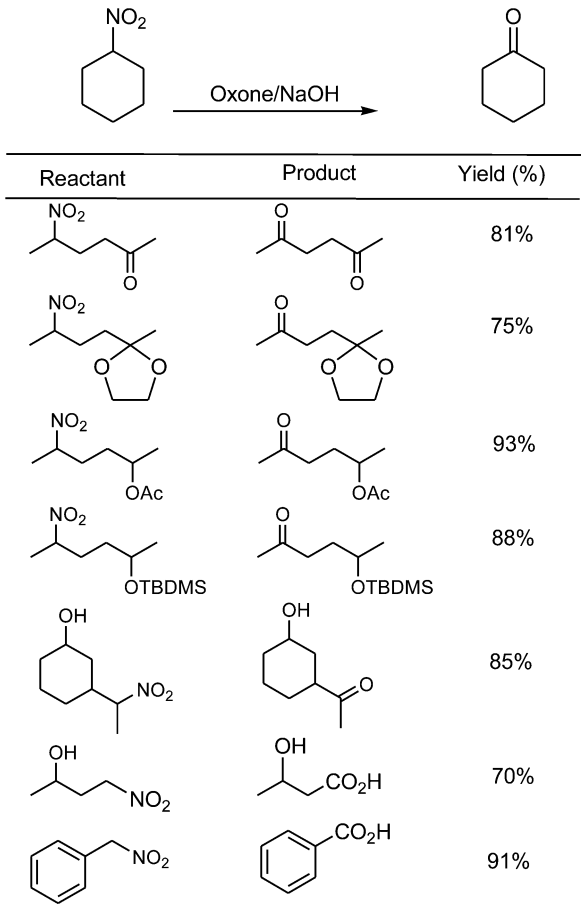
derivatives. Aliphatic nitrocompounds have many applications in organic synthesis, particularly as intermediates in carbon−carbon bond-forming processes or as percursors of many other functional groups. Over the years different procedures have been proposed to effect this transformation, e.g., hydrolytic as well as oxidative methods.[308,309] Ceccherelli et al.[310] reported on the convenient oxidative Nef reaction using Oxone. Initially secondary nitrocompounds were converted into their corresponding ketones such as conversion of nitrocyclohexane to cyclohexanone. On the other hand, primary nitroderivatives provided carboxylic acids as illustrated clearly in Scheme 38. Surprisingly, 5-nitro-hexan-2-ol was not oxidized to the respective hydroxyketone under these conditions.[310]

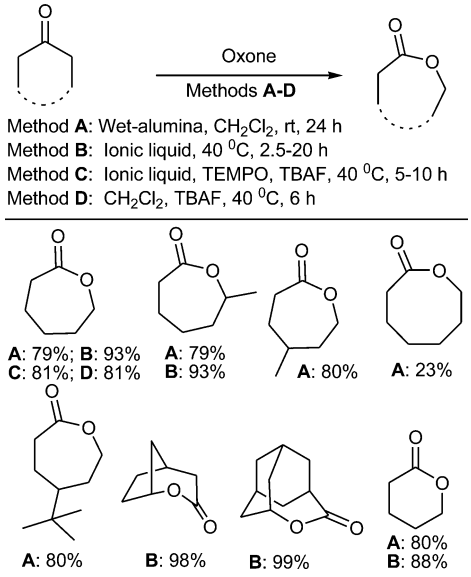
Scheme 38. Oxone-Promoted Generation of Carbonyl Compounds from Nitroalkanes



6.2. Baeyer−Villiger Reaction

The Baeyer−Villiger reaction is among the more important transformations employed in synthetic organic chemistry.[311,312] Although Oxone has since been replaced by organic peracids, hydrogen peroxide, and alkyl hydroperoxides,[313,314] its use in the Baeyer−Villiger reaction has recently been receiving increasing attention. Oxone-mediated Baeyer−Villiger reaction has been reported using method A[315] (wet alumina, CH_2Cl_2, room temperature, 24 h), method B[9] (ionic liquid, 40 °C, 2.5−20 h), method C[316] (ionic liquid, TEMPO, TBAF, 40 °C, 5−10 h), and method D[317] (CH_2Cl_2, TBAF, 40 °C, 6 h). In these methods cyclohexanone was converted to ε-caprolactone in good yields. In method A wet alumina was prepared by vigorous shaking of dried alumina with distilled water until a free-flowing powder was obtained. In particular, methods A and B were effective for the selective Baeyer−Villiger oxidation of variety of cyclic ketones and are illustrated in Scheme 39. It

Scheme 39. Oxone-Mediated Baeyer−Villiger Reaction



should be noted that some differences in reaction times in method A have been mainly ascribed to the differences in the reactivity of the ketones. For example, Baeyer−Villiger reaction of cycloheptanone with Oxone produced the respective lactone in 23% yield after 24 h, while the same reaction applied to cyclohexanone proceeded to give the respective lactone in 8 h and in a 79% yield.[349]

It is interesting to note that method B is an efficient method for synthesis of lactones and esters from the corresponding ketones that utilizes Oxone as oxidant along with environmentally attractive ionic liquids as solvent. Use of an Oxone/ionic liquid system eliminates currently used solvents in Baeyer−Villiger oxidation reactions, such as dichloromethane, chloroform, and acetonitrile.[9] In method C the oxidation process was comprised of a two-phase system consisting of an organic phase (cyclohexanone dissolved in CH_2Cl_2) and inorganic solid phase (Oxone). The results showed that the rate of reaction increased with an increase in the Oxone concentration because extraction of lipophilic pairs ($Q^+ HSO_5^-$) into the organic phase was more efficient.[317]

In another study Wang et al.[318] reported on the enantioselective synthesis of butyrolactones using the *N*-tolyl-substituted oxazolidinone containing ketone as catalyst and Oxone as oxidant in a remarkeble cascade type of reaction on the cyclopropylolefin **107** via a sequential epoxidation, ring opening, and expansion and finally a Baeyer−Villiger oxidation[319−333] to afford product **110** with 91% ee (Scheme 40).

6.3. Hunsdiecker-Type Reaction (Halodecarboxylation of Carboxylic Acids)

Halodecarboxylation of metal carboxylates with molecular bromine, commonly known as the Hunsdiecker reaction, is an extremely useful and selective procedure for syntheses of halogenated organic compounds.[334−336] The efficacy and application of the reaction has been expanded by several groups to include carboxylates of mercury,[337] thallium,[338]

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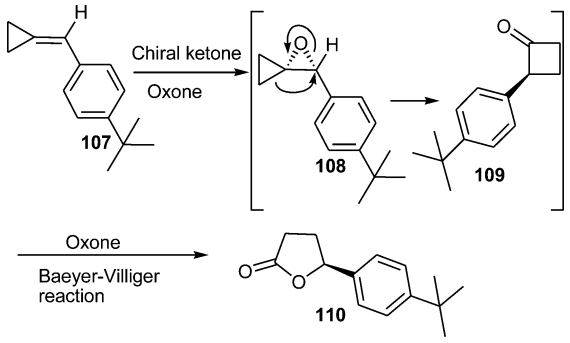
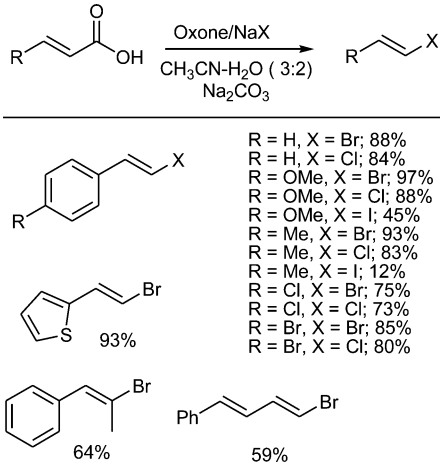
Scheme 40. Synthesis of Compound 110 from 107



lead,[339,340] and manganese[341] besides the original silver metal of the Hunsdiecker. In addition, several innovative oxidative decarboxylation protocols have been reported.[342−344] You and Lee[345] described the halodecarboxylation (Hunsdiecker-type reaction) of various α,β-unsaturated carboxylic acids bearing either an aryl or a styrenyl group at the β-carbon with Oxone and sodium halides in aqueous acetonitrile under relatively mild conditions (Scheme 41). Initially, reaction of cinnamic acid

Scheme 41. Halodecarboxylation of α,β-Unsaturated Carboxylic Acids with Oxone and Sodium Halide



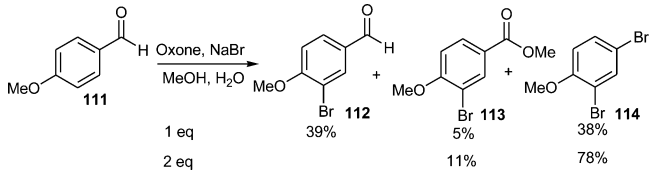
with sodium bromide and sodium chloride with Oxone in acetonitrile/water (3:2) provided β-bromostyrene and β-chlorostyrene in 88% and 84% yields, respectively. However, iododecarboxylation did not proceed at all. On the other hand, electron-rich *p*-methoxycinnamic acids afforded the expected iododecarboxylation product, *p*-methoxy-β-iodostyrene, in 45% yield. The methodology was extended to incorporate *p*-bromo-, chloro-, and iododecarboxylation of different α,β-unsaturated aromatic carboxylic acids with sodium halides with Oxone. Moderate to excellent yields of the corresponding halides except iodides were obtained, and generally acids bearing electron-donating substituents were particularly reactive compared to those having electron-withdrawing groups. Also, in these reactions, a good degree of stereospecificity, wherein (*E*)-acids gave rise to corresponding (*E*)-haloalkenes, was observed.[345]

7. HALOGENATION

7.1. Halogenation of Aromatic Compounds

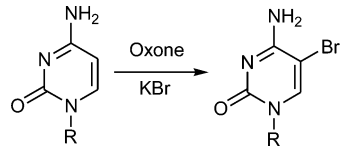
On the basis of the versatility of Oxone as an oxidant, halide generation from sodium halide, and the fact that these strongly acidic solutions may provide some advantage for direct conversion of aldehydes into esters, Koo et al.[346] decided to test the outcome of Oxone and sodium bromide on benzaldehydes in aqueous methanol. The electron-rich aromatic system, *p*-anisaldehyde (**111**), underwent competitive attack on the ring, giving 3-bromo-*p*-anisaldehyde **112** (39%), methyl 3-bromo-*p*-anisate **113** (5%), and unexpectedly the brominated decarbonylation product 2,4-dibromoanisole **114** (38%). When the reaction was conducted using 2 equiv of Oxone, **114** was produced in excellent yield (78%) along with **113** (11%), as shown in Scheme 42. The mechanism is similar to that described in Scheme 3.

Scheme 42. Reaction of *p*-Anisaldehyde with the Oxone/NaBr System



Ross and Burrow[347] used the reaction system of Oxone/KBr in water for halogenation of nucleic acid bases. The authors noted that pyrimidines react faster than purines, and among the different pyrimidines evaluated, cytosine proved to be the most reactive. Halogenation occurs at the C-5 position (Scheme 43).

Scheme 43. Reaction of Nucleic Acid Bases with the Oxone/KBr System

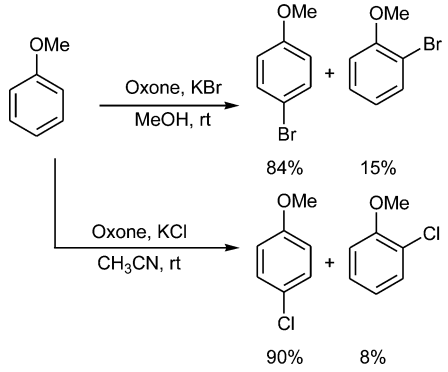


Some authors[348−352] reported on the efficient and regioselective halogenation of aromatic compounds using the binary systems of Oxone/KBr, Oxone/KCl, and Oxone/KI. A large number of different aromatic compounds were subjected to these halogenation protocols, and all proceeded with with good yields and with the expected regioselectivity being observed in acetonitrile or methanol as solvents. It was interesting to note that that the reaction gave high overall yields and para selectivity for a range of substituted benzenes evaluated. It was also found that aromatic compounds having electron-withdrawing groups on the ring underwent halogenation at a much slower rate compared to aromatic compounds with electron-donating groups. Bromination of an aromatic compound in the presence of Oxone proceeds according to Scheme 44, in which it is suggested that halogenation proceeds via formation of hypobromous acid as described in Scheme 3.

