Non-Metal and Enzymatic Catalysts for Hydroperoxide Oxidation of Organic Compounds

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Abstract: Oxidation of different groups of organic compounds, with hydroperoxides catalyzed by non-heavy metal containing low-molecular-weight compounds and enzymes is reviewed. This article is concentrated mainly on the hydrogen peroxide and *tert*-butyl hydroperoxide, however other less common hydroperoxides are also mentioned. Since hydroperoxides themselves are inactive toward most of the organic substrates, *in situ* activation of the oxidant is necessary. For this purpose various activators have been applied in stoichiometric or catalytic amounts. The carboxylic acids, nitriles, amides and urea are representative for the first category. The organocatalysts such as α-halo carbonyl compounds, ketones, imines, iminium salts, nitroxyl radicals and polyaminoacids, selenium compounds and enzymes are presented. They are involved in oxygen, and electron transfer processes whose mechanisms are briefly discussed, and their applications in laboratory and industrial synthesis are indicated.

Keywords: Oxidation, hydrogen peroxide, *tert*-butyl hydroperoxide, catalysts, enzymes.

1. INTRODUCTION

Oxidation reactions are basic processes widely applied in organic synthesis both in research and industry. Among the oxidants, the hydroperoxides have a prominent position. Among them, hydrogen peroxide (**1**) and *t*-butyl hydroperoxide (TBHP) (**2**) are commonly used [1-10]. Both of them are relatively stable, easy to store, commercially available, relatively cheap reagents of low molecular weight which can be used for both laboratory and industrial purposes. They contain relatively high amounts of active oxygen (H_2O_2 – 47% and TBHP - 17.8% weight), and are environmentally friendly since water which is easy to recover from the reaction mixture, *t*-butanol, are the products of their reduction. Hydrogen peroxide is supplied mainly as a 30% aqueous solution and TBHP as a 70% aqueous solution or 5.0-6.0M solution in decane or nonane.

Although several other hydroperoxides are known, they are less common oxidation agents mainly because most of them are not commercially available, their stability is low and they are hazardous substances which can explode during preparation or storage. Nevertheless, some of them, presented in Scheme **1**, have been employed in organic synthesis as the oxygen source. They are represented by cumyl hydroperoxide (**3**) [11], perhydrates **4** also called *α*-hydroxy hydroperoxides derived from strongly electron–deficient aldehydes or ketones [12] (e.g. 2-hydroperoxyhexafluoro-2-propanol (**4**, $R^1 = R^2 = CF_3$), 5-hydroperoxycarbonyl-phthalimide (**5**) [13], hydroperoxyflavines (**6**), related systems, and *α*-azo hydroperoxides (e.g. **7**) [14]. Concerned with the poor stability of hydroperoxyflavines and *α*-azo hydroperoxides and their explosive nature a series of *N*-substituted 3-hydroperoxyindolin-2-ones (**8**) were synthesized as stable alternatives and used as the reagents [15, 16]. Their less stable simpler analogs - hydroperoxypyrrolidones were also obtained and investigated [17, 18]. Sugar hydroperoxides (e.g. **9**) have also attracted some interest in recent years because they have a potentially good chance of applicability in stereoselective oxygen-transfer reactions since they are inherently chiral. They were synthesized and subsequently applied in the base-mediated asymmetric epoxidation of electron-deficient substrates without transition-metal catalysts [19-21].

The usual oxidation catalyst contains a transition metal which activates hydroperoxides for the oxyfunctionalization. The broad spectrum of applications of metal catalysts for hydrogen peroxide and TBHP oxidation have been reviewed elsewhere e.g. in [2-6, 22-25]. Such catalyst must withstand hostile oxidizing conditions, which may curtail the catalytic activity due to oxidative degradation of the metal complexes. Alternatively, one may perceive the use of organocatalysts - the oxidatively resistant organic substances, which mediate catalytic homogenous oxidations without the need of metal complexes. The advantages of the non-metal catalysts include their availability, low cost and low toxicity, which confers huge direct benefits in the production of pharmaceuticals, animal health products, agrochemicals, fragrances and fine chemicals when compared with transition metal catalysts.

Until recently, the catalysts employed for oxidation of organic substrates fell almost exclusively into two general categories: transition metal salts and their oxoacid compounds or complexes and enzymes. More recently a third general approach to the catalytic oxidative transformation has emerged organocatalysis and numerous reactions have been noted. The most prominent catalysts

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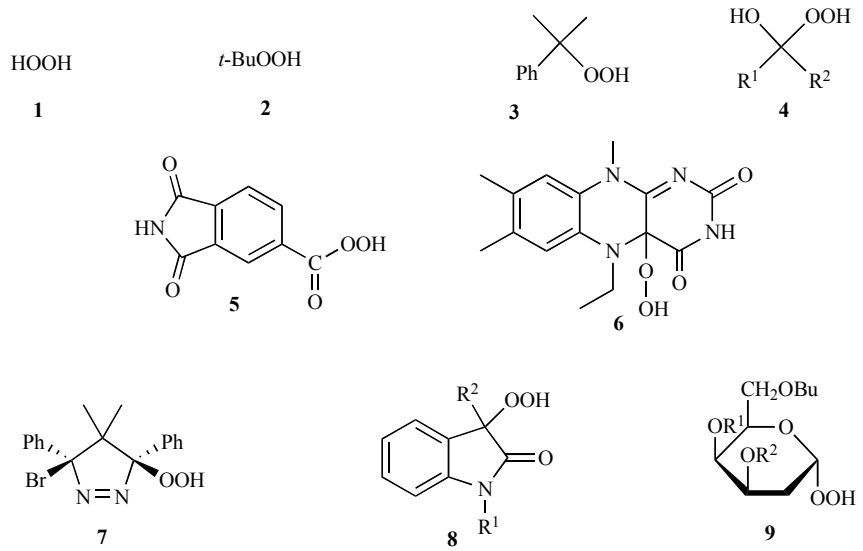


Scheme 1. Hydrogen peroxide and organic hydroperoxides.

have been some carboxylic acids, the perfluoro ketones, imines, polyaminoacids, nitrogen and selenium containing heterocyclic compounds and diaryldiselenides [5, 12, 14, 26, 27]. The alternative group is biocatalysts - the enzymes. Although most of them contain metal atom in the active site, their advantages are high turnover number and high chemo-, and stereoselectivity. The enzyme\oxygen source ratio is several orders lower than when classical catalyst is used. When they are used as oxidation catalysts, the reactions are environmentaly friendly and proceed in aqueous medium under very mild conditions [28-30].

The aim of this review is to highlight efforts made for application of different non transition metal-containing activators and catalysts or enzymes for hydroperoxide oxidation of different groups of organic compounds. The literature survey is up to 2009. We would like to apologize to anyone who finds our description of her or his work inadequate or whose work has been omitted.

2. HYDROPEROXIDE OXIDATION *VIA* ELECTROPHILIC OR NUCLEOPHILIC OXYGEN INTERMEDIATES

2.1. Hydroperoxides in Alkaline Media

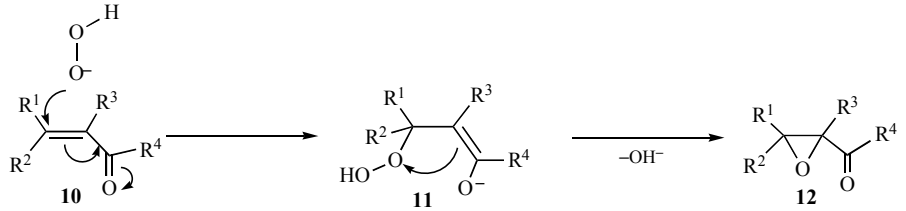
Hydrogen peroxide and TBHP themselves are slow oxidants in the absence of an activator due to the poor leaving tendency of the hydroxide or alkoxide ion and their use without an activator or catalyst is very limited [3-5].

It is well known that the oxygen-donation capacity of hydroperoxides (including peroxyacids) relates inversely to the pK_a of the leaving group, i.e., on the ability of RO^- to stabilize the negative charge, which is equivalent to its thermodynamic stability.

In alkaline medium, hydroperoxides act as nucleophiles, because formed peroxide anion ROO^- can react with electron-deficient substrates. The nucleophilic addition by a Michael – type mechanism (illustrated in Scheme **2**) involving an attack of hydroperoxide anion on the electrophilic carbon atom in α,β-unsaturated carbonyl compound **10** is an example. The subsequent ring closure of the intermediate **11** gives the epoxide **12** [31]. Oxidation, in an inert solvent of a non-aromatic or non-enonic ethylenic bond or of a non-conjugated cyclic ketones in the presence of alkali or alkali metal salts or complex, resulted in epoxide or lactone [32].

Mildly basic conditions ($NaHCO_3$) have also been used to epoxide alkenes. When substrates are water insoluble, aqueous MeCN is a suitable medium [33]. A very similar system is useful for oxidative cleavage of organostannates containing a perfluoroalkyl group to furnish alcohols [34]. α-Formylpyrroles yield 2-pyrrolinones [35]. Amines react with alkaline H_2O_2 and carbon disulfide to deliver isothiocyanates in 84-95% yield [36]. Epoxidations of enones with H_2O_2 can be catalyzed under mild conditions with a new strongly basic porous catalyst obtained by immobilization of the guanidine base (1,5,7-triazabicyclo[4.4.0]dec-5-ene) on silica support MCM-41 [37].

Under the mildly basic conditions aryl 1-imidazoyl sulfones and 1-(arenesulfonimidoyl)imidazoles are useful



Scheme 2. Epoxidation of electrophilic olefine with alkaline hydrogen peroxide.

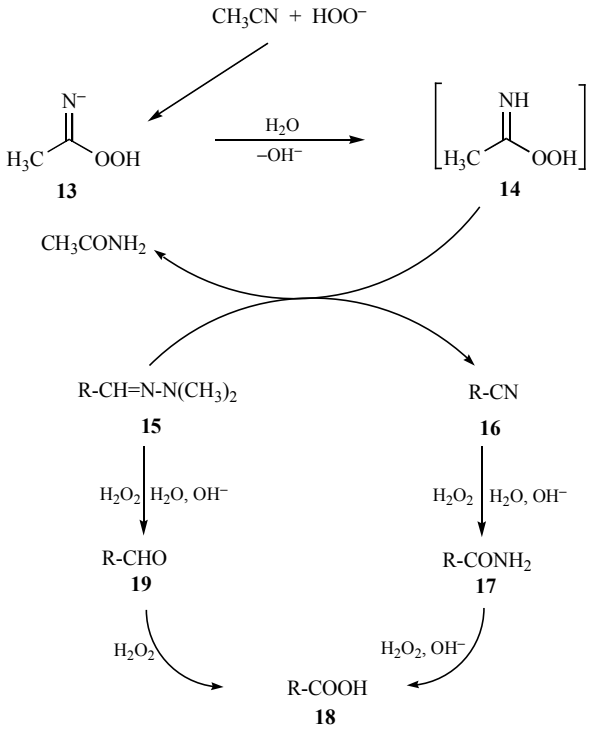
chiral activators of H_2O_2 for diastereoselective epoxidation of olefins, allylic and homoallylic alcohols, and α,β-unsaturated ketones [38,39].

Alkaline hydrogen peroxide is also a convenient reagent for the hydrolysis of nitriles to amides. A number of aromatic and vinylic nitriles were converted under phase-transfer conditions into corresponding amides in high to excellent yields [40].

The reaction of HOO^- ion with nitriles under controlled pH conditions (pH≈8) generated short-lived peroxyimidate anions **13** derived from imidoperoxoic acids **14** (Scheme **3**) [41-44]. These reagents are specially useful for epoxidation when the substrate or oxidized product is sensitive to acidic conditions. Moreover, this oxidation has the advantage of being useful on both a large and small scale. For example (*Z*)-cyclooctene was oxidized in this way in 60% yield [45]. Although benzeneimidoperoxoic acid seems to be an excellent oxidant (Payne reaction), acetonitrile has some advantages over benzonitrile in terms of costs. In addition, it is often easier to remove acetamide rather than benzamide as a by-product [46]. Methaneimidoperoxoic acid, formed *in situ* from acetonitrile, and hydrogen peroxide oxidize sulfides to sulfoxides and sulfones in excellent yields, depending on the amount of the oxidant used [47]. When *N,N*-dimethylhydrazones **15** were oxidized with hydrogen peroxide in alkaline acetonitrile, depending on the substrate, nitrile **16** and/or amide **17** accompanied with carboxylic acid **18** and parent carbonyl compounds **19** were obtained [48].

The oxidation of pyridines using a combined oxidant of hydrogen peroxide and benzonitrile catalyzed by a basic hydrotalcite, $Mg_{10}Al_2(OH)_{24}CO_3$ gave high yields of the corresponding pyridine *N*-oxides [49]. The hydroboration reaction, with subsequent oxidation by alkaline hydrogen peroxide, provides a convenient method for the *cis-anti*-Markovnikov hydration of alkenes from a less hindered site. The oxidation occurs with the total retention of configuration, placing the hydroxyl group in the position occupied by the boron atom in the initial organoborane. The reaction proceeds under mild conditions, with no rearrangements of the carbon skeleton [50].

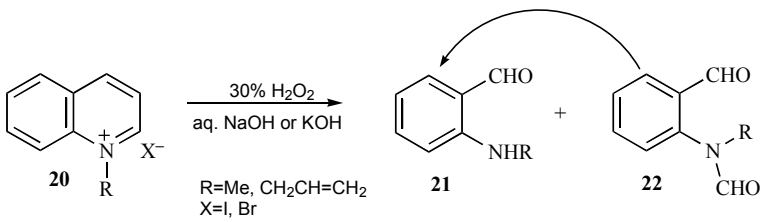
Alkaline hydrogen peroxide is a mild and effective oxidant for the cleavage of α-ketols and corresponding ketones, and carboxylic acids are produced. This reagent is inactive to 1,2-diols, contrary to the case with periodic acid or lead(IV) acetate, and hence may cleave α-ketols selectively in the presence of 1,2-dihydroxy group [51]. Oximes treated with alkaline hydrogen peroxide are converted in to the corresponding carbonyl compounds [52] and aromatic aldehydes or ketones undergo conversion to phenols (the Dakin reaction) [53]. *N*-Alkylquinolinium salts **20** are easily cleaved using alkaline hydrogen peroxide to give 2-formylanilines **21** and **22** in 33-37% yield (Scheme **4**) [54].



Scheme 3. Oxidation of *N,N*-dimethylhydrazones with alkaline hydrogen peroxide-acetonitrile.

In the bicarbonate-activated peroxide (BAP) system, the active oxidant formed from hydrogen peroxide and carbonate ion is a shortly living peroxymonocarbonate ion with ($t_{1/2}$=5 min) and structure $HOOCO_2^-$. The reagent was used for oxidation of sufides, cysteine and related thiols as well as for efficient epoxidation of water-soluble alkenes (e.g. methylvinyl ketone) while competitive diol formation is avoided [55-60].

