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Organoselenium small molecules as catalysts for the oxidative functionalization of organic molecules

Vandana Rathore, D Cavya Jose and Sangit Kumar D*

Organoselenium chemistry has become an exciting topic in synthetic chemistry and pharmaceuticals in the last few decades. Organoselenium molecules as reagents have been developed only recently for the epoxidation or halogenation of olefins by using peroxides and dihalogens or halogenating reagents, respectively. In the past few years, some reports were available but these did not include a clear vision for the catalytic use of organoselenium molecules and despite important breakthroughs, they signify just the very preliminary stages of a nascent field. This perspective highlights the critical analysis of the challenges, in the past decade, which led to the development of organoselenium compounds and their use as versatile catalysts in organic synthesis towards the oxidation of olefins and C-H bonds. Furthermore, the emphasis here differs from the previous reviews of the field by classifying the various types of catalyses and the diverse strategies employed not only for the oxidation of olefins but also carbonhydrogen bond for carbon-carbon and carbon-heteroatom bond formation in the synthesis of various heterocyclic molecules by asymmetric induction.

1. Introduction

The advances in the area of synthesis and reactivity of organoselenium compounds, as well as the discovery of the toxic

Department of Chemistry, Indian Institute of Science Education and Research (IISER), Bhopal, MP 462 066, India. E-mail: sangitkumar@iiserb.ac.in

properties of selenium compounds in the 1930s and the subsequent discovery that selenium is an essential trace element in the diet, has prompted intense studies of the biological properties of both organic and inorganic selenium compounds. The biological and medicinal properties of organoselenium compounds are also increasingly appreciated, mainly due to their



Vandana Rathore

Dr Vandana Rathore was horn in Agra, India. She obtained her BSc and MSc degrees in Chemistry from Dr Bhim Rao Ambedkar University, Agra. In 2018, she received her PhD in chemistry from the Indian Institute of Science Education and Research (IISER), Bhopal, under the supervision of Professor Sangit Kumar. Her doctoral research work focused on the area of organochalcogen chemistry.



Sangit Kumar

Sangit Kumar graduated from Saharanpur, India. After completing his Master's in Chemistry from the University of Roorkee (now IIT Roorkee) in 1999, he joined the group of Professor Harkesh B. Singh, IIT Bombay for a PhD program. In 2005, he joined the group of Professor Lars Engman a post-doctoral position; subsequently, he move to State University at Buffalo (SUNY) continued working and organochalcogen chemistry

under the supervision of Professor Michael R. Detty till 2008. He took an independent position as assistant professor in the Department of Chemistry at IISER, Bhopal, in 2009 and became full professor in 2018. His main research focuses are organochalcogen chemistry and transition metal free carboncarbon and carbon-heteroatom coupling reactions.

antioxidant, anti-inflammatory, antimicrobial, anticancer, neuroprotective⁶ and antiviral⁷ properties.

Organoselenium compounds have been widely utilized by organic chemists in recent years⁸⁻¹² because of their effects on an extraordinary number of different reactions, including carbon-carbon bond formations, under relatively mild reaction conditions. Furthermore, organoselenium compounds can also be used in the presence of a wide variety of functional groups, thus avoiding protecting group chemistry. 13 Selenium can be introduced in an organic substrate via both electrophilic and nucleophilic reagents. Organoselenium anions are powerful nucleophiles, and usually, they are prepared in situ because of their sensitivity to air oxidation. 14 Divalent selenium forms stable bonds with carbon and are structurally analogous to the corresponding organosulfur compounds, namely, selenides (R2Se, analogues of thioethers), diselenides (R2Se2, analogues of disulfides), and selenols (RSeH, analogues of thiols). Representatives of selenides, diselenides, and selenols include selenomethionine, diphenyl diselenide, and benzeneselenol, respectively. Good functional group tolerance, perfect selectivities and mild reaction conditions make this a distinctive research topic. 15 Furthermore, organoselenium catalyzed reactions are often transition-metalfree, hence, it avoids harmful toxic waste in the products, making this method economical and environment-friendly. Particularly in organochalcogen compounds, selenium exhibits variable oxidation states, and therefore, has been utilized as catalysts in several oxidation reactions.16 Notably, selenium element appears in the

Scheme 1 Synthesis of indoles via intramolecular C-H amination.