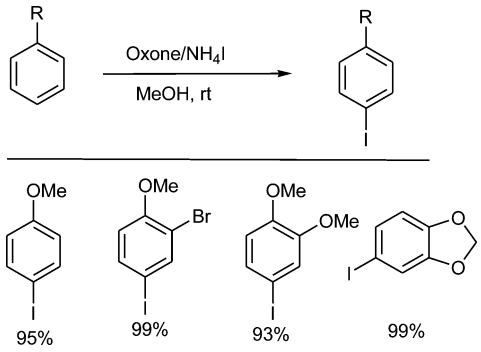
Mohan and colleagues[353] developed a simple method for iodination of aromatic compounds, which is essentially based on generation of electrophilic iodine in situ from NH_4I as the iodine source and Oxone as the oxidant (Scheme 45 and Scheme 3). Mohan's[353] iodination method generally proceeds

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Scheme 44. Oxone/KX System Halgenation of Aromatic Compounds



Scheme 45. Oxone/NH_4I System Halogenation of Aromatic Compounds



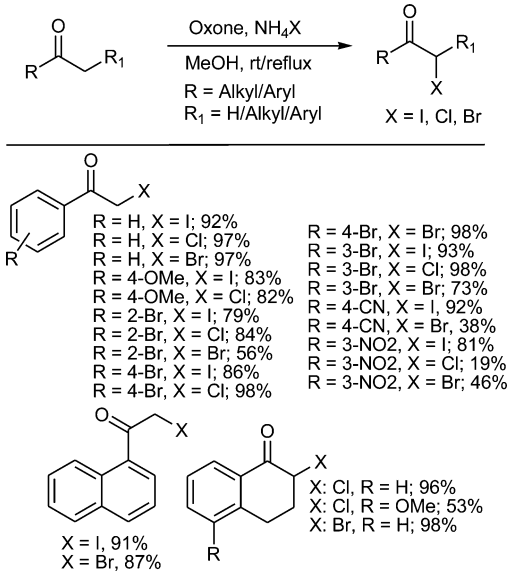
well and with high yields and good regioselectivity. Iodination proceeded with high para selectivity, especially relative to an alkoxy group and for *m*-xylene. However, in the cases of phenols and *o*-xylene the selectivities were only moderate.[353] Nitrobenzene and benzoic acid were not iodinated even under severe conditions and were recovered without change.

7.2. Oxidative Halogenation of Carbonyl Compounds

The chemistry dealing with selective introduction of an iodine atom into organic molecules has attracted considerable interest in the wider scientific community.[354−459] There are a fair number of methods reported for preparation of α-halo ketones,[360−385] but in most of these methods serious drawbacks such as use of expensive and hazardous or toxic reagents are prevalent. Recently, more efficient, environmentally friendly, atom economic (100% with respect to iodine), and selective procedures for α-monoiodination of ketones has been developed using NH_4I−Oxone, NH_4Cl−Oxone, or NH_4Br−Oxone as the halogenation source (Scheme 46).[386−388] Halogenation (iodination, bromination, and chlorination) of a variety of arylalkyl ketones proceeded efficiently to afford the corresponding α-halo ketones in moderate to excellent yields. Acetophenone produced the corresponding α-iodo product in high yields. Moderately activating and deactivating groups present on the aromatic ring of acetophenone gave moderate to high yields of the corresponding α-halo products, along with small amounts of α-methoxy-substituted products. The position of substitution of various groups on the phenyl ring of acetophenone only slightly affects the reaction yield.

It was interesting to note the effect that reaction temperature has on the course of α-bromination. It was also suggested that the presence of highly activating groups on the phenyl ring

Scheme 46. Recation of Ketones with the Oxone/NH_4X System

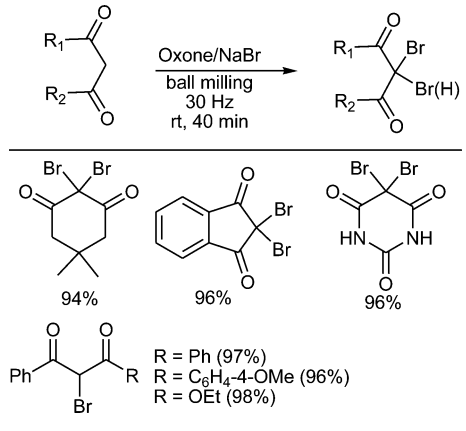


favors bromination, while moderately activating and deactivating groups favor α-bromination. Strong electron-withdrawing groups present on the phenyl ring gave α-brominated products, along with substantial amounts of α-bromodimethyl ketals. Interestingly, cyclic ketones were also found to react well under the Oxone protocol to furnish the corresponding α-bromo cyclic ketones in good to excellent yields. Interesting results were observed when unsymmetrical acyclic ketones were subjected to bromination with this reagent system. Contrary to earlier reports,[376,389,390] bromination took place predominantly at the less substituted α position.[388] The importance of the oxidant Oxone was verified by performing a blank experiment without Oxone in which no reaction occurred between acetophenone and NH_4X.

7.3. Bromination of 1,3-Dicarbonyl Compounds

Solvent-free brominations of 1,3-dicarbonyl compounds were efficiently achieved using sodium bromide and Oxone under mechanical milling conditions.[216] Bromination of representative 1,3-dicarbonyl compounds were investigated (Scheme 47). The cyclic 1,3-dicarbonyl compounds afforded α,α-dibromo derivatives in 94−96% yields. In contrast, acyclic 1,3-dicarbonyl compounds selectively gave α-monobromo derivatives in nearly

Scheme 47. Bromination of 1,3-Dicarbonyl Compounds



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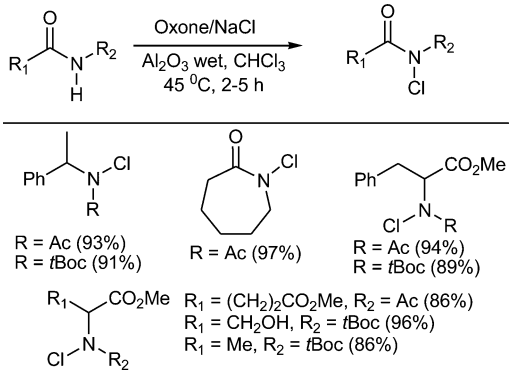
quantitative yields (96−98%), although in these cases an excess amount (2 equiv) of NaBr was employed. It would thus appear that cyclic and acyclic 1,3-dicarbonyl compounds generated α,α-dibrominated and α-monobrominated products, respectively. This difference may be due to the higher activity of the α position of cyclic 1,3-dicarbonyl compounds.[216]

7.4. *N*-Chlorination of Amides and Carbamates

N-Halo compounds are very versatile reagents in organic synthesis,[391−394] and a large number of general methods have been devised for their synthesis.[395−397] Curini et al.[398] reported on the preparation of *N*-chloroamides, lactams, and carbamates using Oxone and NaCl supported on wet alumina. Various substrates were treated with Oxone and NaCl and afforded *N*-chloroamides, *N*-chlorolactams, and *N*-chlorocarbamates in very good yields (Scheme 48). The reaction occurs by reaction

Scheme 48. *N*-Chlorination of Amides and Carbamates with the Oxone/NaCl System



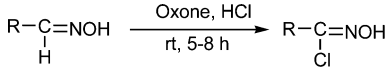
between the species produced as a result of the peroxymonosulfate oxidation of the chloride anion and the respective nitrogenous reagent.[399] It was rather interesting to note that under these reaction conditions the hydroxyl group of the serine side chain remains unreactive.[398]

7.5. Miscellaneous Halogenation of Organic Compounds

Substituted benzohydroximoyl chlorides are important intermediary compounds in synthetic chemistry, and large numbers of reagents have been developed for their synthesis.[400−403] Kim and Ryu[195] developed a protocol, which was particularly selective and by far the most convenient for preparation of benzohydroximoyl chlorides from the corresponding aldoximes (Scheme 49).

Oxone has also been used for preparation of *gem*-chloronitro compounds which are quite versatile intermediates in organic synthesis for synthesis of molecules containing nitro groups. Literature indicates that preparation of *gem*-chloronitro

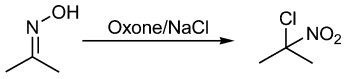
Scheme 49. Halogenation of Oximes with Oxone/HCl



No	R	Yield (%)
1	2-ClC_6H_4	95
2	3-ClC_6H_4	99
3	3-NO_2-C_6H_4	99
4	3-CF_3-C_6H_4	94

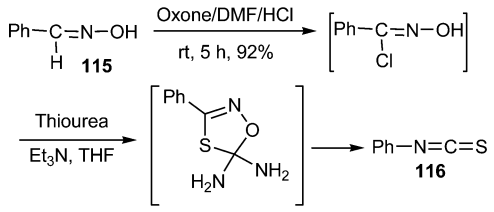
compounds occurs in two steps: chlorination[404,405] at the sp^2 carbon of the oxime followed by oxidation of chlorohydroxylamine to the nitro[406−409] compound. Ceccherelli et al.[410] reported on selective conversion of oximes into *gem*-chloronitro derivatives through a one-pot procedure using Oxone and NaCl, and this this was indeed a viable protocol to such systems (Scheme 50).

Scheme 50. Preparation of *gem*-Chloronitro Compounds Using Oxone/NaCl



Oxone with HCl/DMF is used in the preparation of isothiocyanates in one-pot reaction starting from aldoxime deratives (Scheme 51).[411] The aldoxime **115** was treated with

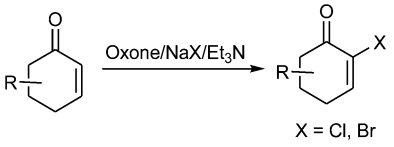
Scheme 51. Preparation of Isothiocyanates Using Oxone/HCl/DMF



the Oxone/HCl/DMF system to afford the corresponding hydroximoyl chloride, which was followed by cyclization with thiourea to finally provide the corresponding isothiocyanate derivative **116**.[411]

Addition of bromine across the double bond of α,β-enones can sometimes be problematic. However, using Oxone with NaBr or NaCl greatly facilitates addition of the halogens to α,β-enones (Scheme 52).[399] Thus, treatment of a CCl_4/aqueous

Scheme 52. Halogens to α,β-Enones Using Oxone/NaX



NaBr/cyclohexenone mixture with Oxone followed by dehydrobromination with Et_3N provided the desired 2-bromo-2-cyclohexenone in modest yield (Scheme 52). Halogenation of simple alkenes was also examined. Both cyclic and acyclic alkenes provided excellent yields of the vicinal dihalo compounds upon treatment with Oxone, and it was evident that in-situ generation of either chlorine or bromine preceded addition across the C═C bond.

Kim et al.[197] reported on the chlorination of alkynes employing the Oxone/DMF/HCl system, and in this case it provided α,α-dichloroketones in good yields (Scheme 53).