TBHP under basic conditions can add, like to hydrogen peroxide, to a double bond that has an electron withdrawing group attached and *t*-butyl peroxides are produced. With acid chlorides in basic media, TBHP acts as a nucleophile, and with acid chlorides give appropriate *t*-butyl peroxy esters [61-64], while epoxides are transformed into *β*-hydroxydialkyl peroxides [65]. TBHP, and other organic hydroperoxides, in the presence of strong bases, react with aromatic nitro compound *via* vicarious nucleophilic substitution of hydrogen to form substituted *o*- and *p*-nitrophenols [66-68].



Scheme 4. Oxidative conversion of alkylquinolinium salts into 2-formylanilines.

2.2. Hydroperoxides in Acidic Media

Relatively strong carboxylic acids such as formic, succinic and trifluoroacetic react with hydrogen peroxide. Substitution of the hydroxyl group with the hydroperoxide group rapidly leads to an equilibrium concentration of the corresponding peroxycarboxylic acids RC(O)OOH (eg. peroxyacetic acid R=CH_3). Addition of strong mineral acid, in catalytic amount accelerates this process. For preparative purposes carboxylic acid can be used both in stoichiometric or catalytical amounts.

Peroxycarboxylic acids oxidize simple alkenes, alkenes carrying a variety of functional groups (such as ethers, alcohols, esters, ketones and amides), some aromatic compounds, furans and *N*-azaheterocycles, sulfides and amines. Ketones and aldehydes undergo oxygen insertion reaction (Baeyer-Villiger oxidation) [69, 70]. Peroxyacetic acid was applied for *N*-oxidation of tertiary amines and the pyridine-like heteroaromatic nitrogen atom [71]. The reaction proceeded in high temperature. Under less severe reaction conditions more reactive groups could be oxidized while *N*-oxidation does not occurs [72].

Phenothiazine sulfones and 4*H*-1,4-benzothiazine sulfones were prepared by oxidation of the corresponding benzothiazines and phenothiazines with 30% hydrogen peroxide in glacial acetic acid [73]. The same reagent was used for the oxidation of phenanthrene to diphenic acid [69]. The method for a large-scale production of 2-methyl-1,4-naphthoquinone (menadione, vitamin K3) through the oxidation of 2-methylnaphthalene is based on using hydrogen peroxide in carboxylic acids or their anhydrides and a strong mineral acid as a catalyst for the formation of the peroxycarboxylic acid [74, 75].

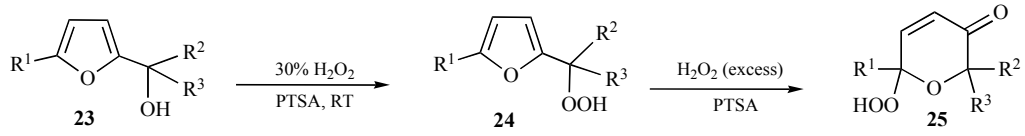
Hydrogen peroxide coordinates the proton of protic acids (HF, HCl, HBr) and HO^+ cations are produced. The Lewis acids ($AlCl_3$, BF_3, $FSO_3H{\cdot}SO_2ClF$, $FSO_3H{\cdot}SbF_5{\cdot}SO_2ClF$) can catalyse oxidation reactions by forming acid-base adducts either with the substrate or with hydroperoxide, enhancing their reactivity and thereby acting as catalysts for the oxidation. These highly electrophilic species are bound to nucleophilic centers of substrate molecules resulting in hydroxylation. In this way, low to moderate yields of phenols can be obtained by the treatment of arenes having electron-donating substituents. Benzylic alcohols are oxidized to aldehydes and thioacetals or thioketals can be deprotected to parent carbonyl compounds. The Baeyer-Villiger oxidation of ketones to esters was also accomplished [76-78]. In the latter reaction acylarenes were readily converted to phenols with H_2O_2-boric acid [79]. When secondary alcohols were oxidized to ketones with hydrogen peroxide in the presence of 20% HBr as an acid catalyst no subsequent Bayer-Villiger oxidation to esters took place [80].

Peroxy groups may replace alcohols, ethers or sulfates directly or can be added to an alkene (with Markovnikov regioselectivity) by reacting an organic compound with TBHP in acetic acid, in the presence of sulfuric acid. The same oxidant reacts with ketones or aldehydes in the presence of strong acid catalyst (e.g. HCl), to give a product with two *t*-BuOO groups in place of carbonyl group [3]. By an acid-catalyzed reaction with TBHP, acetal and enol ethers give the gem-bisperoxides [81]. The similar recation of acetals with hydrogen peroxide, catalyzed by boron trifluoride etherate and boron trifluoride-methanol at room temperature, yields gem-bishydroperoxides $R_2C(OOH)_2$ in various 9-95% yields [82]. Other gem-bishydroperoxides are formed when cyclic benzylic alcohols are treated with 50% H_2O_2 in the presence of sulfuric acid [83]. Furfuryl hydroperoxides **24** and 6-hydroperoxy-2*H*-pyran-3(6*H*)-one **25**, which are valuable regenerable oxygen donors in enantioselective sulfoxidations, are readily prepared from the corresponding 2-furyl alcohols **23** in the reaction catalyzed with *p*-toluenesulfonic acid (PTSA) (Scheme **5**) [84].

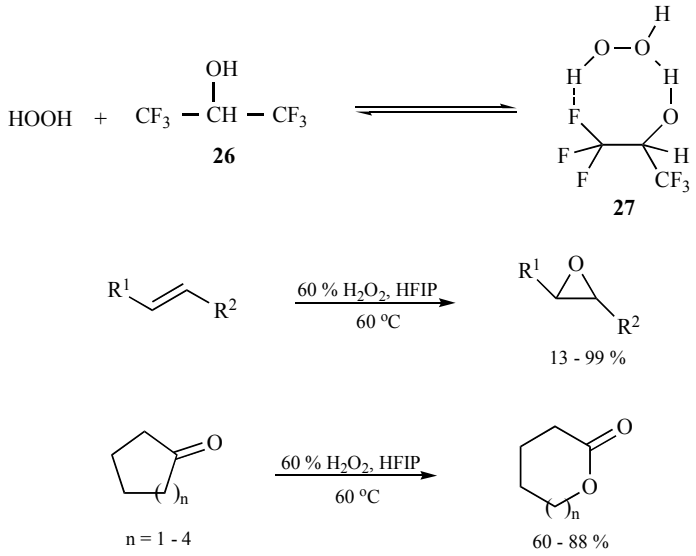
Esters are formed when aldehydes or acetals are oxidized in an alcoholic solvent with H_2O_2 and aqueous HCl [85]. 3-Hydroperoxydioxolanes are synthesized from the corresponding 3-hydroxyderivatives using H_2O_2 with catalytic amount of TsOH. These hydroxyperoxides are effective oxygen-transfer reagents to oxidation of amines and sulfides, and to epoxidation [86].

Unlike in conventional solvents, non-strained ketones such as cyclohexanone react smoothly with hydrogen peroxide in 1,1,1,3,3,3-hexafluoro-2-propanol **26** (HFIP) to give lactones. This reaction proceeds *via* an isolable spiro-bis-peroxide, which undergoes acid-catalyzed rearrangement of two equivalents of lactone [87]. Epoxidation of alkenes in HFIP is efficiently achieved with aqueous 50% H_2O_2 and benzenearsonic acid ($PhAsO_3H_2$) as catalyst. For Baeyer-Villiger oxidation the more common TsOH is also useful. The role of catalyst is not clear. Although it has been postulated that benzenearsonic acid acts *via* active peroxyacid form most probably TsOH is a protic acid catalyst [88]. Nevertheless, it was also reported that in HFIP epoxidation, Baeyer-Villiger oxidation and selective oxidation of sulfides to sulfoxides proceed efficiently in the absence of catalyst (Scheme **6**). In this reaction medium, the strong electron-withdrawing properties of fluorine along with the hydrogen bonding properties of the O-H, hydrogen atom lead to formation of an electrophically activated hydrogen peroxide intermediate **27**. As expected, reactivity is increased as a function of fluorine substitution; (HFIP) is more active than 2,2,2-trifluroethanol (TFE). Alkene epoxidation is also promoted by polyfluoroalkanesulfonyl chloride [89-91].

A new economical and clean route for synthesis of 1,2-diols is based on the dihydroxylation of alkenes with 30% H_2O_2 in the presence of resin supported sulfonic acid under metal free conditions without any organic solvent. The



Scheme 5. Acid catalyzed hydrogen peroxide oxidation of 2-furyl alcohols.



Scheme 6. Hydrogen peroxide epoxidation of alkenes and Bayer-Villiger oxidation of ketones in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).

catalyst can be recycled easily and is effective for the last 10 cycles [92].

Fast oxidation of organic sulfides by hydrogen peroxide by *in situ* generated peroxynitrous acid, was reported. Under the optimized conditions $NaNO_2$ acts as a catalyst in the form of ONOOH, quickly carrying the oxygen from hydrogen peroxide to the sulfide [93].

3. HYDROGEN PEROXIDE-UREA

The hydrogen peroxide forms the adduct with urea $CO(NH_2)_2 \cdot H_2O_2$ (UHP), also called percarbamide. It is a non-toxic, odorless crystalline solid, which has a high proportion of hydrogen peroxide (36 mass %) with the active oxygen content of 17.02 mass %. It is commonly used, commercially available reagent for safe oxidation of different organic substrates. Although, it is more active than hydrogen peroxide itself, in some reactions the catalysts had to be used [94].

In the last years, several reports appeared on use of UHP in oxidations of various organic substrates. Some of them concerned the conversion of amines into nitroalkanes, Baeyer-Villiger oxidation of ketones to lactones, oxidation of sulfides to sulfoxides or sulfones and conversion of pyridines to *N*-oxides under heating in solid state [95-98]. In the presence of trifluoroacetic anhydride, it oxidizes electron-deficient pyridines to the *N*-oxides, being less hazardous than hot H_2O_2-CH_3COOH and more effective than H_2O_2-$MeReO_3$ [99]. This reagent was used, in the presence of maleic anhydride, as a mediator in a simple and convenient method for the oxidation in high yield of some thiols to the corresponding disulfides. Peroxymaleic acid formed *in situ* from the reaction of UHP with maleic acid anhydride has a key role in this oxidation [100].

The hydrogen peroxide-urea adduct oxidizes aromatic aldehydes to carboxylic acids at room temperature [101] and it was found to be an efficient reagent for the benzylic oxidation of various alkyl arenes under microvawe irradiation in solvent-free conditions [102]. This adduct has also been investigated in epoxidation of olefins, using various fluoroketones as catalysts. With reactive olefins, no catalyst was required. With monosubstituted olefins epoxides were obtained, in high yields, by using catalytic amounts (3-5%) of perfluorodecan-2-one [103].

Eco-friendly laboratory procedures allow the oxidative iodination of various activated and deactivated arenes with UHP [104,105] and the same reagent was successfully used for the direct synthesis of hypervalent [bis(trifluoroacetoxy) iodo]arenes avoiding the use of hazardous reagents with the workup being only an aqueous extraction [105].

4. HYDROPEROXIDES AS INTERMEDIATES

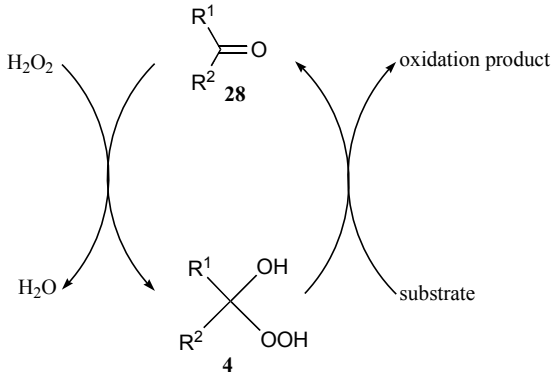
4.1. Perhydrates

Perhydrates (α-hydroxy hydroperoxides), are mainly obtained by the addition of hydrogen peroxide to an aldehyde or a ketone. Most of such perhydrates do not persist isolation and revert to the carbonyl precursor and hydrogen peroxide. Presumably, intramolecular hydrogen bonding is responsible for the persistence of the functionalized perhydrates [12]. That the perhydrate of hexafluoroacetone (**4**, R^1=R^2= CF_3) may be isolated as such is not overly surprising, when it is realized that the corresponding hydrate requires distillation from P_2O_5 to release the ketone [106].

The catalytic cycle for perhydrate-mediated oxygen transfer is shown in Scheme **7**. The process is initiated with the ketone **28** and hydrogen peroxide by exchange of the hydroxy for the required hydroperoxy group to give the perhydrate oxidant **4** under catalytic conditions. Subsequently, the perhydrate transfers an oxygen atom to the substrate to afford the desired oxidation product and it is regenerated by the action of the started ketone or its hydrate.

The perhydrate **4** (R^1 = R^2 = CF_3), the strongly electrophilic oxidant, generated *in situ* by the treatment of hexafluoroacetone with hydrogen peroxide, efficiently oxidizes unactivated olefins to epoxides, ketones are converted to esters and aldehydes to carboxylic acids [106-108]. Phenol, resorcinol, and anisole may be hydroxylated,

but under more severe conditions, phenol and alkyl-activated and polynuclear arenes may be oxidized completely to the respective quinones [109, 110]. Perhydrate **4** ($R^1 = R^2 = CF_3$) also efficiently transfers oxygen to heteroatom substrates such as sulfides, which may be selectively and quantitatively oxidized to the corresponding sulfoxides or sulfones by employing either 1 or 2 equiv of H_2O_2 as the oxygen source. Tertiary amines are oxidized to their *N*-oxides in nearly quantitative yields; this oxidation is performed selectively in the presence of C=C double bonds [111].



Scheme 7. The catalytic cycle for perhydrate-mediated oxygen transfer.

The high toxicity and volatility of hexafluoroacetone has prevented the wide use of this catalytic system. Using high-molecular-weight perfluoroketone (perfluoroheptadecan-9-one) with less volatility, a selective and reusable catalyst for epoxidation with hydrogen peroxide made a suitable improvement [112].

Trichloroacetaldehyde and its hydrate as well as partially chlorinated acetone and chlorofluoroacetone have been employed as catalysts [113, 114]. Hexachloroacetone has been shown to catalyze the hydrogen peroxide epoxidation of a variety of C=C bonds in steroidal compounds with a high π-facial selectivity [115-117]. Differently substituted in benzene ring trichloro-, trifluro- and perfluroacetophenones were also reported as catalysts for hydrogen peroxide oxidadion [118-120]. Trifluoroacetone was used as a catalyst for selective oxidation of organic sulfides to the corresponding sulfoxides, with 35% hydrogen peroxide in chloroform under very mild conditions [121].