4th period after the filling of the 3d-orbitals, which makes it unique from the lighter sulfur and heavier tellurium congeners; for example, selenium in its highest oxidation state of +6 is a stronger oxidizing agent than the lighter sulfur and heavier tellurium elements. Organoselenium catalysts can even be designed in such a manner that they catalyze asymmetric transformations. 17 Several reviews have been presented on organoselenium chemistry; these either focus on their biological applications, structural features or their use as a catalyst in organic transformations. 1b,2c,8 This perspective mainly focuses on organoselenium compounds as catalysts for the oxidation of organic molecules. In addition, the roles of the selenium atom and bonded ligand in organoselenium catalysts are discussed with respect to their catalytic properties for the oxidation of organic substrates.

Selenium catalyzed indole formation

Zhao and co-workers have reported a new organoseleniumcatalyzed method for the formation of indoles via intramolecular C-H amination, where N-fluorobenzenesulfonimide (NFSI) was used as an oxidant in dioxane solvent at 30 °C (Scheme 1).18

A plausible mechanism is depicted in Scheme 2. The addition of the catalyst diphenyl diselenide to the double bond resulted in intermediate I. Then, the removal of the PhSe group from I in the presence of NFSI via intermediate II would provide III, followed by the aromatization of III via the elimination of H⁺ to afford the desired indole product.

Lewis base selenium catalyzed bromoaminocyclization

Yeung and co-workers have developed a chiral selenium catalyzed synthesis of an asymmetric pyrrolidine having two stereogenic centres, where N-bromophthalimide was used as the bromine source (Scheme 3).19 Specifically, the reactions showed excellent diastereoselectivity with dr > 99% and exclusive enantiospecificity of up to 95%.

Scheme 2 Mechanism for the synthesis of indoles.

$$R^{1} = H, Ph, alkyl$$

$$R^{2} = Ph, aryl$$

$$R^{1} = H, Ph, aryl$$

$$R^{2} = Ph, aryl$$

$$R^{2} = Ph, aryl$$

$$R^{2} = Ph, aryl$$

$$R^{2} = Ph, aryl$$

$$R^{3} = Ph, aryl$$

$$R^{4} = Ph, aryl$$

$$R^{2} = Ph, aryl$$

$$R^{4} = Ph, aryl$$

$$R^{5} = Ph, aryl$$

$$R^{5} = Ph, aryl$$

$$R^{5} = Ph, aryl$$

$$R^{6} = Ph, aryl$$

$$R^{6} = Ph, aryl$$

$$R^{7} = Ph, aryl$$

$$R^{7} = Ph, aryl$$

$$R^{7} = Ph, aryl$$

Scheme 3 Lewis base catalyzed synthesis of pyrrolidine

Scheme 4 Possible mechanism for the synthesis of bromoaminocyclization.

The haloaminocyclization of olefinic amides proceeds via the formation of activated selenium brominating species IV, which would interact with the olefin amide substrate resulting in the formation of selenium coordinated bromonium intermediate V (Scheme 4). Nucleophilic attack (S_N2) on the lone pair of the amide nitrogen and intramolecular cyclization would facilitate the formation of the desired bromo cyclic pyrrolidine product with good diastereoselectivity and enantiospecificity. The catalyst was regenerated in the reaction mixture.

4. Selenium catalyzed synthesis of six-membered lactones

In 2011, Wirth and co-workers accomplished a new method catalyzed by selenium for the cyclization of γ , δ -unsaturated pentenoic acids at room temperature in the presence of a hypervalent iodine reagent as the oxidant. By using this method, 6-membered lactones could be synthesized under metal-free conditions (Scheme 5).²⁰

The mechanism of the reaction proceeds via the formation of phenylselenenyl trifluoroacetate VI. The reaction of the γ,δ-unsaturated pentenoic acid with phenylselenenyl trifluoroacetate VI would provide selenolactone VII. The formation of

R¹ COOH Phl(OCOCF₃)₂ (1 equiv) R¹ R₂

R² COOH OCOCF₃)₂ (1 equiv) R₂

$$R_1 = R^2 = H$$
, aryl S1-85%

Scheme 5 Cyclization of γ , δ -unsaturated pentenoic acids.

selenolactone VII was confirmed by the isolation of VII as an intermediate from the reaction. Intermediate VII would be activated by PIFA. The resulting intermediate VIII would undergo elimination, leading to the formation of the desired 6-membered lactones (Scheme 6).