8. PROTECTION AND DEPROTECTION

8.1. Protection of Carboxylic Acids As Their Diphenylmethyl Esters

Diphenylmethyl esters (Dpm, benzhydril) are important protecting groups, especially for α-amino acids,[412] penicillins,

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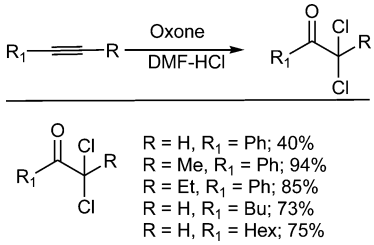
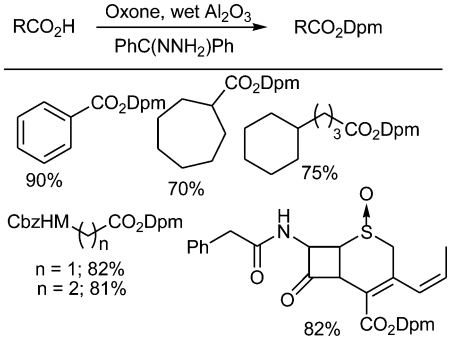
Scheme 53. Chlorination of Alkynes Using Oxone/DMF/HCl



and cephalosporins.[413] Esterification is carried out using Oxone supported on wet Al_2O_3 in methylene chloride at 0 °C and benzophenone hydrazine as reagent. This procedure is of particular importance when contrasted to the previously reported protocols.[413−415] In the current methodology several carboxylic acids have been able to be protected as their diphenylmethyl esters using Oxone oxidation of benzophenone hydrazine in the presence of the carboxylic acids.[416] (Scheme 54)

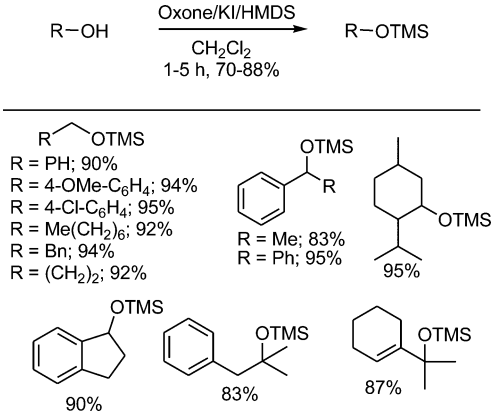
Scheme 54. Protection of Carboxylic Acids As Their Diphenylmethyl Esters with Oxone



8.2. Protection of Alcohols As Their Trimethylsil Ethers

The highly efficient method for trimethylsilylation of alcohols (not phenols) using HMDS catalyzed by molecular iodine in CH_2Cl_2 has been reported.[417] Although molecular iodine is a versatile reagent in organic synthesis,[418] it is highly corrosive, toxic, and easily sublimable which collectively make its broader use somewhat unattractive. In order to overcome these disadvantages of molecular iodine, Kolvari et al.[419] reported a convenient method for in-situ generation of the catalyzing molecular I_2 using Oxone/KI for an improved trimethylsilylation of alcohols in the presence of hexamethyldisilazane (HMDS) (Scheme 55). A variety of alcohols were subjected to the silylation protocol comprised of Oxone and a catalytic amount of KI in the presence of HMDS. All protection reactions were performed under mild and homogeneous conditions at room temperature with good to high yields. Both primary and secondary alcohols underwent reaction rapidly, and interestingly, highly hindered tertiary alcohols were also successfully converted to their corresponding trimethylsilyl ethers in almost quantitative yields at room temperature. Moreover, no side products were observed in these reactions. Additionally, different types of aryl side chain alcohols were successfully converted to the corresponding silyl ethers in short reaction times and in almost quantitative yields. Unfortunately,

Scheme 55. Protection of Alcohols As Their Trimethylsil Ethers with Oxone/KI



amines and thiols were not silylated under these reaction conditions even after prolonged reaction times.[419]

8.3. Deprotection of 1,3-Dithianes and 1,3-Dithiolanes

As a carbonyl protecting group, the *S*,*S*-acetal functional group has found wide use in organic synthesis due to its easy access[420] and high stability toward both acidic and basic conditions. In addition, *S*,*S*-acetals are often used as acyl anion equivalents in C−C bond-forming reactions.[421] A large number of methods are available for deprotection of dithioacetals to their original carbonyl entities.[422−432] Desai et al.[433] earlier reported the combination of Oxone/KBr in aqueous acetonitrile medium for bromination of activated arenes[351] as well as in the synthesis of azo-bis-nitriles.[434] However, this concept was associated with the serious drawback of probable ring bromination[348,351] in the case of activated arenes as well as formation of *α*-bromoketones.[435]

To overcome this problem, Desai et al. planned slow addition of a solution of Oxone in water to the reaction mixture containing KBr. Initially a mixture of the dithioacetal of anisaldehyde and KBr in aqueous acetonitrile (3:1) was added dropwise with stirring to a solution of Oxone in water and furnished anisaldehyde.[433] Interestingly, there was no formation of neither the ring bromination product nor the overoxidation product. To investigate the chemoselectivity in this deprotection, a series of dithioacetals derived from substituted aromatic, conjugated, as well as aliphatic aldehydes was successfully dethioacetalized employing the present reaction conditions (Scheme 56). The absence of formation of ring brominated products and overoxidation products has also been reported by Khan et al.[435,436] In another study a combination of Oxone and wet alumina was used for regeneration of the carbonyl moiety from a new series of 1,3-dithianes and 1,3-dithiolanes (Scheme 56).[437]

8.4. Deprotection of *tert*-Butyldimethylsilyl Ethers

The *tert*-butyldimethylsilyl (TBDMS)[438] group is one of the most frequently used protecting groups for the hydroxyl functional group in organic synthesis due to both its easy installation[438−441] and its general stability to basic and mildly acidic reagents. Although a variety of reagents[442−450] have been developed for deprotection of TBDMS ethers there remain a few niggling drawbacks. Oxone in a 50% aqueous methanolic solution cleaves alkyl and aryl TBDMS ethers with a fair degree of selectivity under mild conditions. The TBDMS ethers of primary alcohols were deprotected within 2.5−3.0 h, whereas

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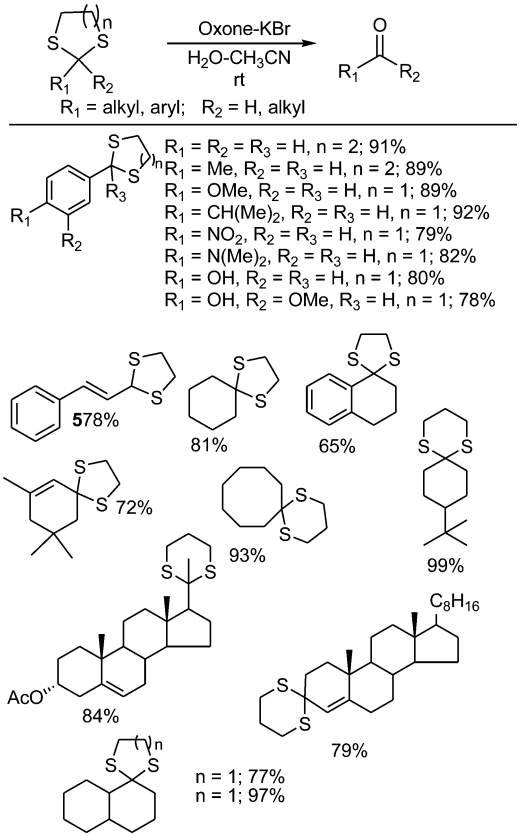
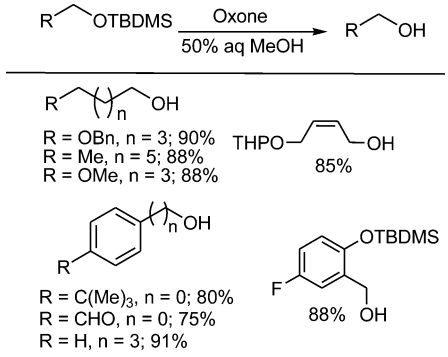
Scheme 56. Deprotection of 1,3-Dithianes and 1,3-Dithiolanes with Oxone/KBr and Oxone/SiO_2 Systems



the phenolic TBDMS ethers remained unaffected (Scheme 57). Prolonged stirring for 20−24 h of phenolic TBDMS ethers was necessary before cleavage was affected. This reveals the very useful selectivity between alkyl and phenolic TBDMS ethers. On the other hand, TBDMS ethers of secondary and tertiary alcohols were unaffected by treatment with Oxone under these same conditions.

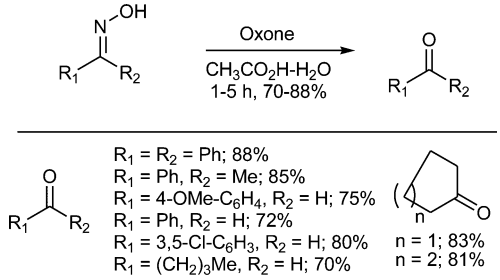
Scheme 57. Deprotection of *tert*-Butyldimethylsilyl Ethers with Oxone



8.5. Deprotection of Oximes

The deoximation reaction to liberate the derived carbonyl compounds under mild conditions is an important process employed in general synthetic organic chemistry,[451,452] and many valuable methods have been developed for deprotection of oximes to their original carbonyl moiety (deoximation of oximes).[453] An Oxone-based protocol was developed for deprotection of oximes to their corresponding carbonyl compounds in water (Scheme 58).[454] Oxidative cleavage of oximes to carbonyl compounds was performed with peroxymonosulfate ion in glacial acetic acid in good yields. The reaction was most suitable for conversion of ketoximes to ketones. However, deoximation of aldoximes requires longer reaction times.[454]

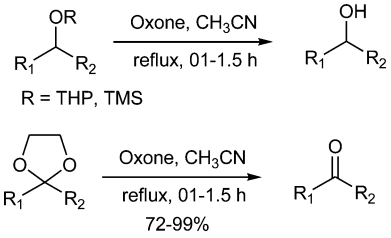
Scheme 58. Deprotection of Oxime



8.6. Deprotection of Silyl, Tetrahydropyranil Ethers, Ketals, and Acetals

Protection of alcoholic functional groups by conversion into their silyl and tetrahydropyranyl ethers is a common practice used by most major research enterprises. Baltork[455] reported that treatment of TMS− and THP−ethers with Oxone in refluxing acetonitrile facilitated deprotection in short times and excellent yields (80−99%) (Scheme 59). It is most interesting and vital to note that this procedure transforms allylic ethers into the corresponding allylic alcohols without any epoxidation of the carbon−carbon double bond. The same conditions may be applied for deprotection of ethylene acetals and ketals. These moieties were cleaved in good yields, and similarly to allylic ethers, deprotection of conjugated enal systems occurred without compromising the double bond. This procedure, when applied to TMS−ethers in the presence of THP−ethers and acetals or ketals, gives chemoselective deprotection of the TMS−ether over the other protecting groups but requires careful monitoring. Another format of this reaction applied to THP− and TMS−ethers as well as ketals involves the use of benzyltriphenylphosphonium Oxone[456] in the presence of $BiCl_3$ under microwave irradiation, and most acceptable results were thus obtained.