A silica immobilized perfluoroacetophenone is an effective heterogeneous recyclable catalyst for the oxidation of different organic substrates using 60% aqueous hydrogen peroxide as oxygen donor. The oxidation of pyridine and derivatives to the corresponding *N*-oxides, showed that the catalyst was quite effective for this reaction. The yields were generally high for some representative substrates such as pyridine, 2- and 4-methylpyridine, quinoline, and 4-methylquinoline; *N*-oxides were the only products. Interestingly, 8-hydroxyquinoline was less reactive, presumably because of steric hinderence and the electron-poor 2,6-dichloropyridine was unreactive as expected. Aniline, alkyl-substituted aniline and halogen-substituted aniline derivatives all yielded the dimeric azoxy compounds as sole products in quantitative yields, while aniline with electron donating hydroxyl substitution or electron withdrawing nitro substitution yielded the corresponding nitro derivatives. The perfluoroketone-silicate also exhibited appreciable activity for epoxidation of alkenes although for less electrophilic substrates its activity was low [12].

4.2. Imine Derived Hydroperoxysulfonyl Amides and Oxaziridines

The reaction of imines with hydrogen peroxide or more often with monoperoxysulfate affords oxaziridines. These relatively weak electrophilic oxidants only manage to oxidize electron-rich substrates such as enolates, silyl enol ethers, sulfides, selenides, and amines; however, the epoxidation of alkenes has been achieved with activated oxaziridines produced from perfluorinated imines. Most of the oxidations by *in situ* generated oxaziridines, have been performed stoichiometrically, with the exception of sulfoxidations. When chiral imines are used as catalysts, optically active sulfoxides are obtained in good enantiomeric excess values. Imine-catalyzed oxidations are scarce and essentially limited to sulfoxidation. The catalyst reacts with the oxygen source, usually $KHSO_5$ or H_2O_2, to afford the oxaziridine as the catalytic oxidant. The electrophilic oxygen atom of the oxaziridine is transferred to the electron-rich substrate, to give the oxygenated product with the release of the imine; thereby, the catalytic cycle has been completed [12].

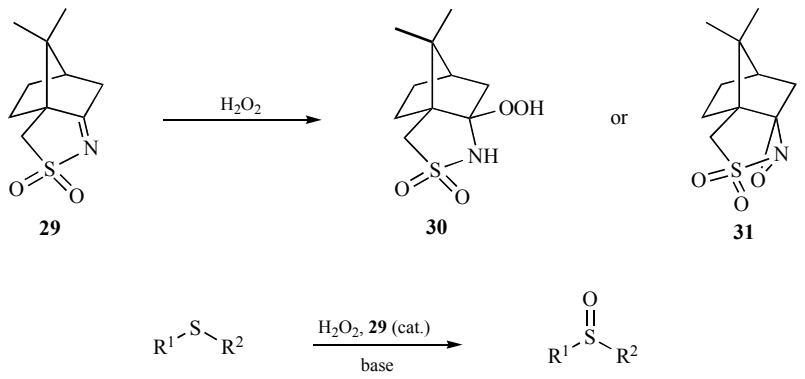
The highly efficient asymmetric sulfoxidations mediated by some camphorsulfonylimines such as **29**, using hydrogen peroxide as the oxidant have been suggested to proceed *via* intermediate *α*-hydroperoxycamphorsulfonyl amides (**30**). However, some experimental data indicate oxaziridine **31** as an active oxidant (Scheme **8**). Details of the results of these investigations have been sufficiently reviewed in the pertinent literature [122-127].

Several simple imines have also been tested as sulfoxidation catalysts with H_2O_2 as the oxygen source. The simple imine *N*-benzylideneaniline gave poor yields of sulfoxides due to hydrolysis to its amine and carbonyl partner. The use of acetone oxime, cyclohexanone oxime derivatives and *N*-cyclohexylidene-benzenesulfonamide, gave moderate yields of sulfoxides. Among these, the cyclohexanone oxime showed the higher activity and was used under catalytic conditions. The cyclic sulfonylimine derived from saccharin, named 3-*tert*-butylbenzisothiazole-1,1-dioxide, gave much higher yields of sulfoxide under catalytic conditions, but a long reaction time was necessary [128].

4.3. Hydroperoxyflavines

The reaction of flavine **32** (R^1,R^2 = Me) and related heterocyclic systems with hydrogen peroxide (also with molecular oxygen) affords hydroperoxy derivatives. This reaction plays an important role in enzymatic oxidation. Moreover, the flavine hydroperoxide **33** (R^1,R^2 = Me) and related hydroperoxides were used in synthetic practice as stoichiometric reagents [14]. Despite the growing interest in these peroxides organocatalytic oxidations of synthetic importance mediated by flavines were reported only in a few works.

Several sulfides oxidized with hydrogen peroxide with flavine perchlorate **32**·$HClO_4$ (R^1,R^2 = Me) as catalyst, gave sulfoxides with excellent yields. For example, from



Scheme 8. Hydrogen peroxide oxidation of sulfides catalyzed by camphorsulfonylimines.

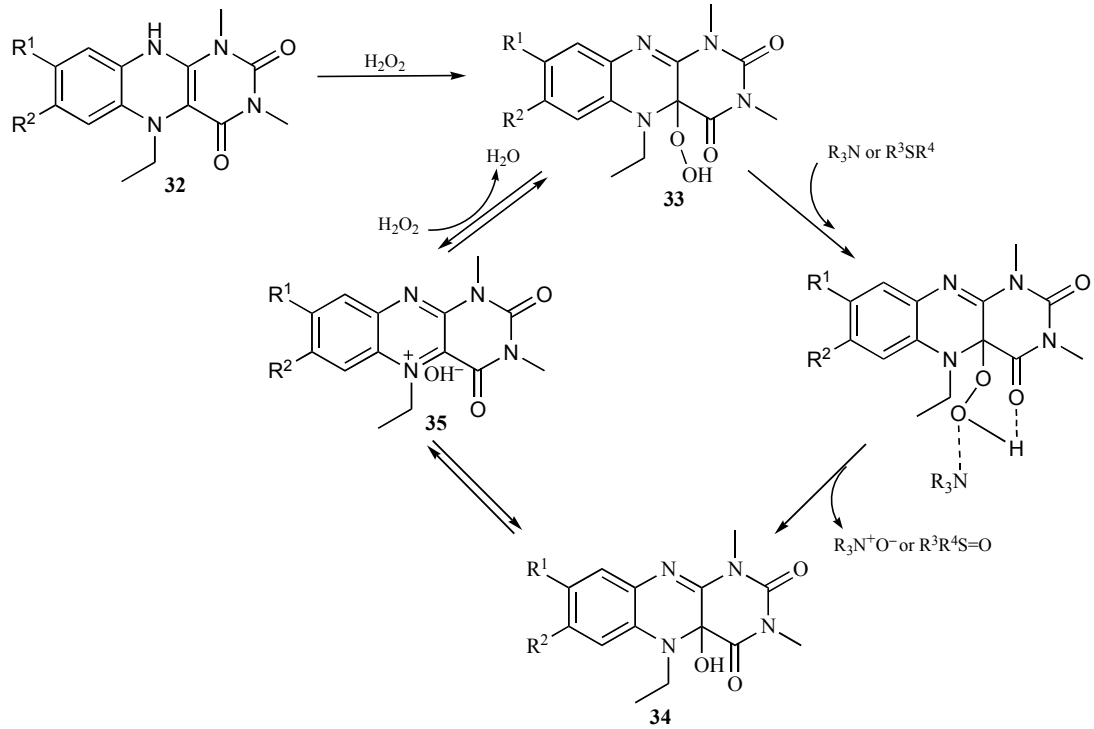
dibenzyl-, dibutyl-, and diphenylsulfides, sulfoxides were obtained in ≥96% yields with 1 equiv of H_2O_2 and 10 mol% of catalyst. Dibenzylsulfoxide treated with 1 equiv of H_2O_2 and 10 mol% of catalyst, gave dibenzylsulfone in 98% yield [129]. The biomimetic oxidation of nicotine with hydrogen peroxide in the presence of 5-ethylflavin mononucleotide perchlorate, gave the nicotine-*N*-oxide [130].

Chemoselective oxidation of a series of sulfides to their sulfoxides and oxidation of tertiary amines (but not heterocyclic pyridine-like systems) to amine oxides by 30% H_2O_2 using the neutral 1,5-dihydroalloxazine (**32**; R^1,R^2 = H) as the catalyst, has been described. Under this catalytic system selective sulfoxidation of thioethers in the presence of many potentially reactive electron-rich functional groups was achieved, while further oxidation to sulfones did not occur even when a large excess of H_2O_2 was used over a prolonged reaction time [131-133].

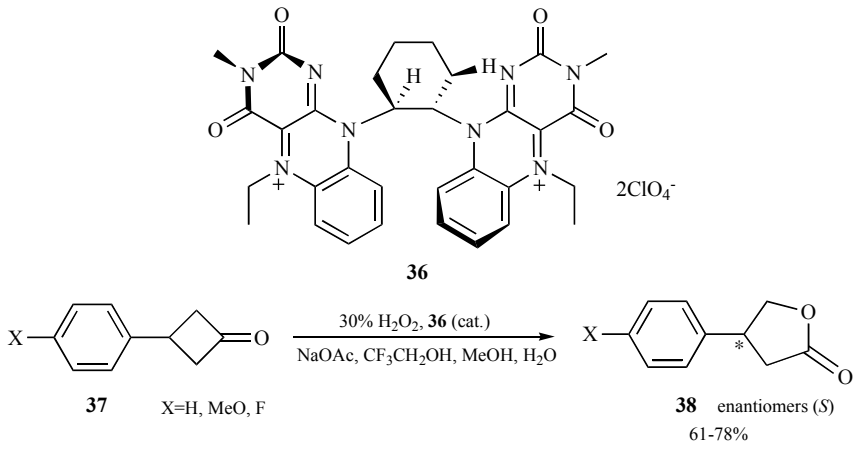
Accordingly to the proposed sequence of reactions, presented in Scheme **9**, the catalyst (for example alloxazine **32** (R^1,R^2 = H) reacts with hydrogen peroxide for conversion to the active oxidant hydroperoxide **33** (R^1,R^2 = H). The hydroperoxide reacts with the nucleophiles (sulfides or amines), to give the oxidation product and the intermediate **34**, that is subsequently converted into salt **35** and finally oxidized to hydroperoxide **33**.

By using the flavinium salt and H_2O_2 as the oxygen source different ketones were converted to the expected lactones in good yields under mild conditions. An interesting feature of this system is that under appropriate reaction conditions, the double bond and the alkoxy group are tolerated. Thus, the reaction is both chemo- and regioselective [14, 134].

In the presence of catalyst **36**, 3-arylcyclobutanones **37** were converted in Baeyer-Villiger reaction to lactones **38** with up to 74% ee, using 30% H_2O_2 as the oxygen source



Scheme 9. The mechanism of hydrogen peroxide oxidation of sulfides and amines catalyzed by 1,5-dihydroalloxazine.



Scheme 10. The stereoselective lactonization of cyclic ketones using H_2O_2/**36** system.

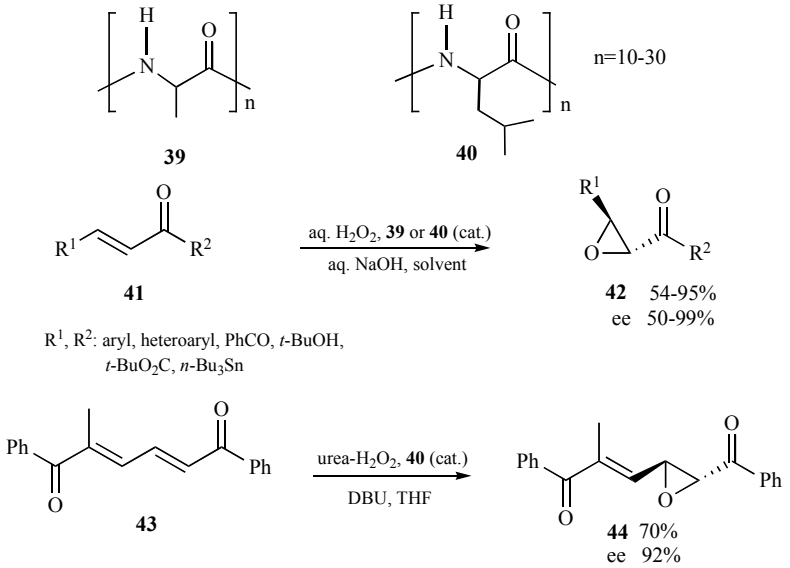
(Scheme **10**). In this case, the flavinhydroperoxide formed *in situ,* is thought to play a dual role as the nucleophile and as the chiral catalyst responsible for asymmetric induction into the products [14, 135].

5. AMINO ACIDS AND POLYAMINO ACIDS

The common amino acids such as L-proline, L-leucine, L-phenylalanine and *N*-benzylproline are efficient catalysts for hydrogen peroxide oxidation of sulfides. The most efficient catalyst was L-proline. The conversion of substrate was almost quantitative and sulfoxide:sulfone ratio was 97:3. Unfortunately, a very low enantioselectivity (4.0% ee) was observed in the case of thioanisole. The experiments strongly suggest, that hydrogen bonding between the carboxylic group of L-proline and H_2O_2 plays a major role in this transformation. When the reactions were carried out with *t*-butyl hydrogen peroxide (TBHP), a mixture of sulfoxides and sulfones was formed [136].

Over a series of papers the group of Juliá and Colonna investigated the method for the catalyzed by poly-L-alanine (**39**) or poly-L-leucine (**40**) hydrogen peroxide oxidation of chalcones (**41**) and simple analogues to epoxides (**42**) under triphasic reaction conditions (Scheme **11**). The catalyst may be readily separated from the reaction products, washed and reused. However, reuse of the catalyst frequently gave reduced enantioselectivity, a phenomenon ascribed to degradation of the catalyst under the strongly basic reaction conditions. A limitation of this methodology is the length of the reaction; even relatively reactive substrates such as chalcone and simple derivatives require 24 h for complete conversion. Less reactive substrates either generate products in low yield and enantiomeric excess or fail to form any epoxide. In particular, enolisable chalcones are poor substrates [137-143].

The biphasic procedure that reduces reaction times for chalcone to under 30 minutes, has been developed. The peroxide is delivered in the form of an anhydrous complex urea–H_2O_2, the inorganic base is replaced with a strong amidine base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the reaction is performed in an organic solvent such as THF. Under these conditions enolisable substrates, such as simple alkyl ketones, can be readily epoxidized [143,144]. These biphasic conditions constitute the most widely tested and reliable of the new class of polyamino acid catalysed



Scheme 11. Polyaminoacid catalyzed epoxidation.

epoxidation systems. Examples reported by Roberts and coworkers typically use polyleucine, however it has recently been disclosed that poly-L-neopentylglycine can offer advantages of increased reaction rate and enantioselectivity [145]. An alternative procedure employs inexpensive sodium percarbonate (NaPc) as both an oxidant and a base. Screening for a range of solvent systems for this oxidant revealed that organic–water mixtures are most effective; in particular DME–water gives rates and enantioselectivities comparable with the urea–H_2O_2/THF/DBU system [146].