Scheme 59. Deprotection of Silyl, Tetrahydropyranil Ethers, Ketals, Acetals, and Ethylene Acetals and Ketals with Oxone



9. MISCELLANEOUS

9.1. Benzylic Oxidation

Numerous methods have been developed for direct benzylic oxidation of alkylarenes using heavy metals.[457−479] Recently, a new heavy-metal-free direct and selective benzylic oxidation

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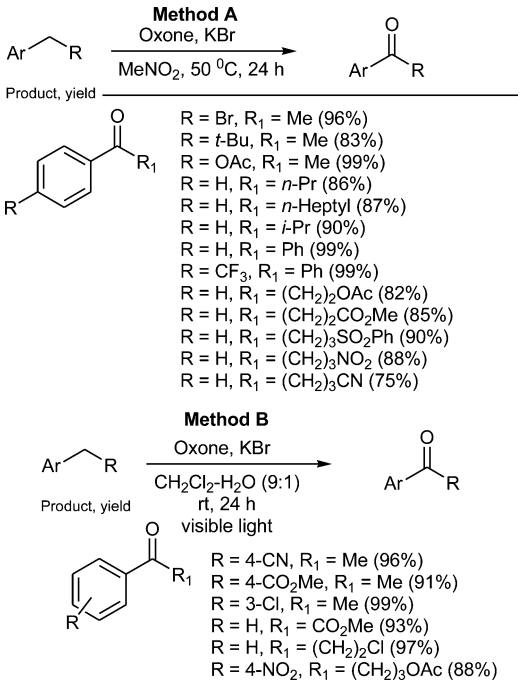
method of alkylarenes was reported by Moriyama et al.[480] as well as Yin et al.[481] using an alkali metal bromide/Oxone system. Different alkylarenes were oxidized by employing this system, which was optimized into methods A and B, the conditions of which are given in Scheme 60. Thus, in method

Scheme 60. Direct Benzylic Oxidation of Alkylarenes with Oxone



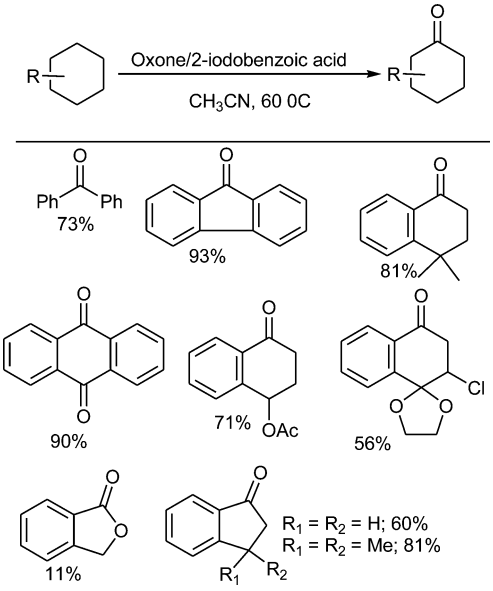
A, para-substituted alkylarenes bearing Br, *t*-Bu, and AcO afforded the oxidized products in excellent yields (83−99%), while reaction of *n*-butylbenzene, *n*-octylbenzene, and isobutylbenzene provided their respective ketones in 86−90% yield. In the photooxidation (method B) protocol, far better yields were obtained compared to thermal oxidation (method A) for direct benzylic oxidation of alkylarenes having an electron-withdrawing group.[480]

In a similar sense oxidation of benzylic C−H bonds could be efficiently achieved using the hypervalent iodine-derived IBS catalyst generated in situ from 2-iodobenzoic acid and Oxone in the presence of the phase-transfer catalyst, n-Bu_4NHSO_4, in anhydrous acetonitrile.[482] Different alkylbenzenes, including toluenes and ethylbenzenes, several oxygen-containing functionalities substituted alkylbenzenes, and a cyclic benzyl ether, were all evaluated and gave oxidative products with good yields (Scheme 61). It was further proved that Oxone was a more powerful oxidant than IBX, and acetonitrile was the best solvent among all tested.

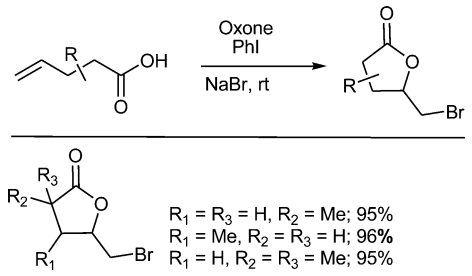
9.2. Lactone Formation

Halolactonization serves as one of a host of key reactions in synthetic chemistry.[483−486] Recently, bromolactonization of alkenoic acids was reported to occur in the presence of Oxone and iodobenzene and during which cyclization of various 4-pentenoic acids with NaBr was easily carried out in CF_3CH_2OH as the solvent (Scheme 62).[487] Although reports suggest most reactions provide good to excellent yields of five-membered bromolactones, the product obtained for the same reaction of 2-cyclopentene-1-acetic acid was isolated only in

Scheme 61. Benzylic C−H Oxidation of Alkylarenes with Oxone



Scheme 62. Halolactonization with Oxone



moderate yield due to the restrictive effect of the ring. Unfortunately, reaction of 3-butenoic acid and *trans*-3-hexenoic acid provided unsaturated lactones and not the desired bromolactones. Experiments suggested that that the desired five-membered lactones and in some instances the four-membered lactones were first formed followed by their transformation into the unsaturated lactones during the workup procedure by elimination. Efforts for preparation of six-membered lactone, viz., 6-bromomethyltetrahydropyran-2-one from 5-hexenoic acid, were only partially successful with only 27% yield of product being isolated.[487]

In a further study by Schomaker et al.[488] the group reported on direct lactonization of alkenols via OsO_4−Oxone oxidative cleavage lactonization (Scheme 63). Conversion of 4-penten-1-ol and 5-hexen-1-ol to butyrolactone and valerolactone, respectively, was achieved in good yields, thus demonstrating that alkyl-substituted olefins can also undergo lactonization in preference to oxidation to carboxylic acids. Formation of five- and six-membered lactones was achived in good yield, but the yield dropped off considerably for larger rings, viz., formation of caprolactone. Longer chain alken-1-ols gave no discernible amounts of lactone with the carboxylic acids being isolated as the sole products. The yield of seven-membered lactones could however be improved, provided that conformational freedom was restricted, but similar attempts to form an eight-membered lactone were unsuccessful and led only to the carboxylic acid products. However, tertiary alcohols with steric crowding of the

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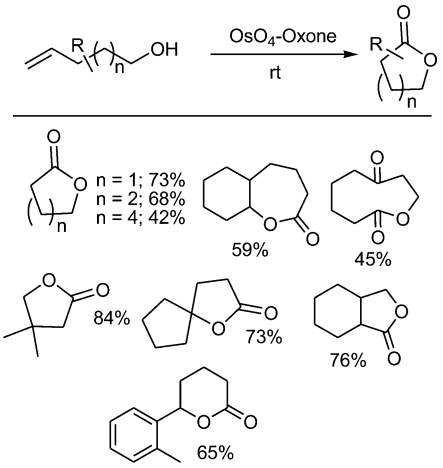
Scheme 63. OsO_4/Oxone Oxidative Cleavage Lactonization

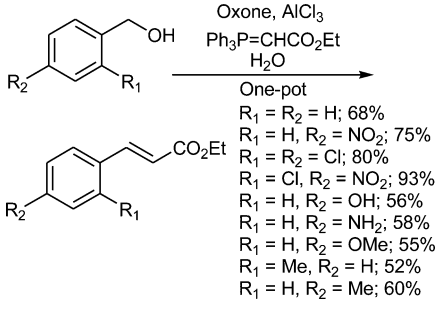


hydroxyl groups, surprisingly, reacted efficiently to yield lactone products. Fused 5/6- and 6/7-ring systems could also be obtained in good isolated yields.[488]

9.3. Domino Synthesis of Alkenes

Treatment of ylides with aldehydes (Wittig reaction) provides, through the products, access to alkenes with either high *E*- or *Z*-geometrical selectivity and has been utilized extensively over many years.[247] In order to extend the application of Wu et al.,[247] who used a clean reaction system (combination of Oxone and $AlCl_3$), domino synthesis of alkenes was developed which started from oxidation of a primary alcohol and then immediately followed by olefination. Under the optimized conditions developed, adding the ylides afforded only alkene as the final product. Wu et al.[247] examined the scope of the aqueous Wittig reaction for synthesis of a variety of alkenes, and the results are depicted in Scheme 64. The Wittig reaction

Scheme 64. Domino Synthesis of Alkenes with Oxone/$AlCl_3$

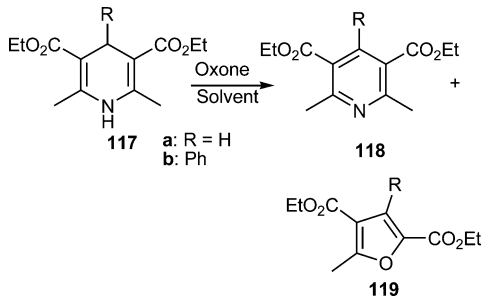


in water is a relatively straightforward protocol that works favorably between ylids and benzyl alcohols having electron-donating or electron-withdrawing groups. All products were isolated in moderate to excellent yields, and the reaction gave preferentially the *E*-isomer. The presence of electron-withdrawing groups gave increased reaction yields, whereas electron-releasing groups gave the corresponding product in lower yield.

9.4. Hantzsch 1,4-Dihydropyridine Transformation to Furan

Oxidation of Hantzsch 1,4-dihydropyridines (DHPs), a class of model compounds of the NADH coenzyme,[489,490] has attracted continuing interest by organic chemists, and a number of protocols has been developed for such purposes.[491−499] In the initial part of this study, DHP (**117a**) was treated with 2 equiv of Oxone in CH_3CN at room temperature and the fully aromatized product **118a** was generated as expected in 65% yield. However, when 4-phenyl DHP (**117b**) was treated with Oxone under the same condition, two products were isolated from the reaction mixture. One was the normal pyridine derivative **118b** (28%) along with a 12% yield of the unexpected tetrasubstituted furan **119b** (Scheme 65).[500] In

Scheme 65. Hantzsch 1,4-Dihydropyridine Transformation to Furan with Oxone



light of this finding, the reaction conditions were optimized to increase the yield of **119b**. Various solvent systems were tested, and it turned out that nonpolar solvents such as toluene and CH_2Cl_2 were unfavorable for formation of **119b** even in the presence of a typical phase-transfer reagent, viz., *n*-Bu_4NHSO_4. Polar solvents such as CH_3CN, CH_3OH, and C_2H_5OH were better solvents to effect the reaction, especially in the presence of H_2O. Interestingly, however, no furan product was generated in the solvent DMF. The best result was obtained in MeCN at refluxing temperature, which afforded **119b** in 44%.[500]

9.5. Dearomatization of *p*-Alkyl Phenols to *p*-Peroxyquinols and *p*-Quinols

Previous literature showed that a good number of methods are available for preparation of the *p*-peroxyquinols[325] and that these methods included the use of oxygen and H_2O_2.[501−504] However, despite their efficiency, these methods have not yet been applied extensively. Treatment of 3,4,5-trimethylphenol (**120**) with Oxone in a basic medium afforded *p*-peroxyquinol **131** in 93% yield (Scheme 66). The structure of **131** was confirmed by its reduction to the *p*-quinol **142** by treatment with PPh_3. Unfortunately, purification of *p*-quinol **142** from the resulting mixture with PPh_3=O was troublesome.[505] To overcome the purication problem a one-pot procedure was developed in which the water-soluble reducing agent $Na_2S_2O_3$ was used, and this lead to formation of *p*-quinol **142** in 83% yield, without any troublesome purification. Scheme 65 illustrates the products obtained when this same methodology was applied for preparation of *p*-peroxyquinols and *p*-quinols. For comparison, the maximum yields, in brackets, are included for previous transformations of *p*-alkyl phenols into *p*-peroxyquinols or *p*-quinols. Oxidative dearomatization of *p*-alkyl phenols **121−130** with Oxone was very fast (15−140 min), and *p*-peroxyquinols **132−141** were obtained in good to excellent yields (53−100%) in method A. The direct access method to *p*-quinols **142−152** was also achieved by adding $Na_2S_2O_3$ to the crude mixture and stirring for 30 min at room temperature (method B). Interestingly, method B provided access to the *p*-quinols in moderate to excellent yields (33−98%). The above methodlogy was also applied for synthesis of some simple natural products, viz., hallerone (**150**) or

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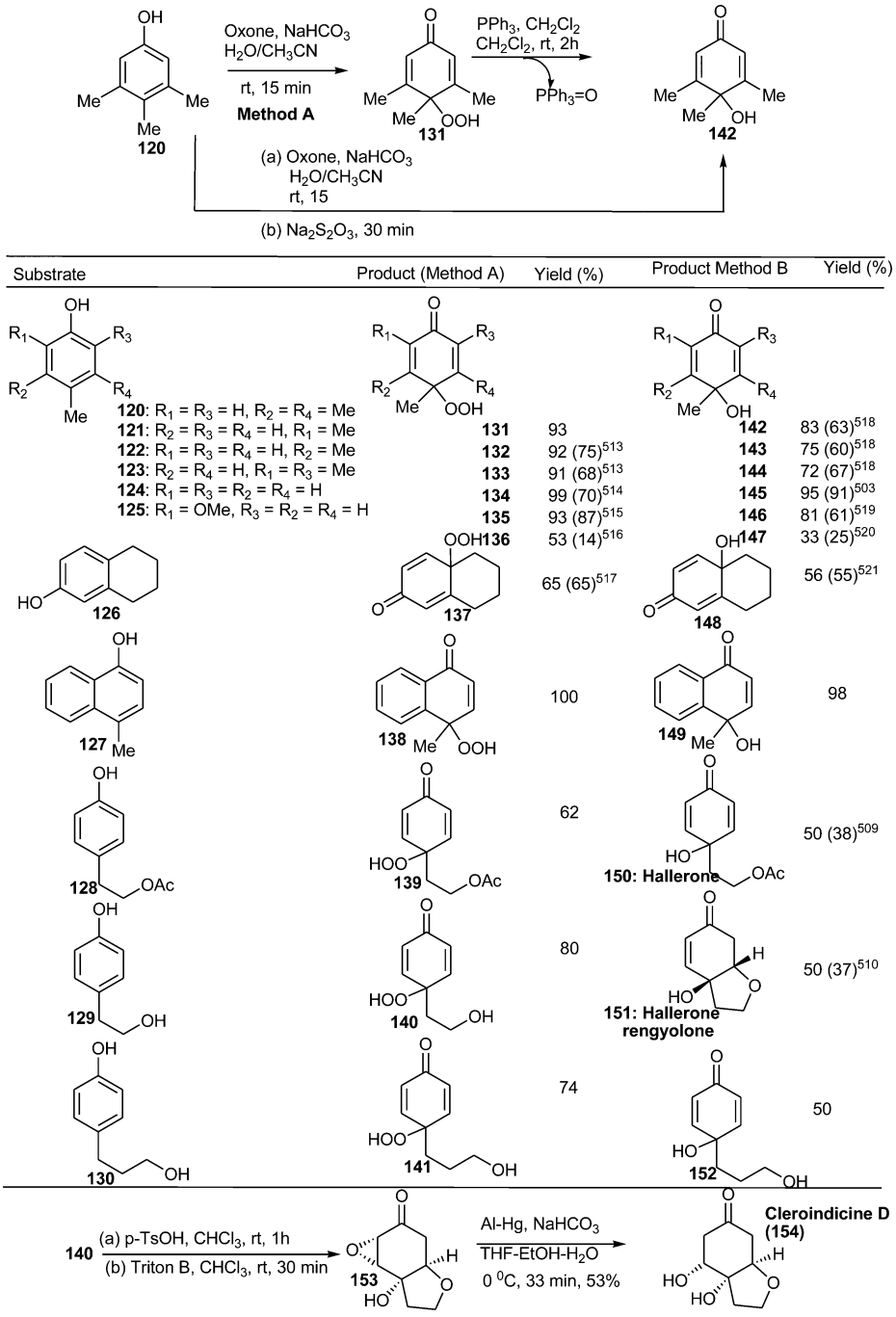
Scheme 66. Dearomatization of *p*-Alkyl Phenols with Oxone



halleridone (rengyolone) (**151**) isolated from *Halleria lucida*,[506] with interesting biological and therapeutic properties.[507,508] Both compounds have been prepared previously in yields of 38% and 37%, respectively, by sensitized photooxygenation of the respective phenols.[509,510] Thus, oxidative dearomatization of phenol **128** under method B provided hallerone (**150**) in 48% yield. Similarly, halleridone (rengyolone) (**151**) was prepared from **129** via method B in 50% yield.[505] The same authors also synthesized natural product cleroindicin D (**154**),[511] reported by Sun et al. to be isolated from the aerial parts of *Clerodendrum indicum* in 1997.[512]

9.6. Synthesis of 3,4-Dihydrocoumarins

Coumarin and its derivatives is one of the most privileged structural motifs frequently found in natural products and pharmaceuticals.[522−525] As an important class of coumarins, 3,4-dihydrocoumarins are widely distributed in nature[526−528] and exhibit some interesting biological activities, such as antiherpetic, anti-inflammatory, antioxidative, antiaging, and anticancer activities.[529−532] For this reason development of efficient protocols for synthesis of dihydrocoumarins have attracted great interest among the major research groups in recent years.[533−535] Thus, Gu and Xue[536] reported the direct oxidative cyclization of 3-arylpropionic acids to afford 3,4-dihydrocoumarins using Oxone in the presence of $BF_3{\cdot}OEt_2$. Generally, 2.0 equiv of Oxone and 1.5 equiv of $BF_3{\cdot}OEt_2$ were

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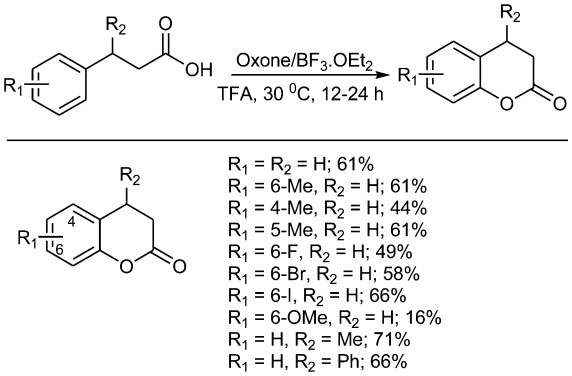
found to be the best ratio for smooth conversion of acids in TFA into their corresponding cyclized products in 16−71% yields (Scheme 67). This transformation could be applied to

Scheme 67. Synthesis of 3,4-Dihydrocoumarins Using Oxone/BF_3·OEt_2

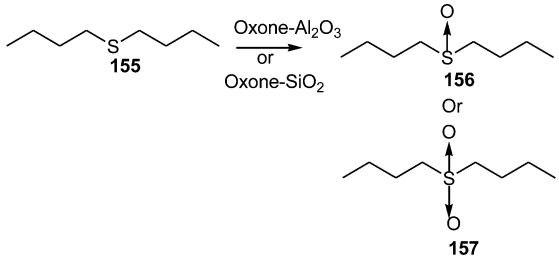


precursor acids containing a range of functional groups, including methyl, phenyl, halide, and methoxy groups. However, when the substrate contains an electron-withdrawing group, e.g., in 3-(4-carbomethoxyphenyl)propionic acid, the reaction was not successful.[536]

9.7. Oxidation of Sulfides to Sulfoxides and/or Sulfones

Sulfones are valuable synthetic intermediates for construction of chemically and biologically important molecules,[537−541] especially those that have demonstrated biological activities.[542−549] It has been reported that Oxone dispersed on "wet alumina" suspended in organic solvents effects oxidation of phenyl alkyl sulfides to their corresponding sulfoxides and sulfones.[550] Kropp et al.[300] found that oxidation of sulfide **155** and sulfoxide **156** or sulfone **157** occurs equally well when the Oxone is dispersed on either alumina or silica gel (Scheme 68).

Scheme 68. Oxidation of Sulfides to Sulfoxides and/or Sulfones with Oxone



Initially mixing of solid Oxone with moist silica gel or alumina, either as a suspension in CH_2Cl_2 or solvent free, apparently results in its dispersion or at least dispersion of the active component $KOSO_2OOH$ on the surface of the adsorbent, thereby facilitating oxidation. A small amount of water is necessary to facilitate adsorption[551−553] as well as promote heating when microwave irradiation is applied. Sulfoxide **156** underwent oxidation substantially slower than sulfide **155** with Oxone over both silica gel and alumina, which might be expected from both its weaker nucleophilicity and its higher degree of adsorption to the surfaces. Oxone is extensively used for oxidation of sulfides to their corresponding sulfoxides and sulfones, and results are summarized in Table 2.

9.8. Oxidation of Alkylcyanohydrazines to Azo-Bis Nitriles

The chemistry of azo-bis nitriles, a useful class of organic compounds, has been the subject of intensive studies over many years. Commercially, they are used as initiators for free radical polymerization of common vinyl monomers like styrene, vinyl chloride, vinyl acetate, and alkyl methacrylates.[619] Azo-bis nitriles are prepared in good yields and high purity by oxidation of the corresponding 1,2-bis-dialkylcyano hydrazines using Oxone/KBr in aqueous medium.[489] A variety of such 1,2-bis-dialkylcyano hydrazines were smoothly oxidized using the Oxone/KBr reagent system to form the corresponding azo-bis nitriles in good yields except for the levulinic acid-based hydrazino compound in which case the yield was low (Scheme 69).[489]

9.9. Thiocyanation of Aromatic Compounds

Thiocyanation of aromatic and heteroaromatic compounds is presently one of the more important reactions for synthesis of sulfur-containing heterocycles[620,621] and is particularly useful for producing drugs and pharmaceuticals.[622] Wu et al.[623] reported on the regioselective approach for thiocyanation of indoles, anilines, pyrrole, and carbazoles using ammonium thiocyanate as a thiocyanation reagent and Oxone as an oxidant. Interestingly, monothiocyanation of indoles and 2-methoxycarbazole uniquely occurred at the 3 position of the indole ring (Scheme 70). Similarly, pyrrole was also easily transformed into the monothiocyanated product. The aromatic amino compounds were readily converted to the monothiocyanated products with high para selectivity. Since aromatic amino compounds could be oxidized, some highly polar byproducts, easily dissolvable in water, were formed which led to correspondingly decreased yields of thiocyanated products.[623]

9.10. Synthesis of Benzimidazoles

Benzimidazole derivatives have found commercial application in veterinarian medicine as anthelmintic agents and in such diverse human therapeutic areas as antiulcer agents, antihypertensives, antivirals, antifungals, anticancers, and antihistaminics.[624,625] Addition of Oxone to a mixture of a 1,2-phenylenediamine and an aldehyde in wet DMF at room temperature results in rapid formation of benzimidazoles under what can only be described as very mild conditions. The reaction was successfully applied to a wide range of substrates including aliphatic, aromatic, and heteroaromatic aldehydes and is not significantly affected by steric or electronic effects (Scheme 71).[626] In most cases crude products are isolated in good to excellent yields (59−95%) and homogeneities (86−99%) by simple precipitation or extraction from the reaction mixture and do not require additional purification. Some nitrogen and the one sulfur-containing heterocycles were not affected by the oxidizing power of Oxone, and additionally, electron-rich aldehydes were well tolerated. Functionalities such as carboxylic acid and phenolic hydroxyl groups do not require protection. Limitations to the scope of this methodology were encountered in cases of aldehydes, which were sensitive to Oxone under acidic reaction conditions. In most cases, reasons for unsuccessful reactions could be traced to the aldehyde component and its incompatibility toward Oxone. For example, α,β-unsaturated aldehydes and indole 3-carboxaldehyde gave complex reaction mixtures.[626]

9.11. Oxidation of selenides

While oxidation of sulfides to sulfoxides and sulfones using Oxone has been presented vide infra, few examples of a similar