One further improvement, reported by Roberts and coworkers, is the introduction of a silica-supported polyamino acid catalyst. Polyleucine was stirred as a suspension in THF with a range of solid supports and the properties of the resultant adsorbed materials were investigated. It was found that silica provided the best combination of improved activity and ease of filtration/recycling. Generally the silica-adsorbed material is active enough to allow as little as 2.5 mol% catalyst (based on 1 equivalent being a single polyamino acid chain) to be used without any reduction in enantioselectivity [147,148]. The polyleucine catalyzed epoxidation shows some interesting selectivity. For example, the diene **43** is selectively epoxidized on the disubstituted double bond to afford the mono-epoxide **44** in reasonable yield and good enantiomeric excess [149].

The epoxidation of 2-substituted naphthoquinones with *t*-BuOOH, in an aqueous buffer solution containing a small amount (up to 5 molar% equiv.) of bovine serum albumin (BSA), gives the corresponding epoxides with enantiomeric excess (ee) up to 100%. The enantioselectivity is very sensitive to the addition of water, miscible or immiscible cosolvents and to the length of the alkyl chain in position 2 [150].

6. CYCLODEXTRINS

Asymmetric oxidation of sulfides to sulfoxides catalzsed by *β*-cyclodextrins was reported by Drabowicz and Mikolajczyk. The resulting sulfoxides had optical purities of 0.03-30.00% [151]. The procedure elaborated more recently allows the highly chemoselective formation of sulfoxides from sulfides and sulfones from sulfoxides [152].

The groups of Colonna [153-155] and Takahashi [156] have both reported on the modification of Weitz–Scheffer conditions by the addition of *β*-cyclodextrin. Under Colonna, s optimized conditions, the enantiomeric excesses recorded for the epoxidation of a range of naphthoquinones and chalcone derivatives were below 48%; the highest enantiomeric excess observed by Takahashi and coworkers in the epoxidation of cinnamaldehyde was 2.5%.

β-Cyclodextrin borate catalyses oxygenation of aryl substituted alkenes with TBHP to afford *β*-dioxyalcohols in good yields (63-86%) [157]. It was shown that 2,2'-ditlellurobis(2-deoxy-*β*-cyclodextrin), in the presence of structurally distinct hydroperoxides (H_2O_2, TBHP, cumyl hydroperoxide), acts like the enzyme glutathione peroxidase in thiol oxidation [158].

A series of new *α*-cyclodextrin derivatives were evaluated for their ability to affect amine and alcohol oxidations with hydrogen peroxide. Oxidation of aromatic amines gave corresponding nitrocompounds, or in some cases azo-, azoxy-, or other dimerization products. Oxidative cyclocondensation of 2-aminophenol results in 2-aminophenoxazinon-2-one. The catalysis was found to follow enzyme kinetics, giving a rate increase (k_{cat}/k_{uncat}) up to 1100 in the best case [159-161].

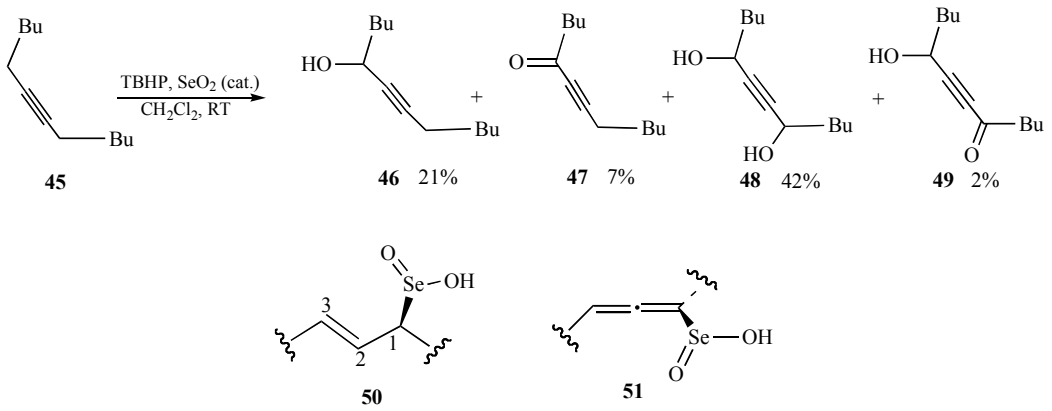
7. SELENIUM AND TELLURIUM COMPOUNDS

7.1. Selenium(IV) and Tellurium(IV) Oxide

The first publication on the use of selenium(IV) oxide (SeO_2) in oxidation reactions appeared in 1932 [162] and since then it has been applied as a versatile reagent for the synthesis of various types of organic compounds [163-167]. Due to its toxicity when taken orally, intense local irritation of skin and eyes, and the sometimes malodors volatile selenium-containing by-products are formed, SeO_2 is used in modern synthesis only when it competes favourably well with other methods, provides unique reactivity or when used in catalytic amounts [4,167-171]. Contrary to selenium(IV) oxide, use of the tellurium(IV) oxide as the reagent, has been strongly limited [171]. The TBHP/SeO_2 or H_2O_2/SeO_2 system is more convenient in use than SeO_2 alone, particularly when it is used in catalytic amounts, very often in 5 mol%. Reaction conditions are much milder and as a result, yields are higher with less oxidation, dehydration, rearrangement of by-products and the problem of the removal of colloidal selenium is circumvented.

Like selenium(IV) oxide alone, the reagent TBHP/SeO_2 oxidizes alkenes, cycloalkenes and alkynes in the allylic position. Hydroxylation of cycloalkenes carrying alkyl substituents at the allylic position takes place preferentially on the ring *α*-carbon atom. Oxidation of terminal alkenes results in C=C bond migration and primary allyl alcohols formation. Terminal and non-terminal vinyl fluorides have been hydroxylated regioselectively in the allylic position adjacent to the fluorine bearing carbon [172,173]. TBHP/SeO_2 was used in the allylic hydroxylation of isolated double bonds in straight-chain hydrocarbons, e.g. mono-unsaturated fatty acids, esters and alcohols. Either allylic position was hydroxylated or both positions reacted, to give dihydroxy isomers. Yields of monohydroxy compounds in which the OH group was between the double bond and C(1) were usually higher than those in which the OH group was between the double bond and the methyl terminus [174-176]. When an *α*-methylene group is oxidized, the reaction proceeds under mild reaction conditions [177-179].

Unlike alkenes, alkynes show a strong tendency to *α*,*α*'-dihydroxylation upon reaction with TBHP/SeO_2. The oxidation of different acetylenes allowed assignment of the reactivity sequence $CH_2 = CH > CH_3$. Alkynes bearing one methylene and one methine substituent afforded the enynone as the major product. When internal alkynes e.g. **45** were treated with TBHP/SeO_2 in addition to the expected products **46** and **47**, substantial amount of dioxygenated products **48** and **49** were also found (Scheme **12**). Considering stereochemical aspects, an interesting difference between SeO_2 oxidations of alkenes and alkynes is worth pointing out. In the case of alkenes, the allylic selenic acid intermediate **50** can in principle give rise to allylic alcohol by a [2,3]-sigmatropic shift to either face of the olefinic bond. This is a consequence of free rotation about C(1) to



Scheme 12. Oxidation of alkyne with TBHP/SeO_2.

C(2) bond in **50**. However, in the case of alkynes, the putative allenic seleninic intermediate **51** arising from an ene reaction of SeO_2 with the alkyne, has a fixed geometry and only one [2,3]-transition state is feasible. Thus, in the case of acetylenes, the stereochemistry of the oxidation product should be determined only by the stereochemistry of the initial ene reaction, which produces the allenic seleninic acid **51** [179].

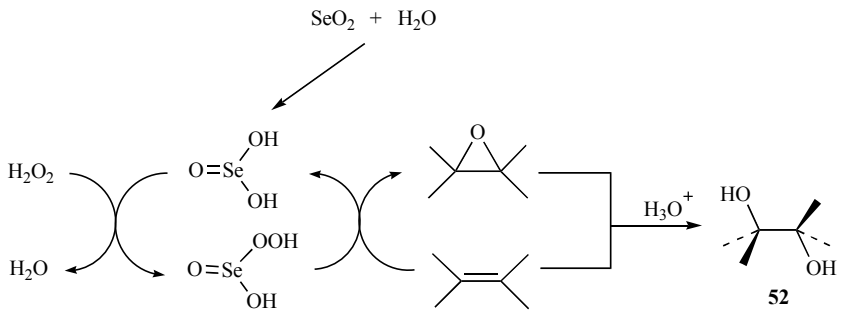
The TBHP/SeO_2 has been used to convert alkenes to their corresponding *α,β*-unsaturated ketones [180] or aldehydes [181-183]. It was also found to be a highly selective for the oxidation of allylic methyl groups to *trans*-*α,β*-unsaturated aldehydes [184] and it was applied for the synthesis of 1,2,3-triones from 1,3-diketones [185]. The urea-hydrogen peroxide, in the presence of catalytic quantities of SeO_2 under microwave irradiation has successfully led to the allylic oxidation of alkenes while keeping the other chemical functionalities intact [186]. The TBHP/SeO_2 reagent allowed the oxidation of activated methyl groups of *N*-heterocyclic compounds under milder conditions than SeO_2 alone without the formation of the over-oxidized carboxylic acids [187]. Claisen rearrangement based on vinyl fluorides took place when 2-fluoroalkenes were treated with TBHP/SeO_2 [188].

A number of alkenes were *trans* dihydroxylated with 30% aqueous hydrogen peroxide in the presence of 20 mol% of SeO_2 at room temperature. The isolated yields of the diols were in a range 55-88%. Cyclic, acyclic, terminal and internal alkenes were smoothly converted to their corresponding diols and no *α*-hydroxylation or *α*-oxygenation to aldehydes or ketones was observed. It was found, that aliphatic alkenes exhibited better results than their aromatic analogues and the sterically hindered double bonds exhibited poor yield compared with less hindered one. When arylidenemalononitriles were used as substrates, they produced the corresponding carbonyls due to the presence of the two electron-withdrawing groups on one terminal of the olefins. The peroxyselenic(IV) acid is responsible for the epoxidation of alkenes, which in the presence of water and selenic(IV) acid forms the corresponding diols **52** (Scheme **13**) [189].

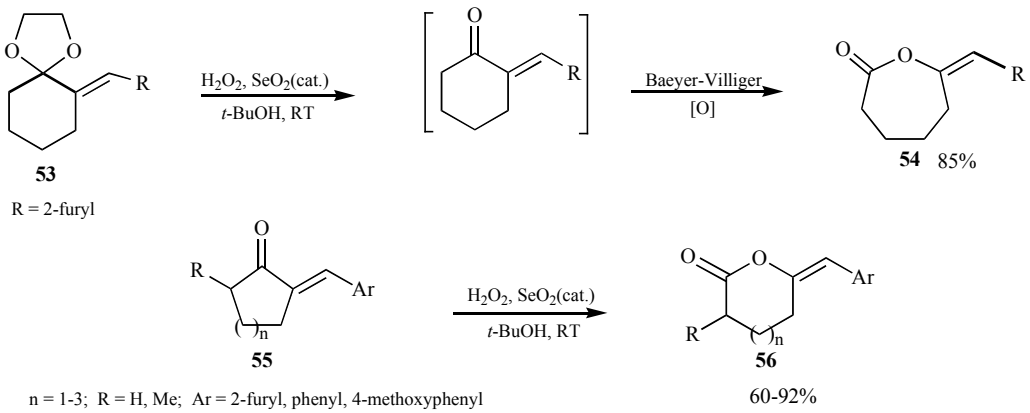
A synthetic method for some aryl pyridines involved H_2O_2/SeO_2 dihydroxylation and methoxyhydroxylation of 4-aryl-1,2,3,6-tetrahydropyridines [190]. Selenium(IV) oxide that mediated dihydroperoxidation of 3-aryl-1,4,5,6-tetrahydropyridine, was also examined [191].

Long chain alkenes and unsaturated acid esters oxidized with H_2O_2/SeO_2 at ambient temperature gave, depending on the reaction time, vicinal diols, selenite esters and epoxides. For methyl oleate after a short reaction time (4 h) the epoxide was produced, while the time was prolonged for 24 h ester, accompanied with diol, was a major product. It supported the hypothesis that the product sequence is epoxides→selenite esters→vicinal diols [192].

Ring transformations using H_2O_2/SeO_2 resulted in the ring contraction of cycloalkanones to norcycloalkane carboxylic acids [193,194], and related rearrangements in acyclic ketones [193-197] as well as 3-ketosteroids [198,199]. Moreover, it was observed that ketal **53** was rapidly converted, in high yield, into the ε-enollactone **54**. A simple explanation for the formation of **54** involves acid-catalyzed hydrolysis of the ketal protecting group, followed by a Baeyer-Villiger type oxidation of intermediate ketone



Scheme 13. Hydrogen peroxide *trans*-dihydroxylation of alkenes catalyzed by SeO_2.



Scheme 14. Lactonization of cycloalkanones with H_2O_2/SeO_2.

53. The reaction extended on the other 2-alkylidenecycloalkanones **55** yielded corresponding enollactones **56** [200] (Scheme **14**).

Oxidative cleavage of ene-lactams can be performed efficiently by SeO_2 catalyzed oxidation with H_2O_2 to give the corresponding ketoimides. The reaction provides convenient methods for the preparation of macrocyclic ketoimides and construction of *N*-fused azabicyclic ring systems such as indolizidine and cephalotaxine skeletons [201].

The Baeyer-Villiger reaction using H_2O_2/SeO_2 for various benzaldehydes possessing hydroxy or methoxy substituents mainly in *ortho* and *para* position, and/or a furan ring, afforded phenols rapidly in good yield or mixtures of the phenols and carboxylic acids. On the other hand, *meta*-substituted benzaldehydes or benzaldehydes carrying less effective electron donating groups, electron-deficient heteroaromatic and aliphatic aldehydes were oxidized to the corresponding carboxylic acids [200, 202, 203].

N-Oxidation of secondary amines with H_2O_2/SeO_2 is a convenient way of synthesizing nitrones [204-206]. Differently ring substituted anilines were oxidized to nitroso compounds or azoxybenzenes using hydrogen peroxide in the presence of catalytic amounts of selenium(IV) oxide. As it has been shown for methyl 4-aminobenzoate the result strongly depends on the solvent. Treating this compound with H_2O_2/SeO_2 in methanol at room temperature, furnishes the azoxyarene exclusively. The same oxidation in aprotic, nonpolar dichloromethane, gives nitrosoarene as a major product in 80% yield [207,208].

Despite using of tellurium(IV) oxide as a stoichiometric oxidant it was applied in small molar ratio as catalyst while H_2O_2 or TBHP were the reoxidants [209,210]. The H_2O_2/TeO_2 system was used for the selective oxidation of sulfides to the corresponding sulfoxides. Reaction occurs at room temperature and is highly chemoselective. Neither over-oxidation of the formed sulfoxide to sulfone occurs, nor are double bonds or other functional groups such as hydroxyl or carbonyl group affected even in the presence of one equivalent of TeO_2. An initially observed disadvantage of the method, which is a long reaction time, was circumvented by the addition of a small amount of concentrated hydrochloric acid [211].

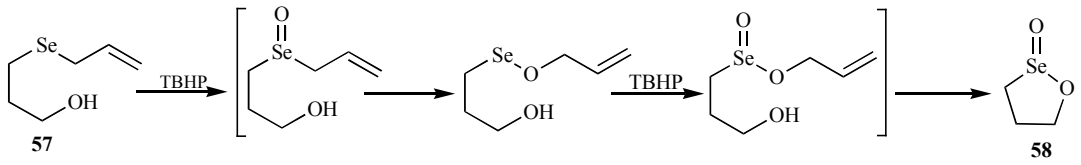
Oxidation of cyclohexanone with TeO_2/H_2O_2 under reflux afforded 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide in 42% yield [194] whereas oxidation with SeO_2/H_2O_2 resulted in a ring contraction and cyclopentanecarboxylic acid was produced. TeO_2/H_2O_2 reagent was also applied for oxidative conversion of *N*,*N*-dimethylhydrazones derived from aliphatic and heteroaromatic aldehydes into nitriles, although the more efficient catalyst was phosphomolybdic acid [212].

7.2. Organoselenium and Organotellurium Compounds

For hydrogen peroxide oxidation, selenoxides R_2SeO and selenides R_2Se have been used as the catalysts since the selenoxides are generated *in situ* from selenides and returned to the reaction cycle. 2-Carboxyphenyl phenyl selenide was successfully used as a catalyst for oxidation of sulfides into sulfoxides and/or sulfones [213]. 3,5-Di(trifluoromethyl) phenyl benzyl selenoxide is an efficient catalyst for the epoxidation of various olefinic substrates and the Baeyer-Villiger oxidation of aldehydes and ketones [214]. Another oxygen-transfer, easy to regenerate, catalyst 2,4-bis(perfluorooctyl)phenyl butyl selenide was used for epoxidation of alkenes by 60% hydrogen peroxide in fluorinated solvents. Oxidation of aldehydes and ketones under mono-, bi-, or triphasic conditions with 3,5-bis(perfluorooctyl) phenyl butyl selenide gave the carboxylic acids or carboxyesters, respectively. The active intermediates were corresponding bis(perfluorooctyl)benzeneseleninic acids [215,216].

Epoxidation in combination with a subsequent ring-opening reaction leading to dihydroxylated products was developed recently. The alkene is epoxidized by peroxyselenic(IV) acid generated *in situ* by oxidation of diphenyl diselenide with hydrogen peroxide and the epoxide is opened by an S_N2-type reaction. The stereocontrol in these reactions depends on the steric and electronic properties of the substrate [217].

Allyl selenides are good catalysts for the oxidation of benzyl thioalcohol with TBHP. 3-Hydroxypropyl allyl selenide (**57**) proved to be exceptional in this reaction. It was found, that this selenide is a procatalyst which undergoes a series of rapid oxidation and sigmatropic [2,3]-rearrangement steps to form a cyclic seleninate ester (**58**), the true catalyst for hydroperoxide oxidation (Scheme **15**) [218]. The ester (**58**), aromatic cyclic seleninate esters and spirodioxyselenuranes also exhibit glutathione peroxidase mimic activity as catalysts [219,220].



Scheme 15. TBHP oxidation of hydroxypropyl allyl selenide (**57**) into seleninate ester (**58**).

Dendrimeric polyphenyl selenide can catalyse the oxidation of bromide with hydrogen peroxide for subsequent reaction with alkenes [221]. A dendrimer with twelve PhSe groups showed an autocatalytic effect which resulted in the turnover of numbers of above $6 \cdot 10^4$. The reaction is initiated by the bromonium cation generated in the uncatalyzed background reaction [222]. The impressive catalyst for the bromination of arenes and for bromolactonization is (4-hydroxymethyl) phenyl selenoxide. The catalyst is easily separated from the reaction mixture by filtration and the recovered catalyst can be reused without loss of activity [223].

Dimethyl ditelluride and diphenyl ditelluride, which may be regarded as precursors for tellurinic acids, assuming that H_2O_2 acts upon them as it does upon diselenides also, were found to be inactive in this reaction. It was assumed that when tellurinic acids were treated with hydroperoxides, even in aqueous medium, they formed anhydrides instead of peroxytellurinic acids [224]. The exception is cross-linked to polystyrene-tellurinic acid used as a catalyst for selective hydrogen peroxide epoxidation of olefins. In the presence of this catalyst, cyclohexene treated with H_2O_2 in *t*-BuOH at 60°C for 24h quantitatively yielded the epoxide [225]. Despite of lack of success in epoxidation of alkenes catalyzed by ditellurides, diaryl ditellurides, have been found to be a thiol peroxidase like catalysts for hydrogen peroxide oxidation of thiols to the corresponding disulfides [226].

In the last two decades different, easily accessible seleninic acids, or more frequently their precursors diselenides RSeSeR, have been used as catalysts for the oxidation of different organic compounds with hydrogen peroxide, TBHP and other oxygen donors [165,168,227-230].

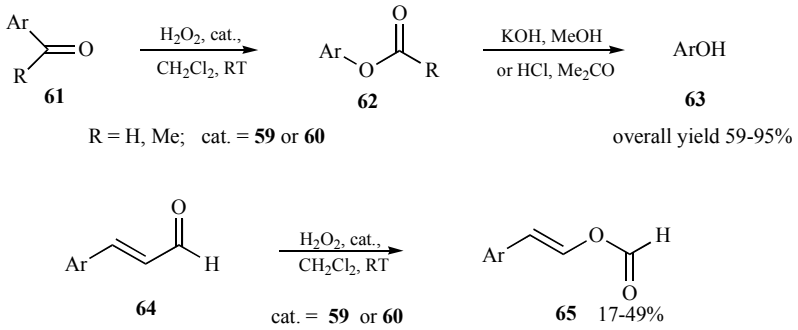
Peroxybenzeneseleninic acid PhSe(O)OOH, generated from diphenyl diselenide and hydrogen peroxide, was applied for the oxidation of primary aromatic amines to aromatic nitroso compounds, which can be used in a one-pot hetero Diels-Alder reaction with conjugated dienes to form oxazines as well as for preparation of azoxyarenes [208,231]. An improved protocol for selective oxidation of activated alcohols with TBHP, was devised resulting in significantly decreased catalyst loading (< 1 mol%) [231].

2-Nitro- and 2,4-dinitrobenzeneseleninic acids 2-$NO_2C_6H_4Se(O)OH$ (**59**) and 2,4-$(NO_2)_2C_6H_3Se(O)OH$ (**60**) and related diselenides, have been applied as catalysts for hydrogen peroxide and TBHP oxidation of different groups of organic compounds [232-234]. Oxidation of aldehydes and aryl methyl ketones **61** (R = Me) into phenol formates or acetates **62**, which in one-pot procedures are subsequently hydrolyzed to phenols **63**, is a useful way of synthesizing phenols with electron-donating substituents or polycondensed ring systems [235].

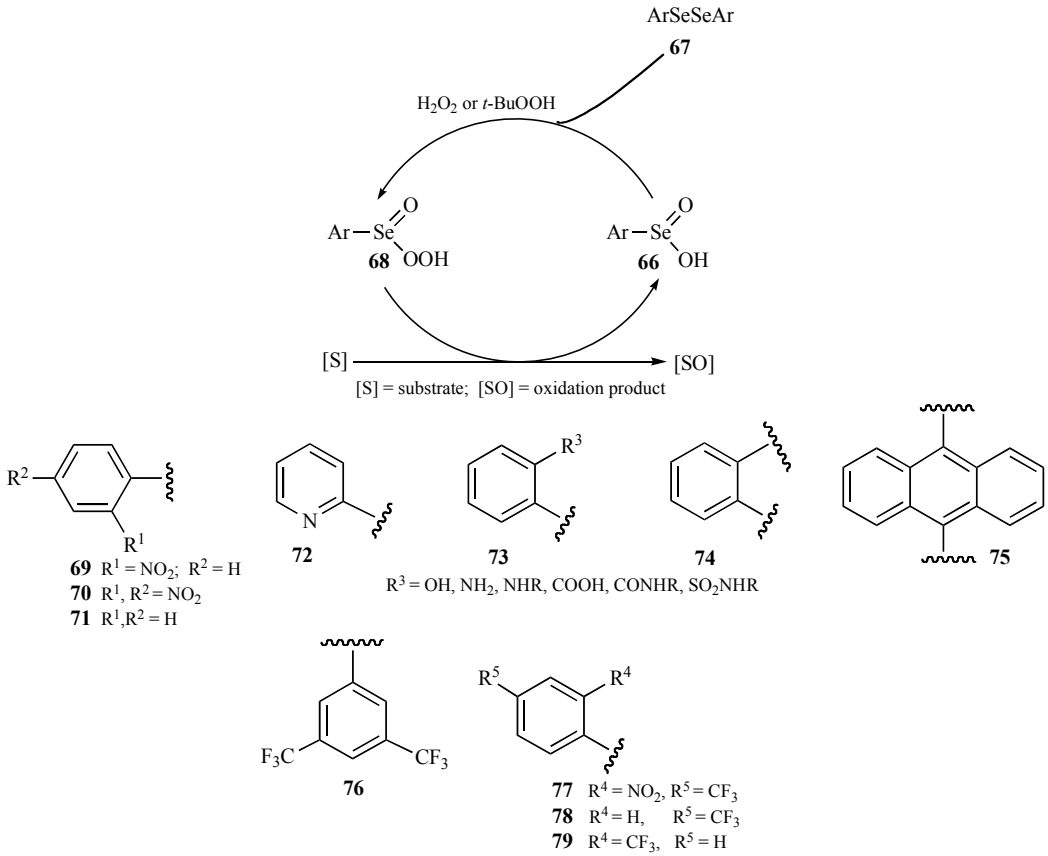
In a similar reaction, α,β-unsaturated aldehydes **64** give vinyl formates **65**, accompanied by the products of their subsequent transformations (Scheme **16**) [236]. Recently, Ichikawa and coworkers described bis(2-phenyltrifluoromethanesulfonate) diselenide (2-$TfOC_6H_4Se)_2$ as a catalyst for the Baeyer-Villiger oxidation. Reaction with hydrogen peroxide generates the peracid, which reacts with cyclic ketones to yield the corresponding lactones in high yields [237].

The proposed mechanism of the oxidation of organic substrate in the presence of areneseleninic acid **66** or its precursor the diaryl diselenide **67**, is presented in Scheme **17**. Both of them are oxidized *in situ* with hydrogen peroxide or TBHP into areneperoxyseleninic acid **68**, the active oxygen donor. Peroxybenzeneseleninic acid and its 2-nitro- and 2,4-dinitro analogues were obtained by hydrogen peroxide oxidation of the corresponding diaryl diselenides and were fully characterized [238, 239].

Diselenides **69-79** used more recently as catalysts for oxidation of different groups of organic substrates are presented in Scheme **17**. They are easily available in the reaction of alkyl, aryl, and heteroaryl halides with dilithium



Scheme 16. Hydrogen peroxide oxidation of aromatic aldehydes and ketones, and α,β-unsaturated aldehydes catalyzed by seleninic acids or diselenides.



Scheme 17. The mechanism of hydroperoxide oxidation of organic substrate catalyzed by diaryl deselenide or areneselenenic acid.

diselenide formed *in situ* from elemental lithium and selenium in aprotic media [240-242].

It has been observed, that the effectiveness of selenium catalysts strongly depends on the substrate used. While *ortho*-substituted diphenyl diselenides are the best catalysts for hydrogen peroxide oxidation of sulfides into sulfoxides and ketazines into their parent ketones [243, 244], the poly(bis-1,2-phenylene) diselenide (**74**) was selected for preparative oxidation of various aromatic aldazines, aldoximes, and conversion of tosylhydrazones into arenecarboxylic acids [245].

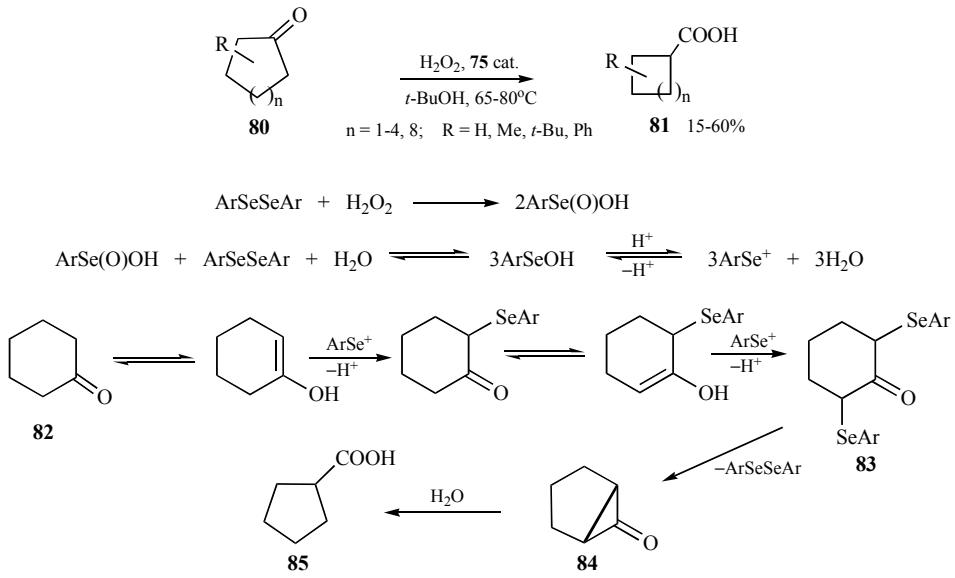
In the presence of poly(bis-9,10-anthracenylene) diselenide (**75**) a broad spectrum of aliphatic, unsaturated and aromatic nitriles was obtained, in excellent preparative yields, by oxidation of the corresponding *N*,*N*-dimethylhydrazones [48]. It was the catalyst of choice for oxidation of cycloalkanones **80** to cycloalkanecarboxylic acids **81**. The results of more detailed studies on the chemo- and stereoselectivity of this reaction support the mechanism, presented for cyclohexanone (**82**) in Scheme **18**. Most probably, the reaction involves addition of two bulky arylselenium cations in both α-positions of the ketone, the elimination of diaryl diselenide from adduct **83** and finally the Favorski-like rearrangement of intermediate **84** to the acid **85** [246].