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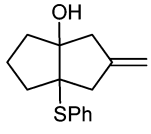
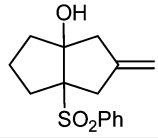
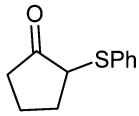
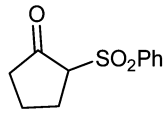
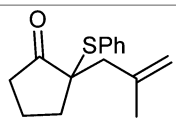
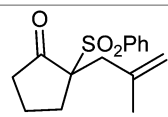
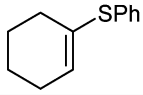
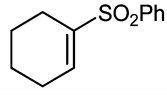
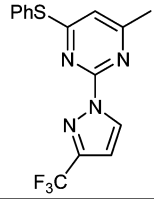
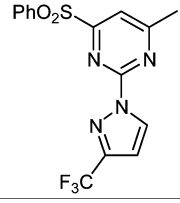
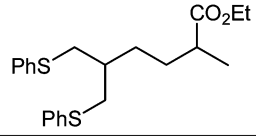
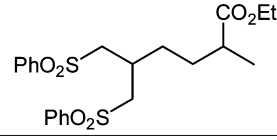
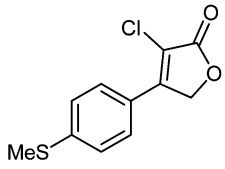
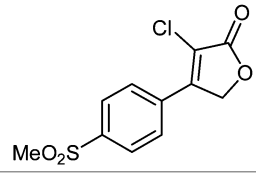
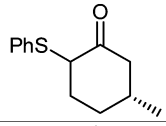
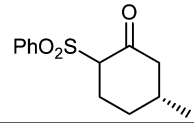
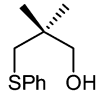
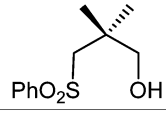
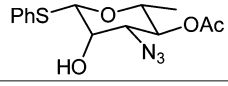
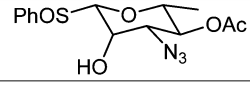
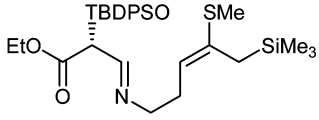
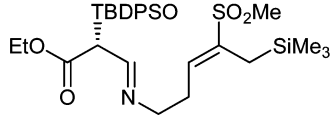
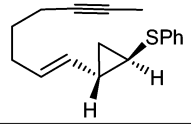
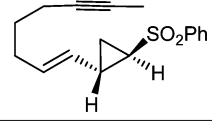
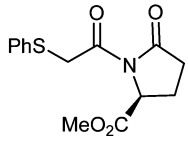
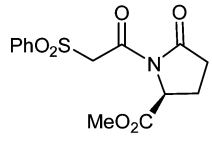
Table 2. Oxidation of Sulfies to Sulfoxides or Sulfones Using Oxone

No.	Substrate	Product	Yield (%)	Ref.
1			94	554
2			98	554
3			92	554
4			98	554
5			91	555
6			99	556
7			85	557
8			95	558
9			89	559
10			64	560
11			92	561
12			62	562
13			67	563

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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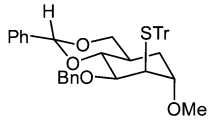
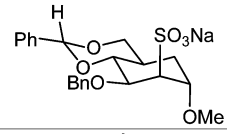
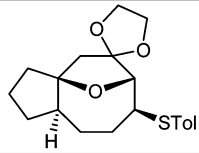
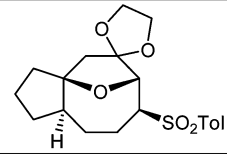
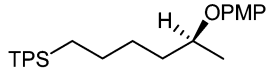
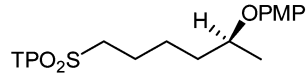
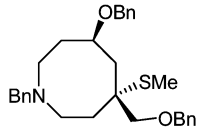
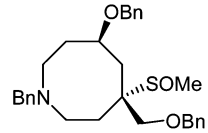
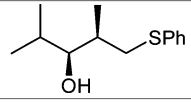
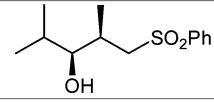
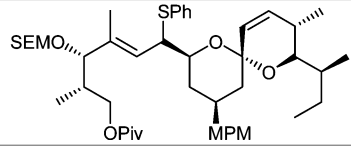
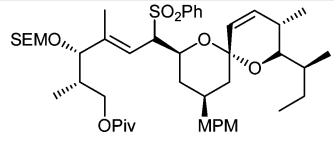
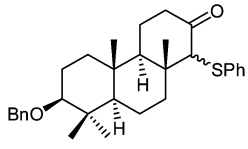
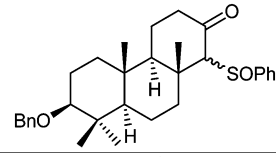
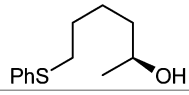
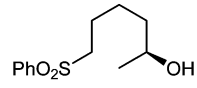
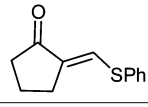
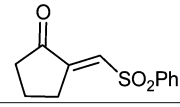
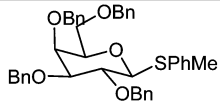
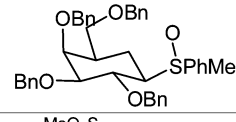
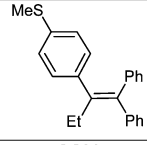
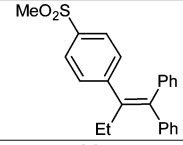
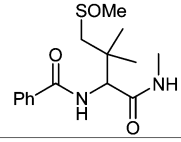
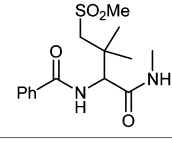
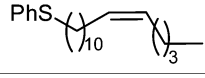
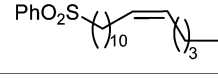
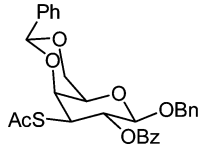
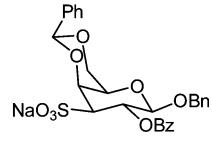
14			35	564
15			97	565
16			88	566
17			NA	567
18			80	568
19			80	569
20			NA	570
21			57	571
22			75	572
23			71	573
24			76	574
25			90	575
26			92	576
27			68	577

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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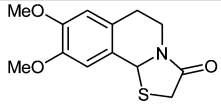
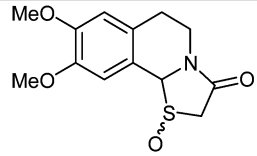
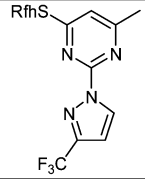
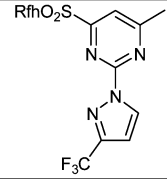
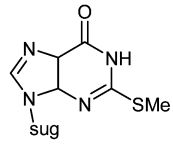
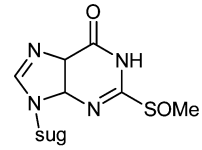
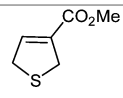
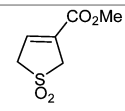
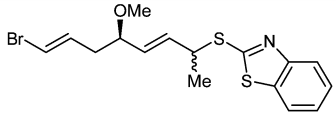
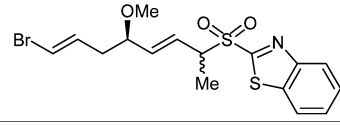
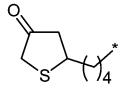
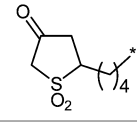
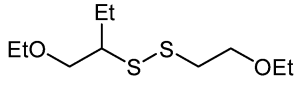
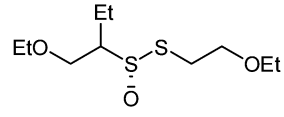
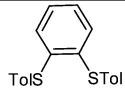
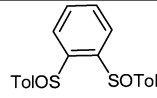
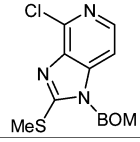
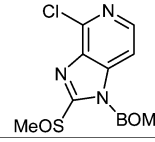
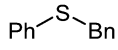
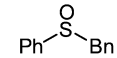
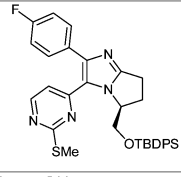
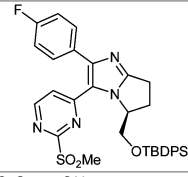
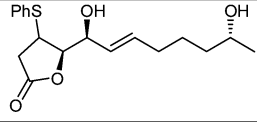
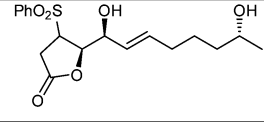
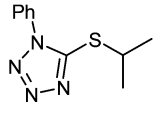
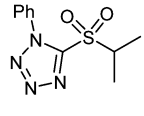
28			96	578
29			91	579
30			NA	580
31			NA	581
32			NA	582
33			78	583
34			80	584
35			40	585
36			91	586
37			95	587
38			79	588
39			82	589
40			85	590

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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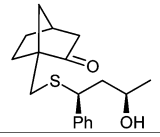
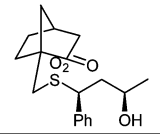
41			97	591
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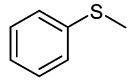
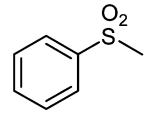
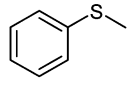
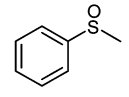
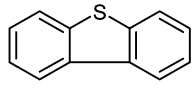
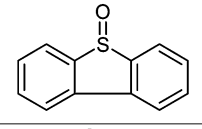
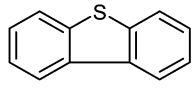
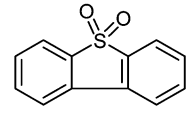
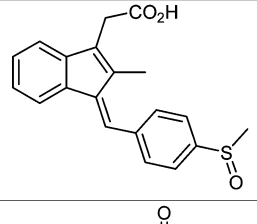
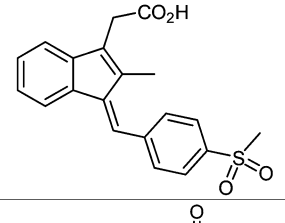
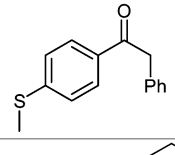
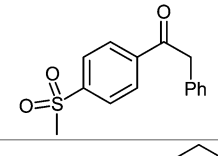
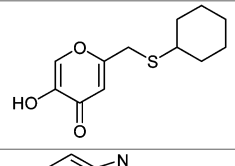
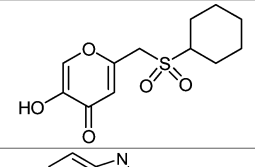
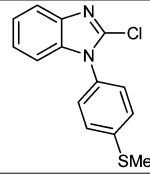
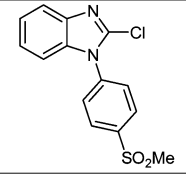
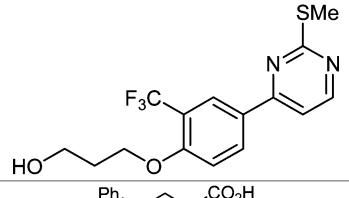
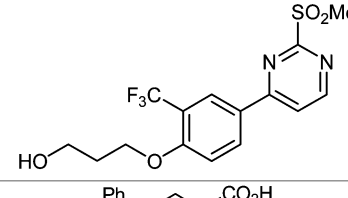
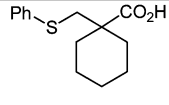
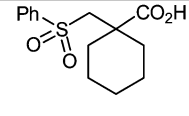
43			99	593
44			96	593
45			48	593
46			97	593
47			NA	594
48			NA	595
49			NA	596
50			NA	597
51			NA	598
52			NA	599