Although preparative yields of the cycloalkanecarboxylic acids did not exceed 60%, they were substantially higher than those obtained when selenium(IV) oxide was the catalyst. Since the cycloalkanones are cheap and easily available substrates, the elaborated method is suitable for the synthesis of acids **81**, particularly those having five-, six- and seven-membered rings.

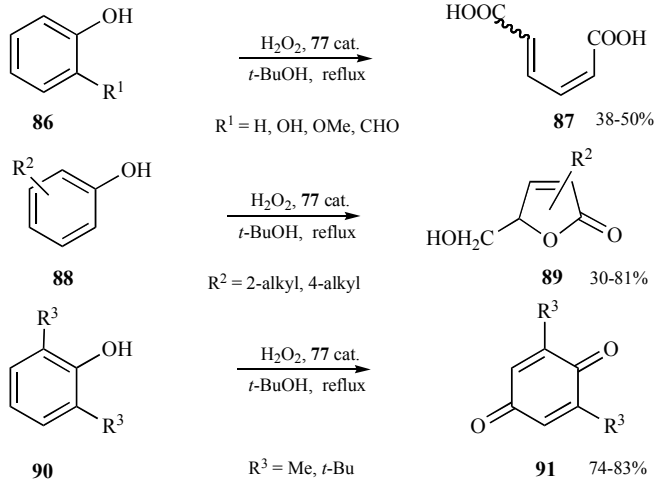
The bis[2-nitro-4-(trifluoromethyl)phenyl] diselenide (**77**) was found to be an efficient catalyst for hydrogen peroxide oxidative degradation of electron-rich benzene ring in the phenol or its *ortho* substituted derivatives **86**, **88** and **90**. Depending on the substrate used, muconic acid (**87**), muconolactones **89** or 1,4-benzoquinones **91** were produced in satisfactory to good yields. Similar ring-degradation took place when substituted naphthalenes were oxidized. Cinnamic acid or benzofurane derivatives were the final products [241,242,247] (Scheme **19**).

Recently it was reported that bis[3,5-bis(trifluoromethyl) phenyl] diselenide (**76**) has been significantly more active than other previously described selenium catalysts for epoxidation and Baeyer-Villiger oxidation of carbonyl compounds with hydrogen peroxide [248,249].

Areneseleninic acids and selenoxides can be used as catalysts for the oxidation of bromide, with hydrogen peroxide, to hypobromite and bromine in a two-phase reaction mixture. Among various areneseleninic acids tested as catalysts, the most effective were benzeneseleninic acid and 4-methoxybenzeneseleninic acid. Generated *in situ* Br_2 and NaOBr bring on the cyclization of unsaturated enolic acids, such as for example, 4-pentenoic acid (**92**) or related unsaturated alcohols, give the lactone **93**, accompanied with a small amount of dibromo acid **94**. Similarly, the



Scheme 18. Oxidative conversion of cycloalkanones into cycloalkanecarboxylic acids catalyzed by poly(bis-9,10-anthracenylene) diselenide (**75**).



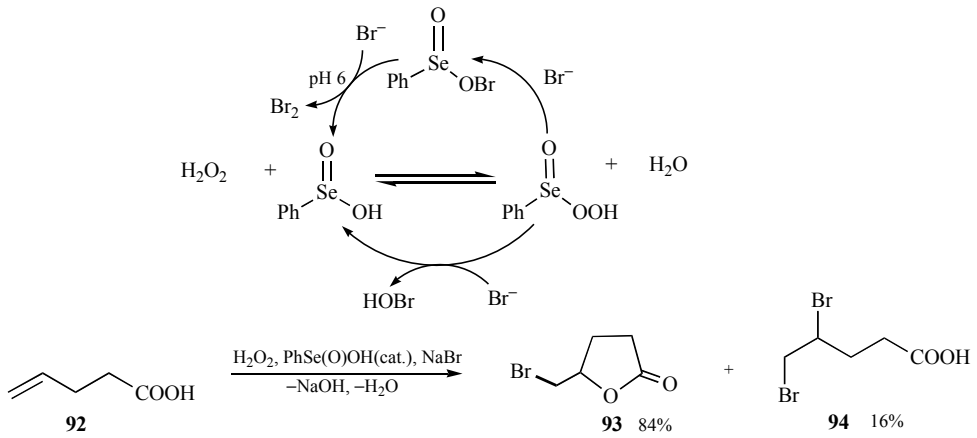
Scheme 19. Oxidation of the benzene ring of phenols with H_2O_2/ bis[(2-nitro-4-trifluoromethyl)phenyl] diselenide (**77**).

electrophilic bromination of activated aromatic rings can be performed with high yields (Scheme **20**) [250,251].

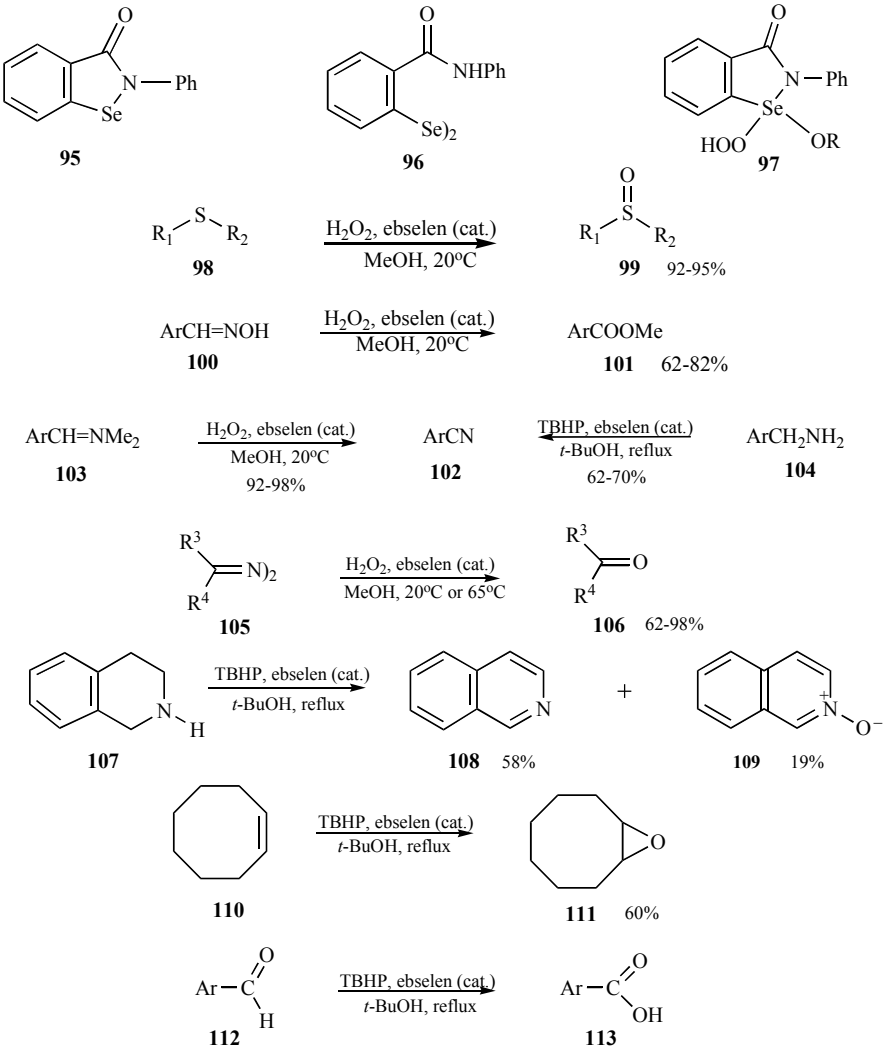
Other works showed the evidence that well known glutathione peroxidase mimic the ebselen (**95**), related selenenamides and diselenides could catalyze the hydroperoxide oxidation of various organic compounds. The catalyst **95** was used in 5 mol%, and diselenide **96** in 2.5 mol% while the stoichiometric oxidant was 30% hydrogen peroxide or 80% TBHP and results are presented in Scheme **21** [27,228,229,241,252-254]. It was postulated, that all these reactions have ionic character and that active intermediate is hydroperoxyselenurane **97** [255].

The sulfides **98** are exclusively oxidized into sulfoxides **99** [243]. Aromatic aldoximes **100** oxidized in methanol give carboxymethyl esters **101** [256]. Nitriles **102** are produced from *N*,*N*-dimethylhydrazones **103** by oxidation with hydrogen peroxide [238,243] or from benzylamines **104** oxidized with TBHP [257]. Hydrogen peroxide oxidation of ketazines **105** gives the parent ketones **106** [243]. 1,2,3,4-Tetrahydroisoquinoline (**107**) is dehydrogenated to isoquinoline (**108**) which undergoes subsequent oxidation into the *N*-oxide **109** [258]. Cyclooctene (**110**) treated with TBHP gives epoxide **111**, accompanied with trace amounts of 3-hydroxycyclooctene, resulting from α-hydroxylation [259], while oxidation catalyzed by selenium(IV) oxide obtains 3-hydroxycyclooctene as a major product and epoxidation is not observed [171,259]. Oxidation of aromatic aldehydes **112**, having electron-donating substituents, with TBHP in the presence of ebselen, led almost exclusively to the acids **113**, thus avoiding the Baeyer-Villiger rearrangement [255], contrary to mentioned earlier, oxidation with hydrogen peroxide in the presence of selenium(IV) oxide, where mixtures of arenecarboxylic acids and phenols or even phenols as the sole products, were produced [203].

Despite the ionic reactions presented above, some other reactions can proceed *via* a free-radical mechanism. Catalyzed by ebselen, TBHP oxidation of alkylarenes **114** to alkyl aryl ketones **115** [257], anthracene (**116**) to



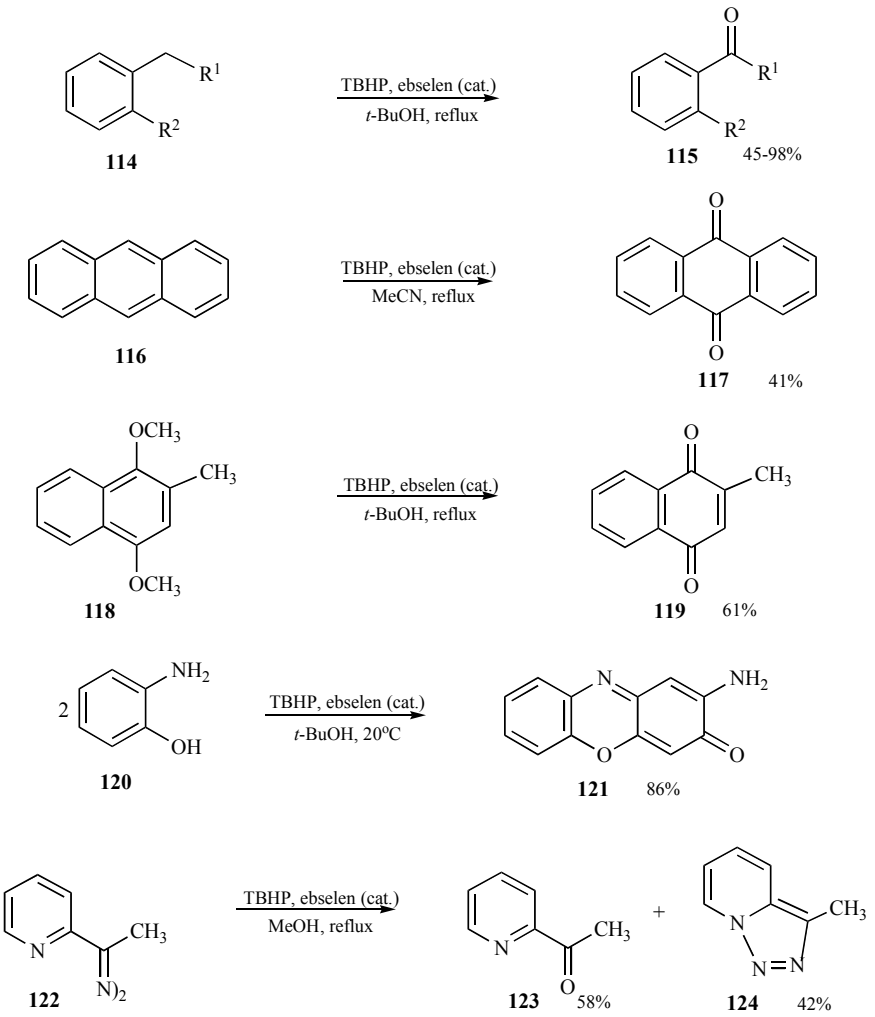
Scheme 20. Bromolactonization of an enolic acid *via* benzeneseleninic acid catalyzed oxidation of NaBr with H_2O_2.



Scheme 21. Oxidation of ionic character catalyzed by ebselen.

anthraquinone (**117**) [260], 1,4-dimethoxyarenes to 1,4-quinones (e.g., 2-methyl-1,4-dimethoxynaphthalene (**118**) to menaquinone (**119**) [261] and oxidative coupling of 2-aminophenols (e.g., **120** to phenoxazinones **121**) [262] gave results similar to those with the one-electron oxidants Ce(IV), Ag(II), or Mn(III) (Scheme **22**).

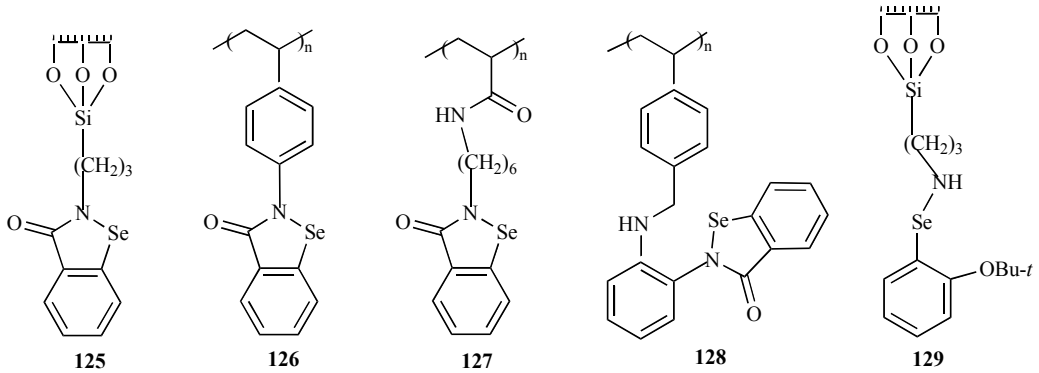
Moreover, oxidation of ketazine (**122**), derived from 2-acetylpyridine, gave a mixture of ketone **123** and condensed triazole **124** [257]. The same result was found when cerium ammonium nitrate was used as the reagent. This suggests, that the reaction proceeds *via* cation-radicals. Both of the postulated mechanisms, ionic and free-radical, were discussed in greater detail in a review article [27].