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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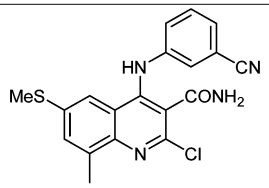
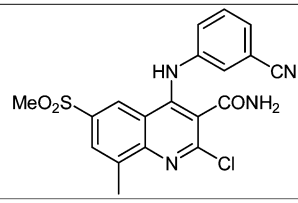
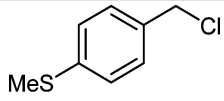
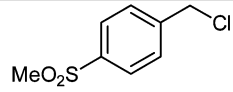
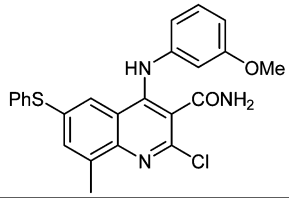
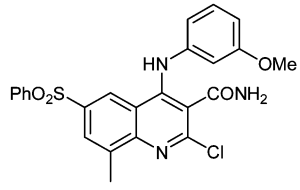
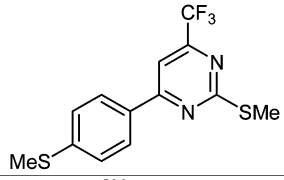
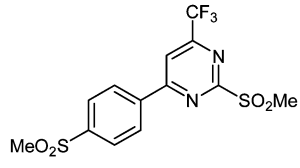
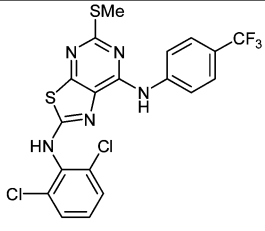
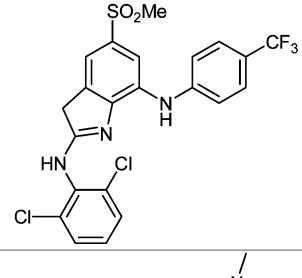
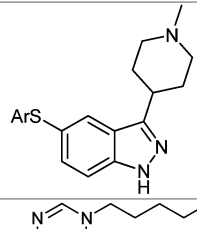
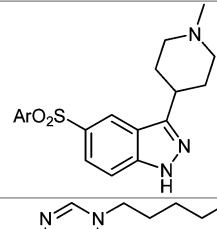
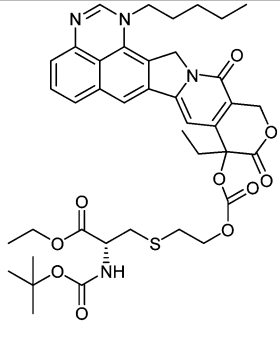
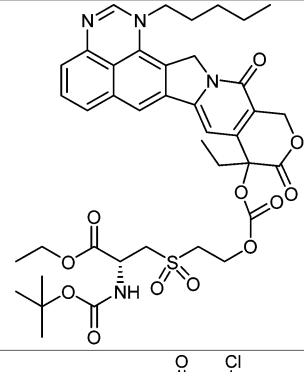
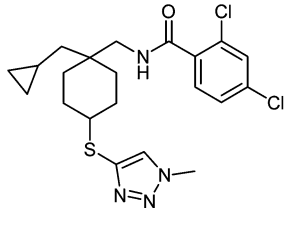
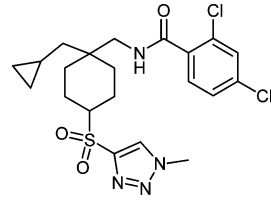
53			NA	600
54			NA	601
55			NA	602
56			91	603
57			90	604
58			90	605
59			88	606
60			NA	607

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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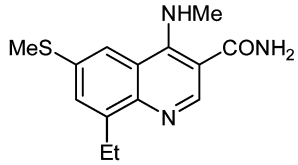
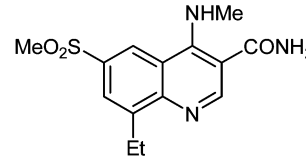
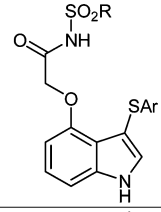
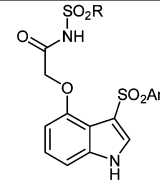
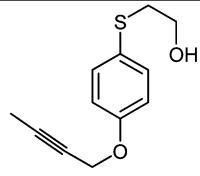
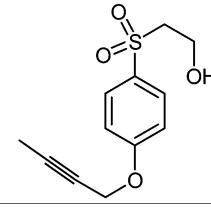
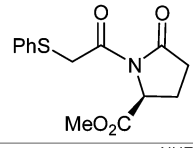
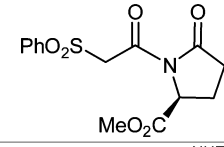
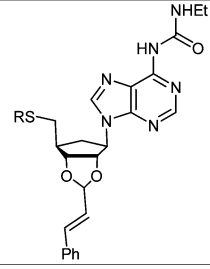
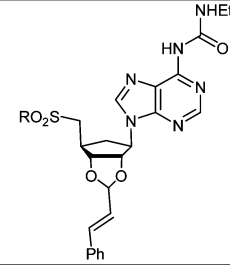
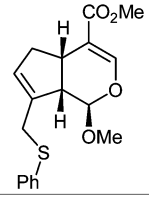
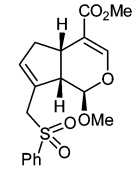
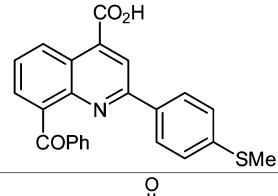
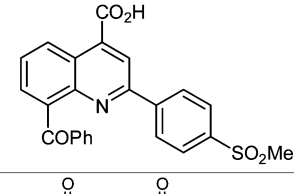
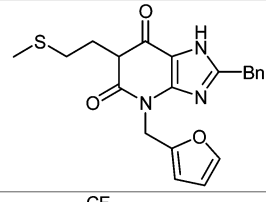
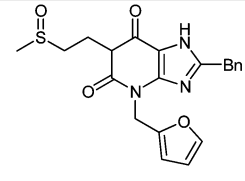
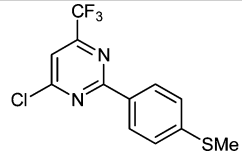
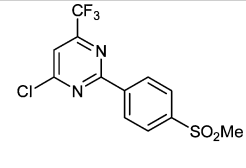
61			NA	608
62			94	609
63			82	610
64			NA	611
65			NA	612
66			NA	613
67			NA	614
68			NA	615
69			NA	616

dx.doi.org/10.1021/cr3004373 | Chem. Rev. 2013, 113, 3329−3371

Table 2. continued

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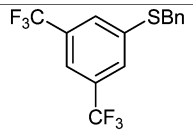
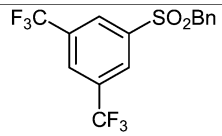
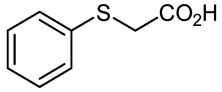
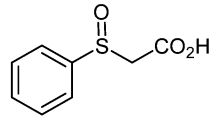
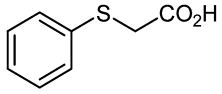
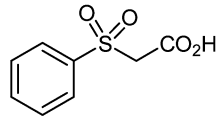
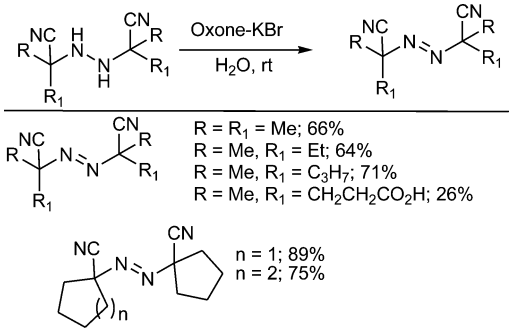
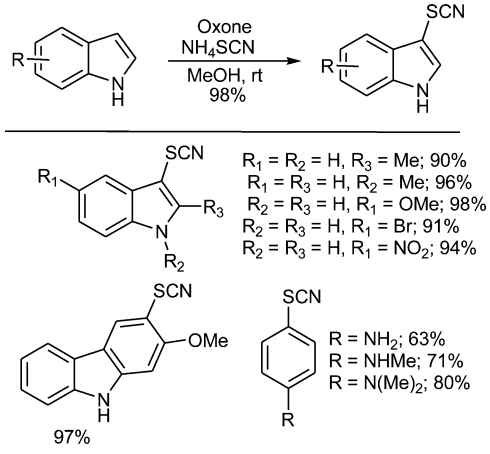
70			93	617
71			98	618
72			96	618

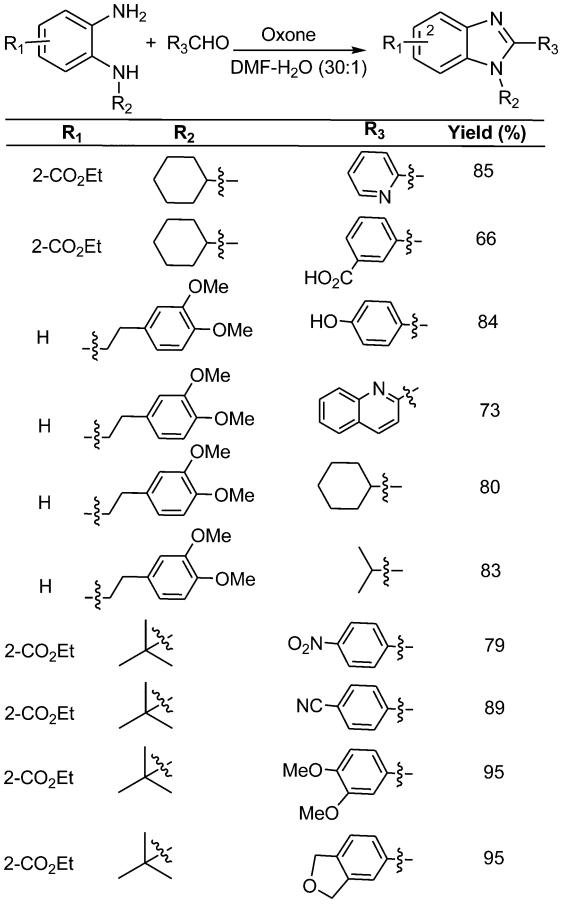
Scheme 69. Oxidation of Alkylcyanohydrazines to Azo-Bis Nitriles with Oxone/KBr



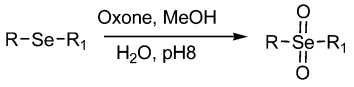
Scheme 70. Thiocyanation of Aromatic Compounds



Scheme 71. Synthesis of Benzimidazoles with Oxone



Scheme 72. Oxidation of Selenides Using Oxone



type of oxidation of selenides to selenoxides and selenones have been reported.[627] One of the first reports in this regard is preparation of selenones using Oxone in methanolic aqueous-buffered solution described in 1995[628] (Scheme 72).

The protocol was applied to oxidation of three classes of substrates, viz., alkylaryl selenides, β-methoxyalkyl selenides, and β-hydroxyalkyl selenides. Selenones were obtained in good yields, representing improvements on the already described methods, in shorter times, and under milder conditions for oxidation of alkyaryl selenides and β-methoxyalkyl selenides. In the oxidation of β-hydroxyalkyl selenides however, only the corresponding epoxides were obtained. It is interesting to note that when using this procedure it is possible to avoid skeletal rearrangements that are always observed when using alternative methods during attempted selenone formation of β-hydroxy and β-methoxy selenides illustrated in Scheme 73.[629]

9.12. Olefin Metathesis−Ketohydroxylation

Chiral α-oxygenated carbonyl compounds (acyloins) are extremely useful building blocks in organic synthesis and serve as structural motifs in a variety of biologically active natural products.[630] A report has been written which describes

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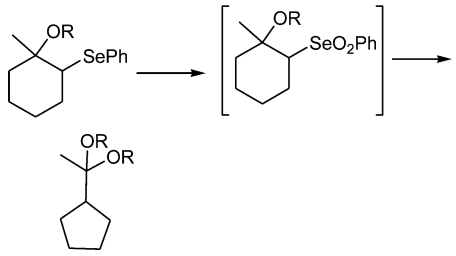
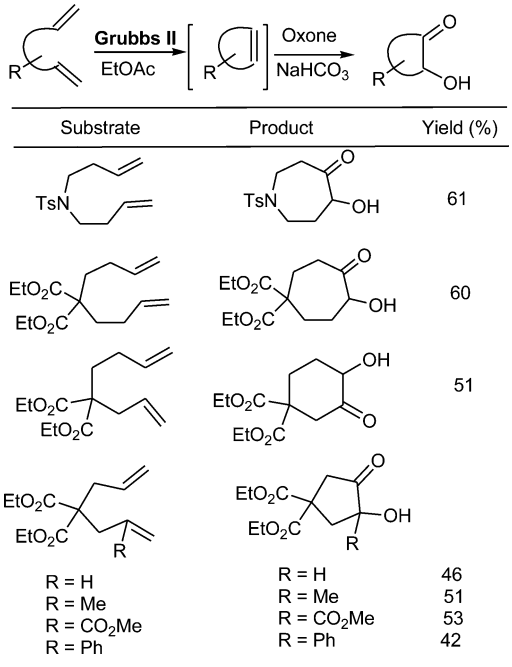
Scheme 73. Oxidation of Selenides Using Oxone



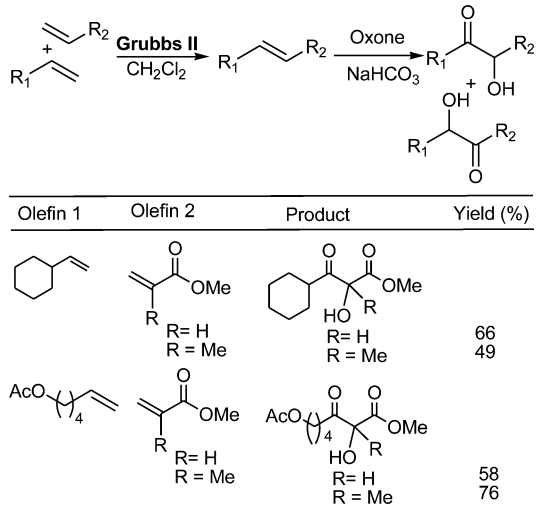
how the Grubbs' second-generation catalyst has been used in the metathesis/oxidation of olefins to generate α-hydroxy ketones employing Oxone and $NaHCO_3$.[631] Ketohydroxylation was performed in a 6:6:1 mixture of MeCN/EtOAc/H_2O in the presence of Oxone, $NaHCO_3$, and 5 mol % of the ruthenium catalyst. Oxidation was rapid (ca. 10−20 min) and provided the α-ketohydroxylated products in 42−61% overall yields (Scheme 74).

Scheme 74. Olefin Metathesis−Ketohydroxylation Using Oxone



Given the success of the tandem RCM/α-ketohydroxylation sequence, the strategy was then expanded to include cross metatheses (CM). Initial olefinic reaction partners were chosen to afford the corresponding CM products in good yield and *E*/*Z* selectivity.[632] Evaluation of the CM conditions indicated that performing the metathesis in CH_2Cl_2 with a 1:2 mixture of olefins gave the desired CM products in excellent yield (Scheme 75). For the ketohydroxylation step, the excess cross-metathesis partner and solvent were removed in vacuo prior to addition of the Oxone. Yields for this tandem process ranged from 49% to 76%, and like the RCM examples, the regioselectivity of the oxidation was generally low. It was proposed that the mixtures observed were due to a selective oxidation followed by isomerization of the resulting β-keto esters under the reaction conditions.[631]

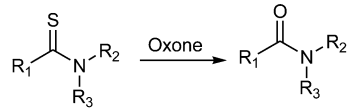
Scheme 75. Cross-Metatheses Reactions Using Oxone



9.13. Conversion of Thioamides into Amides

Conversion of thioamides into their respective amides represents both an unusual but a valuable reaction in synthetic organic chemistry. Many methods and reagents[633−639] have been reported for transformation of thiocarbonyl compounds into their corresponding carbonyl analogues. However, some of these methods have certain limitations. Mohammadpoor-Baltork et al.[639] reported on the mild and convenient procedure for tranformation of thioamides, thioureas, and thioesters into their corresponding carbonyl analogues using Oxone (Scheme 76). The yields for most of the reactions were more than 90%,

Scheme 76. Transformation of Thioamides into Amides



R_1	R_2	R_3	Time (min)	Yield (%)
Me	H	H	5	95
NH_2	H	H	5	96
Ph	Ph	H	15	90

and reaction times were less than 30 min. Similary, Bahrami et al.[640] reported on the transformation of thiocarbonyls into their corresponding carbonyl compounds using Oxone.

9.14. Preparation of Disulfides from Thiols

The vital biological role of thiols and disulfides in living systems has mainly focused on their interconversion reactions. Oxidative conversion of thiols to disulfides is of importance from both biological and synthetic points of view.[641,642] A new method for effective conversion of thiols to their corresponding disulfides was reported by Zolfigol et al.[643] using an Oxone−MX system. Different types of thiols were subjected to oxidation in the presence of Oxone−MX (MX = NaCl, KCl, KBr) and wet SiO_2 to afford good to excellent yields of disulfides (Scheme 77). Of interest to note is that KI was not suitable for this transformation since the oxidation reaction with Oxone−KI proved to be rather sluggish. This reagent system was an effective source for the in-situ generation of halonium species[644] because oxidation did not occur in the absence of metal halide and only using Oxone.[643]

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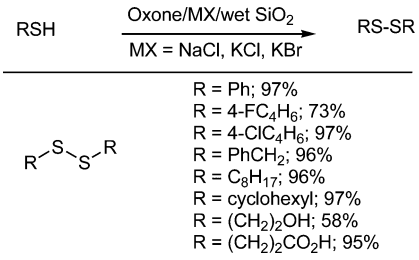
Scheme 77. Preparation of Disulfides from Thiols



10. SUMMARY

The various synthetic methods discussed in this review reveal that Oxone is a versatile reagent used in organic synthesis. Oxone is a cheap commercially available oxidant that easily oxidizes numerous functional groups. It is an efficient single oxygen-atom donor since it contains a nonsymmetrical O−O bond which is heterolytically cleaved during the oxidation cycle. It is an inexpensive reagent ($0.02−0.04/g), which compares favorably with hydrogen peroxide and bleach. Its byproducts do not pose an immediate threat to aquatic life upon disposal, and unlike chromium trioxide and bleach, it does not emit pungent vapors or pose a serious inhalation risk. The aqueous components of an organic Oxone reaction are oxidizing and acidic and should thus be quenched with sodium bisulfite followed by neutralization with sodium bicarbonate, thereby resulting in formation of a mixture of nonhazardous sulfate salts in water. These features make Oxone attractive for large-scale applications. Uses of other oxidizing agents lack the desired ingredients to attract the interest of industry because of tedious purification processes from their deoxygenated counterparts.

The dioxirane (generated from reaction between Oxone and a ketone) epoxidation offers many advantages over traditional methods of epoxidation. Oxone is about one-half as expensive as *m*-chloroperoxybenzoic acid (*m*CPBA) and converted to $KHSO_4$. $KHSO_4$ during the reaction, while being relatively acidic, can easily be neutralized with dilute NaOH solution to produce nontoxic Na_2SO_4. Furthermore, the reaction conditions require the use of relatively nontoxic organic solvents plus water. Another advantage of dioxirane epoxidation is that acetone is recycled in the reaction, which means all of the extra oxygen in Oxone is incorporated into the respective alkenes. Dioxirane is also capable of oxidizing very unreactive olefins, and thus, isolation of some relatively unstable epoxides produced from glycals is possible. This represents a major advantage over the Sharpless and *m*CPBA protocols, which only epoxidize electron-rich olefins and allylic or homoallylic alcohols. These latter reagents also require a directing group. One drawback that dioxirane does have is the fact that it can also oxidize very reactive heteroatoms, hydroxyl groups, and unactivated C−H bonds during the epoxidation procedure.

Oxone does have some disadvantages: (a) it is insoluble in organic solvents, (b) buffering is needed due to its acidity, and (c) it sometimes bleaches the metal catalysts and donor ligands during oxidation reactions. To overcome the need for aqueous conditions, some authors have used ionic liquids as solvent, and additionally, several tetraalkylammonium salts of Oxone have been reported. It has been found that when the cation in Oxone (i.e., K^+) is changed to, e.g., *n*-Bu_4N^+, the oxidant also shows higher solubility in organic solvents, especially in dichloromethane. Tactical utilization of Oxone in synthetic plans is that it may replace tedious organic transformations with simpler routes. One other drawback which needs to be mentioned is that a relatively large excess of Oxone may be required in some reactions to consume all of the starting material. However, militating against this is that Oxone can be reused when it is in stoichiometric excess. Owing to the discovery of a variety of novel applications, Oxone is becoming an increasingly important reagent in synthetic organic chemistry. We hope that this review may act as a catalyst in boosting applications of Oxone in organic synthesis.

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Notes

The authors declare no competing financial interest.

Biographies

Hidayat Hussain received his B.Sc. degree from Govt Degree College Parachinar and his M.Sc. degree from Gomal University Dera Ismail Khan, Pakistan. He received his Ph. D. degree under the supervision of Prof. Viqar U Ahmad in 2004 from H. E. J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Pakistan, in Synthetic Organic Chemistry and Natural Product Chemistry. From June 2004 to September 2007 he was a postdoctoral fellow at the University of Paderborn, Germany, under the supervision of Prof. Karsten Krohn. He was awarded a Region Pays de la Loire postdoctoral fellowship and worked at the Laboratory of Organic Synthesis, University of Maine, Le Mans, France, with Dr. Gilles Dujardin for 1 year. His research topic was asymmetric Robinson annulation via [4 + 2] heterocycloaddition and design and synthesis of a tin catalyst for [4 + 2] heterocycloadditions. In December 2008, he rejoined the group of Prof. Karsten Krohn as Senior Postdoctoral Associate, working until October 2010. Currently, he is working at the Department of Biological Sciences and Chemistry, University of Nizwa, Oman. His research interests include design and synthesis of anticancer, antimalarial, and antimicrobial compounds, asymmetric catalysis of [4 + 2] heterocycloadditions, total synthesis of anthrapyran antibiotics, and biodiversity and characterization of natural products produced by endophytic microorganisms and plants. To date he has authored and co-authored over 140 scientific publications and given 15 podium lectures at International Conferences. He is a referee for 15 international journals.

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I. R. Green received his Ph.D. degree in Organic Chemistry in 1973 from the University of Cape Town. He was made Full Professor in 1986 and Senior Professor in 1990 at the University of the Western Cape, where he lectured for 39 years until his retirement in July 2011.To date he has authored and co-authored over 120 scientific publications, given 40 podium lectures at international conferences, and supervised 30 M.Sc. and 18 Ph.D. students locally and 6 Ph.D. students internationally. He is a referee for 8 international journals. Upon retirement he moved to the University of Stellenbosch, where he is involved in mentoring research students, gives seminars, and is involved in alkaloid research.

Ishtiaq Ahmed was born in 1975 and received M.Sc. and M.Phil. degrees from Quaid-i-Azam University Islamabad Pakistan in 2000 and 2002, respectively. He joined Prof. Henning Hopf's group in October 2003 at the Technical University of Braunschweig, Germany, and worked on synthesis of liquid crystalline materials having a perhydroazulene ring. He obtained his Ph.D. degree in 2007 under the supervision of Prof. Karsten Krohn with a thesis on the study of enantioselective epoxidation, asymmetric reduction, and synthesis of bioactive oligomeric flavonoids. He carried out his postdoctoral research in the same group working on synthesis of chiral macrolide building blocks from sugar, synthesis of anthrapyran antibiotics, and isolation and structure elucidation of secondary metabolites from fungi and medicinal plants. He moved to DFG Centre for Functional Nanostructures, Karlsruhe Institute of Technology (KIT). in November 2010 as a postdoctoral researcher. He is currently working on design of photoswitchable, multifunctional linkers for nanoparticle, DNA, and protein modification under the supervision of Dr. Ljiljana Fruk.

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