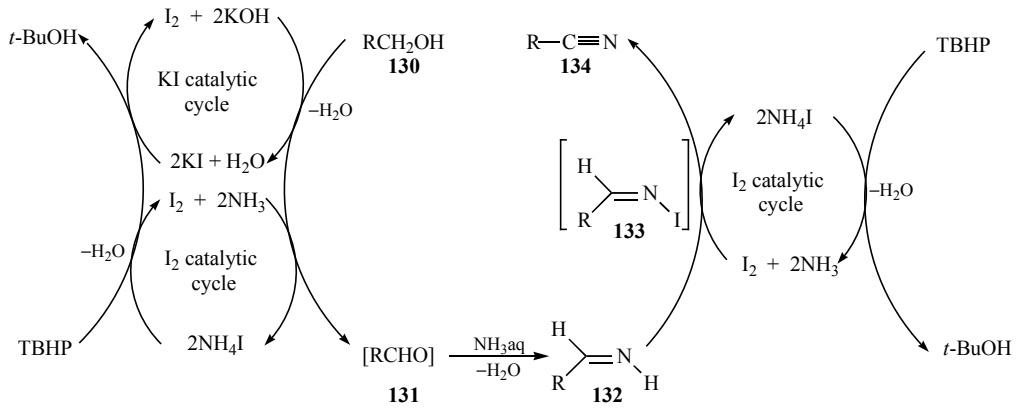
Scheme 22. Catalyzed by ebselen oxidations of free-radical character.

A few benzisoselenazol-3(2*H*)-ones **125-128** and open-chain selenenamide **129** were covalently immobilized to the solid support, either silica or polymer (Scheme **23**) [260,263,264]. They exhibited appreciable catalytic activity similar to the activity of ebselen, and could be easily recovered by filtration, and reused. The most prospective oxygen-transfer recoverable catalyst is benzisoselenazolone covalently bound to a silica support **125** named HALICAT. It has been applied to hydrogen peroxide oxidation of sulfides and TBHP oxidation of the aromatic aldehydes to acids and alkylarenes to alkyl aryl ketones [263].

It should be noted that ebselen (**95**) is a stable, non toxic compound. It can be obtained easily from anthranilic acid *via* bis(2-carboxyphenyl) diselenide and aniline. The method has a more general value because, by using various amines and other compounds with primary amino groups, different benzisoselenazol-3(2*H*)-ones and 2-substituted diphenyl



Scheme 23. Benzisoselenazol-3(2H)-ones and selenenamide covalently immobilized on the solid supports.



Scheme 24. Oxidative transformations of alcohols, aldehydes and amines using KI/I_2 -TBHP system.

diselenides, also these bounded to solid support, can be obtained in high yields [244,253,254,265,266].

8. OTHER CATALYSTS

Recently, the use of catalytic amount of KI or molecular iodine for the facile oxidative amidation of aldehydes and alcohols to form amides using TBHP as an external oxidant has been reported [267]. The same reagent and catalysts were used for direct oxidative conversion of alcohols, aldehydes and primary amines to the nitriles. Aromatic primary amines were oxidized to the corresponding nitro compounds. The present catalytic system works well for both electron-rich and electron-poor substrates [268, 269].

Based on the obtained results, the plausible mechanism, as shown in Scheme **24**, was proposed. In the case of alcohol **130** an aldehyde **131** could be an intermediate, which could be achieved by using either KI or I_2 as a catalyst. Aldehyde **131** thus formed reacts with ammonia to form an imine **132**. Imine further reacts with iodine to form *N*-iodo aldimine **133**, finally transformed into nitrile **134** by β-elimination of HI with ammonia. In case of direct conversion of primary amines to nitrile, a similar mechanism *via* imine and *N*-iodo aldimine was expected. It has been proposed earlier that under alkaline conditions, iodine is involved in multiple equilibriums, in which hypoiodous acid is one of the possible intermediates [268]. Similar intermediate was also proposed under acidic conditions with NaI and H_2O_2 for the α-iodination of ketones [270].

Silica gel has been found to mediate the efficient *t*-butyl hydroperoxide oxidation of sulfides to sulfoxides (80-88% yield), and sulfoxides to sulfones (93% yield). These studies afforded insights into the mechanism of surface-mediated processes. It was found that oxidation of sulfides or sulfoxides by TBHP/silica gel occurs at least predominantly *via* nucleophilic attack by the substrate molecule on the hydroperoxide, which is activated by being bound to isolated silanol sites on the silica gel surface [271].

Under aqueous/biphasic organic conditions aqueous hydrogen peroxide oxidizes aldehydes to carboxylic acids without affecting olefinic or alcoholic function. The phase-transfer catalyst is $[CH_3(n\text{-}C_8H_{17})_3]HSO_4$ ($QHSO_4$) and the reaction is catalyzed simply by acid [272].

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was used as a catalyst for selective hydrogen peroxide oxidation of benzylic alcohols to the corresponding aldehydes. Using TEMPO/HBr/H_2O_2 system and ionic liquid [bmim]PF6 at room temperature the aldehydes were obtained in 72-92% yield. The catalyst was simple to recover and reuse [273].

9. ENZYMES

Enzymes are proteins that catalyze a lot of biological reactions *in vivo*. They are large molecules with unique stereostructures, therefore they can be highly selective for certain types of substrates and reactions. As versatile catalysts they act also *in vitro* with natural and man-made organic compounds. They can be selective for substrates and stereoselective in reactions they catalyze, their selectivity can range from very narrow to very broad.

The active sites of enzymes are chiral, and enzymes are well suited as catalysts for reactions generating specific, mostly the enantiomerically pure intermediates and products. Therefore they are being increasingly used in pharmaceutical industry, agrochemistry, analytical chemistry and polymer science to create novel attractive materials [28].

In broader terms, enzymes play an important part of the spectrum of catalysts available to synthetic chemists. Biocatalytic procedures (including immobilization of enzymes on various supports, application of organic solvents, methods of coenzymes regeneration) may offer practical routes to chemoenzymatic synthesis as a challenging alternative to classical synthetic methods [29].

The demand of novel highly active enzymes stimulates their search in pro- and eukcaryotic world. Particularly, various methods of screening microorganisms or plants for enzymatic activities provide new approaches to the discovery of useful biocatalysts and work out their production on the large scale. The generation of novel tailor-made proteins, mainly due to molecular engineering techniques also creates the fascinating opportunity of providing new catalysts with specific activities [30, 274-278].

An unique group of biocatalysts, belonging to the oxidoreductase class of enzymes, are peroxidases performing oxidation of selected organic compounds using hydroxyperoxides [279, 280]. Due to their catalytical versatility and stability, peroxidases are of particular interest as potential biocatalysts for industrial oxidation processes. Some commercialy available ones have received extensive attention in the last decades as biocatalysts for organic

synthesis, chemiluminescent assays, radiochemistry, immunochemistry and for construction of biosensors used in analytical diagnostics and bioremediation of pollutants [281].

Peroxidases are widely distributed in nature, found in all domains of life: microorganisms, plants and animals. They perform a variety of biological functions, such as the synthesis of macromolecules and the detoxification of hydrogen peroxide, accepting a broad range of substrates [282]. Traditionally, their names are derived from their sources or from their substrates, but based on their structure of active center, peroxidases are classified into three groups: heme peroxidases, vanadium peroxidases and non-metal peroxidases. From the first group, horseradish peroxidase (HRP), lactoperoxidase (LPO), soybean peroxidase (SBP) and several fungal peroxidases like lignin (LiP), manganese (MnP) and haloperoxidase (CPO) are mostly used as biocatalysts [283-286]. Vanadium peroxidases (VPBO), enzymes belonging to the second group, possessing a single bound vanadate ion in the inactive centre occurig in seeweeds were found to be attractive novel catalysts [287,288]. Representatives of the third group: glutathione peroxidases (GPx), enzymes containing selenocysteine in active site also have gained attention [289].

There are several novel peroxidases under study, produced mainly by basidiomycetous wood rotting fungi. They show unique catalytic properties potentially very challenging in several biotechnological processes [290,291].

Peroxidases are versatile enzymes, they catalyze a variety of reactions depending on the conditions and kind of oxidizing agent (hydroxyperoxide or atmospheric oxygen), electron transfer, disproportionation, halogenation, sulfoxidation, epoxidation, demethylation, dehydrogenation, hydroxylation, α-oxidation. In the presence of hydroperoxides biooxidation of aromatic compounds, heteroatomatic compounds, epoxidation, sulfoxidation and halogenation occurs [280]. Therefore these biocatalysts can be used as a tool in asymmetric synthesis. The transformation of a broad range of substrates performed by peroxidases leads to valuable compounds for the synthesis of biologically active molecules. The small-scale applications of peroxidases in the area of synthetic organic chemistry, especially when regio- and enantioselective oxidations are sought, are both numerous and appealing, and have been summarized in many reviews [279,280,292-295]. Oxidative coupling of phenols and aromatic amines is promising for the synthesis of complex molecules with high biological activities, conductive polymers, resin manufacture and removal of pollutants. Halogenation reactions make it possible to obtain radiolabeled compounds or halohydrins used in organic synthesis. The highly selective epoxidation and sulfoxidation of a variety of substrates to yield useful chiral synthons are particularly important.

Useful peroxidase catalysed reactions, when hydrogen peroxide (or other hydroperoxide) is an oxygen source can be divided on three groups: (1) oxidative dehydrogenation, (2) oxidative halogenation, (3) oxygen transfer reactions: (Scheme **25**)

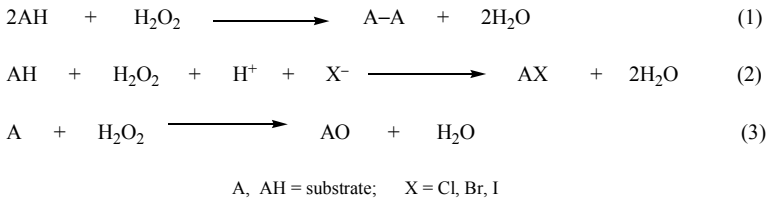
9.1. Oxidative Dehydrogenation

A variety of peroxidases effecitvely catalyze oxidation of phenols **135** to generate phenoxy radicals which react with each other to form in non-enzymatic way dimeric and polymeric products **136** (Scheme **26**) [296,297].

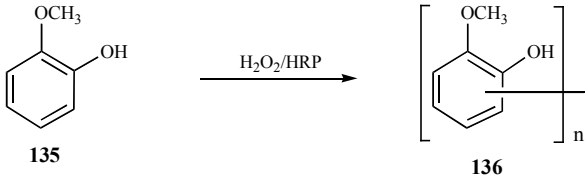
Peroxidases may be useful for the removal of phenolic contaminants from water, wastewater [298] and used for the synthesis of phenolic polymers in industry as an alternative method to harmful phenol-formaldehyde procedures [299, 300]. Syringaldehyde (**137**), one of the major derivatives of lignin, was copolymerized with bisphenol A (**138**) to a polymer **139** harboring an active aldehyde group in the backbone using fungal peroxidase CiP (*Coprinus cinnereus)* (Scheme **27**) **[**301].

The oxidative coupling of phenols catalyzed by peroxidases is a very attractive method for preparing various phenolic dimers showing biological activity. Using HRP as a biocatalyst (*E*)-stilbene-3,4-diol (**140**) (resveratrol analogue) was oxidized to dimeric product, novel phytoalexin (**141**) (Scheme **28**) [302]. Two monomeric *Vinca* alkaloids, catharantine and vindoline were oxidized under similar conditions to the heterodimeric product vinblastine which is an antitumor agent [303].

Enzymatic oxidative polymerization of phenols and its derivatives using peroxidases has several advantages over conventional harsh chemical methods. Phenolic monomers having various substituents are polymerized to give a new

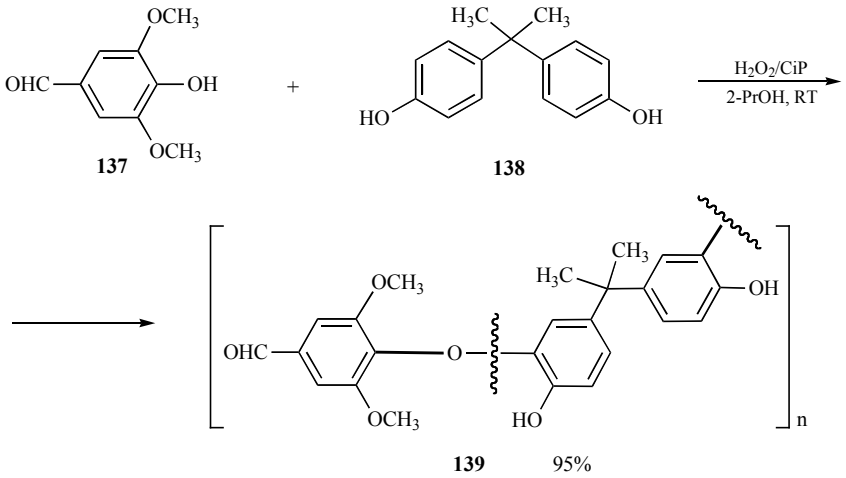


Scheme 25. Hydroperoxide oxidations catalyzed by peroxidase.

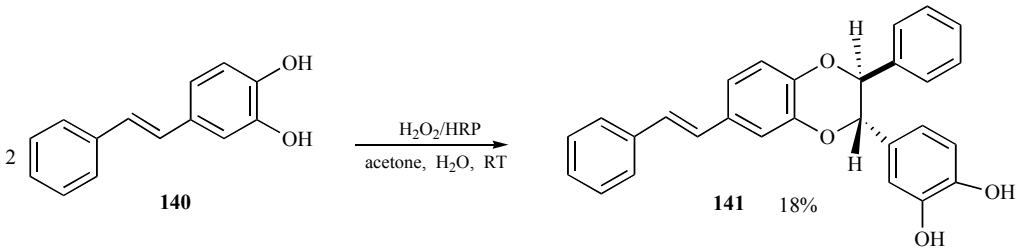


135 **136**

Scheme 26. HRP catalyzed oxidation of phenols.



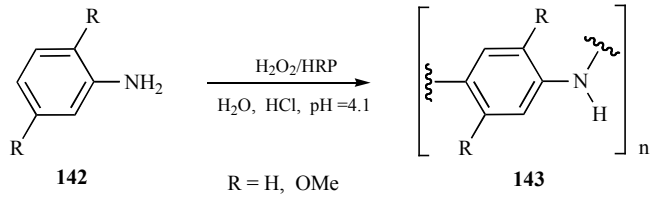
Scheme 27. Copolymerization of syringaldehyde and bisphenol A by fungal (*Coprinus cinnereus*) peroxidase.



Scheme 28. HRP catalyzed oxidative cyclocondensation of (*E*)-stilbene-3,4-diol.

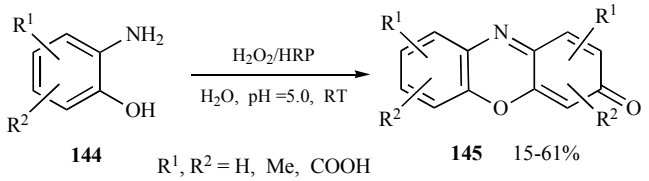
class of functional polyaromatics, the structure and solubility of which can be controlled by changing the reaction conditions.

Using hydrogen peroxide in the presence of HRP, aniline (**142**, R=H) and its derivatives polymerize to polyanilines **143**, one of the most investigated conducting polymers for the electronic industry (Scheme **29**) [304].



Scheme 29. Biocatalytic synthesis of polyanilines.

Oxidative coupling of *o*-aminophenols **144** with hydrogen peroxide in the presence of HRP lead to aminophenoxazinones **145** (Scheme **30**) [305]. Phenoxazinones are widely distributed in nature as insect pigments, fungal metabolites and antitumor antibiotics [306, 307]. Synthetic analogues are used as fluorescent dyes in analytical chemistry [308].



Scheme 30. Oxidative cyclocondensation of aminophenols to aminophenoxazinones.

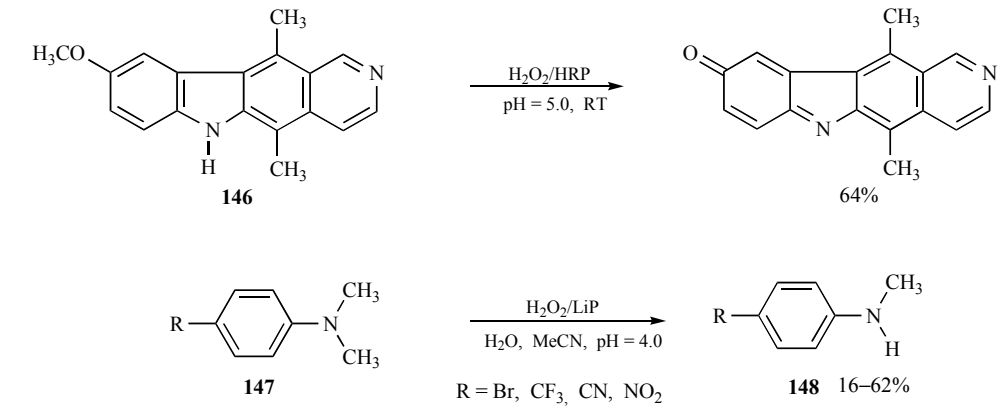
Particularly interesting are the reactions of *O*-dealkylation catalyzed by peroxidases involved in nature in lignin biodegradation processes [309]. In preparative organic chemistry, *O*- as well as *N*-dealkylation reactions require severe conditions while, due to biocatalytic procedures, removal of alkyl groups can be easily performed as it is shown for *O*-demethylation of 9-methoxyellipticine **146** [310] and conversion of *N,N*-dimethylanilines **147** into *N*-monomethylanilines **148** (Scheme **31**) [311].

In spite of synthetic chemistry, peroxidase-catalyzed polymerization as well as *O*- and *N*-demethylation, have been exploited for the treatment of industrial wastewater polluted with polyphenols and phenylenediamines, removal of lignins degradation products accumulated in wood decomposition procedures for bio-fuel production and degradation of azo dyes used in textile industry [312,313].

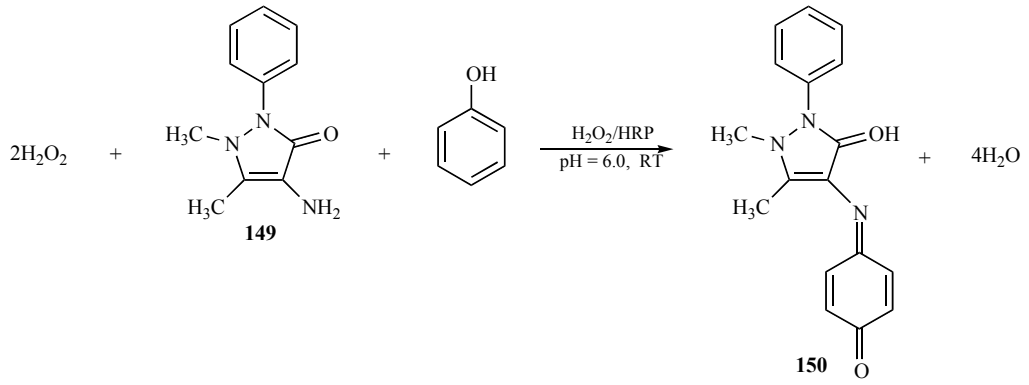
Peroxidases are able to catalyse formation of chromogenic products, e.g **150** from amine **149** and phenol as shown in Scheme **32** [314]. These reactions have been utilized in several immunoassay procedures, chemiluminescence and construction of biosensors [307,314,315].

9.2. Oxidative Halogenation

Several peroxidases, named haloperoxidases, isolated from various sources catalyze oxidation of chloride, bromide and iodide by hydrogen peroxide. They are divided into three groups. In the first group there are enzymes without prosthetic group, mainly found in bacteria. The second group comprises heme-dependent peroxidases derived from different sources. In this group the most well known is lactoperoxidase (LPO) isolated from milk and haloperoxidase (CPO) found in marine fungus *Caldariomyces fumago*.



Scheme 31. Enzymatic *O*- and *N*-demethylation.



Scheme 32. Formation of chromogenic product derived from 4-aminoantipyrine by peroxidases (HRP, LPO) used in analytical metodology.

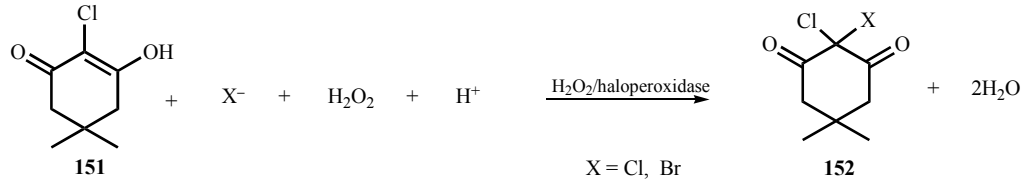
Third group includes vanadium-containing peroxidases (VPOs) produced by several species of alga and marine fungi. According to the oxidized halogen haloperoxidases are classified as chloro, iodo- and bromo-peroxidases. A common substrate to evaluate enzymatic activity of all haloperoxidases is monochlorodimedone **151** oxidized to 2,2-dihalogeno-1,3-diketone **152** (Scheme **33**) [293].

Haloperoxidases can be used as biocatalysts for the preparation of halohydrins from alkenes [293, 316]. Both enantiomers **154** and **155** are obtained from propene **153**, which can be subsequently converted chemically or with halohydrin epoxidases to chiral 2-methyloxirane **156** (Scheme **34**) [292].

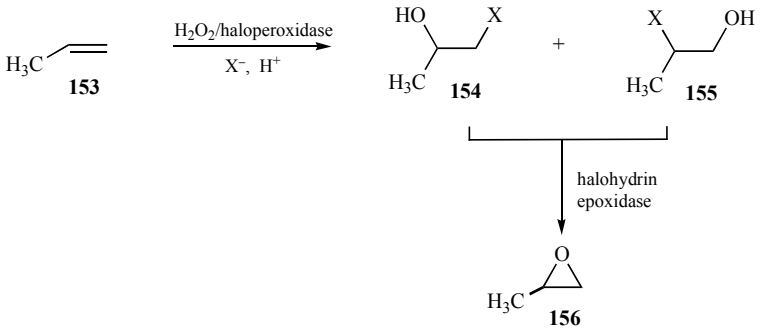
Haloperoxidases, mainly bovine milk lactoperoxidase (LPO) are commonly used to produce radiolabelled compounds and for radioiodination of proteins and nucleic acids [317,318] Halogenation reactions facilitate to obtain several novel intermediates for the synthesis of biologically valuable compounds such as 2-deoxy-2-halo-sugars. For example, when using unprotected glycal **157** as substrate and chloroperoxidase as catalyst, single haloisomers **158-160** were obtained (Scheme **35**) [319].

9.3. Oxygen Transfer Reactions

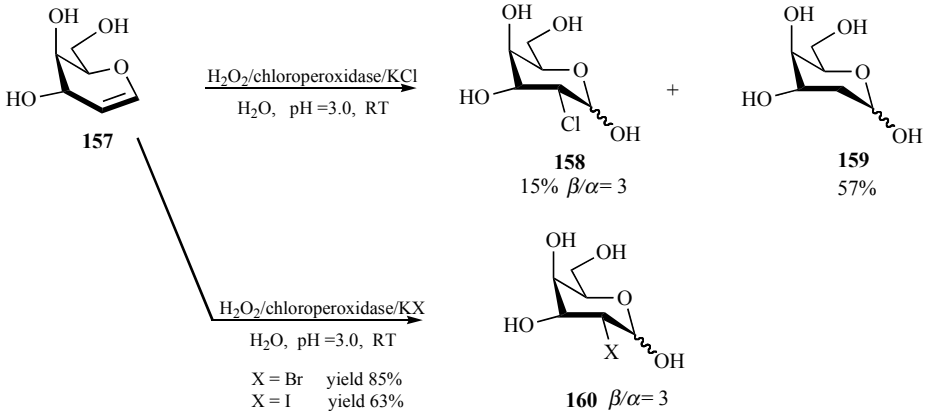
In asymmetric synthesis of natural products optically active epoxides are important building blocks. Among the peroxidases so far tested, only chloroperoxidase from *Caldariomyces fumago* (CPO) in the absence of chlorine ions catalyzes useful oxygen transfer reactions, i.e. asymmetric epoxidation of olefins and sulfoxidation. This versatile enzyme was used to oxidize several olefins: aliphatic and aromatic (styrene and its ring-substituted derivatives). Results reported from various laboratories [280,292,293,320] indicate that CPO catalyzes oxidation of olefins, using both H_2O_2 and TBHP as oxygen donors, affording the corresponding epoxides mostly in good enantiomeric excesses values. The examples presented in Scheme **36** illustrate this type of reaction. The selectivity of bioconversion depends on the structure of the substrate used. In general *cis*- substituted olefins were epoxidized with good yields and excellent enantiomeric excess, whereas *trans*-compounds were poorly accepted.



Scheme 33. Oxidative halogenation of monochlorodimedone catalyzed by haloperoxidases.

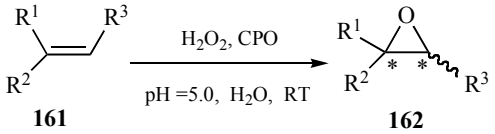


Scheme 34. Formation of halohydrins catalyzed by haloperoxidases.



Scheme 35. Biohalogenations of glycals.

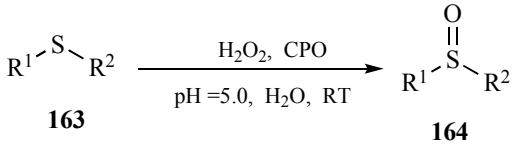
A number of heme and vanadium peroxidases were tested to catalyze enantioselective sulfoxidation. The highest yields were observed when chloroperoxidase from *Caldariomyces fumago* (CPO) was a catalyst. The dialkyl and alkyl aryl sulfides **163** were oxidized to sulfoxides **164** in excellent yields and high (*S*)-enantiomers dominated [280,293,321]. The examples are presented in Scheme **37** [280]. Some conformationally restricted sulfides (dihydrobenzenotiophenes) were also accepted by CPO but in such case (*R*)-isomers prevailed. The variations in products formation were dependent on substrate structures [322].



R^1, R^2 = H; R^3 = Ph	yield 89%, ee 49%
R^1 = H; R^2 = Me; R^3 = Ph	yield 67%, ee 96%
R^1 = H; R^2 = Et; R^3 = *n*-Bu	yield 20%, ee 95%

Scheme 36. Epoxidation of olefins catalyzed by CPO.

Peroxidases catalyzing a variety of reactions are readily inactivated by their substrate, particularly hydrogen peroxide , when concentration of H_2O_2 is high, above 25 mM. Such inactivation of hemoprotein is described as "suicide inactivation" [323]. This problem can be solved by using a very low and controlled hydrogen peroxide supplementation, nessesary just for the maintenance of an effective oxidation level. This can be achieved using a direct pulsated addition, electrogeneration *in situ* [324] or an enzymatic formation of hydrogen peroxide [325].



R^1 = Ph; R^2 = Me	yield 90%, ee 99%
R^1 = $PhCH_2$; R^2 = Me	yield 100%, ee 90%
R^1 = *t*-Bu; R^2 = Me	conversion 80%, ee 85%
R^1 = CH_2=CH; R^2 = Me	conversion >98%, ee >98%

Scheme 37. Enzymatic oxidation sulfides to sulfoxides.

CONCLUSIONS AND OUTLOOK

In this work an attempt has been made to summarize the progress in the exploitation of the non-metal-containing catalysts and enzymes for hydroperoxide, mainly hydrogen peroxide and *tert*-butyl hydroperoxide, oxidation. Among catalysts have been perhydrates, hydroperoxysulfonylhalides, oxazilidines, hydroperoxyflavines, aminoacids and polyaminoacids, cyclodextrins as well as selenium and tellurium compounds (oxides and organoselenium, and organotellurium compounds). Other hydroperoxide activators such as bases, acids and urea have also been presented. The described oxidant/catalyst systems are ecologically friendly reagents, convenient for modern organic synthesis and have been used for oxidative transformations of various groups of organic compounds. The most important reactions have been allylic hydroxylation, α-oxygenation of alkenes and enolizable ketones, epoxydation of alkenes, oxidation of

methyl groups in arenes and heteroarenes, 1,2-hydroxylation of alkenes, dehydrogenation and oxidative C-O and C-C cleavage, oxidative ring closure and ring transformation, heteroatom *N*- and *S*-oxidation, Baeyer-Villiger conversion of ketenes into lactones and other. The mechanisms and stereochemistry of some important reactions have been discussed and their scope and limitations have been indicated. Where possible, links have been made to enzymatic oxygenations where hydroperoxides are oxygen sources. Although an effort has been made to include all relevant literature, authors do not claim completeness. However, this review can serve as a valuable critical overview of the area, and it is hoped that the contribution helps in encouraging further research in this field.

ABBREVIATIONS

BAP = Bicarbonate-activated peroxide

BSA = Bovine serum albumin

CPO = Chloroperoxidase

DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene

HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol

HRP = Horseradish peroxidase

LiP = Lignin peroxidase

LPO = Lactoperoxidase

MnP = Manganese peroxidase

PTSA = *p*-toluenesulfonic acid

SBP = Soybeen peroxidase

TBHP = *t*-Butyl hydroperoxide

TEMPO= 2,2,6,6-Tetramethylpiperidine-1-oxyl

TFE = 2,2,2-Trifluroethanol

THF = Tetrahydrofurane

UHP = Percarbamide, hydrogen peroxide and urea adduct, $CO(NH_2)_2 \cdot H_2O_2$

VPO = Vanadium-containing peroxidase

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