Furthermore, Breder and co-workers devised the aerobic dehydrogenative esterification of alkenoic acids, which facilitates the formation of five- and six-membered lactones with good yields. 21 The reaction proceeds via the interaction of a selenium- π -acid catalyst and photocatalyst. 2,4,6-Tris(4-methoxyphenyl)pyrylium

Scheme 6 Mechanism of the synthesis of cyclic lactones.

tetrafluoroborate was used as the photocatalyst under air atmosphere for the oxidative lactonization of alkenes.²¹

5. Selenium catalyzed oxytrifluoromethylthiolation of alkenes

In 2017, Zhao and co-workers reported diaryl selenide catalyzed vicinal CF₃S hydroxylation of alkenes by using N-CF₃S-saccharin as a trifluoromethylthiolating agent and nitromethane as the solvent under oxygen atmosphere at room temperature (Scheme 7A).²² Alkenes having carboxylic acid, hydroxy, sulfamide, or ester groups tethered to them could also successfully cyclize intramolecularly by using this protocol (Scheme 7B). The mechanism of this reaction suggests that the redox cycle between Se(II) and Se(IV) is pivotal for the complete conversion.

The mechanism of the reaction involves the generation of diaryl selenoxide IX by the oxidation of the selenium catalyst under O₂/CH₃NO₂ conditions, which is reduced to the selenium catalyst by the CF₃S-saccharin reagent (Scheme 8). The CF₃S reagent reacts with the catalyst to produce the intermediate X. An alkene reacts with X, which would generate episulfonium ion XI. Finally, the attack of H₂O on XI afforded the desired product and regenerated TfOH and the catalyst.

Organoselenium catalyzed electrophilic fluorination of olefins

In 2018, Zhao and co-workers disclosed an efficient organoselenium catalyzed method for oxidative allylic fluorination. N-Fluoro-2,4,6trimethylpyridinium triflate (TMFP-OTf) was used as the fluorine source, which also acted as an oxidant in the presence of TEMPO (Scheme 9).²³ The reaction proceeds through electrophilic selenium catalysis (ESC); TEMPO as an additive affects the fluorination and provides a better substrate scope with excellent functional group tolerance.

The mechanism started via the oxidative cleavage of the diselenide catalyst, generating benzyl selenium fluoride XII (Scheme 10). The reaction of the olefinic ester with benzyl selenium fluoride XII provided seleniranium ion XIII. The nucleophilic attack of the fluoride anion on the intermediate XIII

$$\begin{array}{c} \textbf{A} \\ \textbf{R}^1 \\ \textbf{R}^2 \\ \textbf{R}^4 \\ \textbf{R}^4 \\ \textbf{R}^4 \\ \textbf{R}^5 \\ \textbf{R}^4 \\ \textbf{R}^5 \\ \textbf{R}^4 \\ \textbf{R}^5 \\ \textbf{R}^5 \\ \textbf{R}^5 \\ \textbf{R}^6 \\ \textbf{R}^6$$

Scheme 7 (A) CF₃S hydroxylation of alkenes. (B) Oxytrifluoromethylthiolation of nucleophile tethered alkenes.

N-CF₃S-saccharin
TfOH

N-CF₃S-saccharin
TfOH

$$Ar$$
 Ar
 Ar
 Ar
 Ar
 R^3
 R^4
 R^4
 R^3
 R^4
 R^4

Scheme 8 Proposed mechanism for trifluoromethylthiolation

$$R^{1} = Me, Et, aryl$$

$$R^{3} = COOMe, COOBn, CN$$
Se catalyst (10 mol %)
$$TMFP-OTf (2 equiv)$$

$$TEMPO (0.5 equiv)$$

$$DCE, rt, 20 h$$

$$R^{2} = R^{3}$$

$$R^{2} = R^{3}$$

$$R^{3} = COOMe, COOBn, CN$$
Se catalyst (10 mol %)
$$R^{1} = R^{3}$$

$$R^{2} = Me, Et, aryl$$

$$R^{3} = COOMe, COOBn, CN$$

$$R^{3} = R^{3} = R^{3}$$

$$R^{4} = R^{3}$$

$$R^{5} = R^{3}$$

Scheme 9 Allylic fluorination via olefin isomerization.

Scheme 10 Mechanism for the allylic fluorination of alkene.

would give fluoroselenenylated intermediate XIV. At this stage, intermediate XIV would undergo oxidation by TMFP-OTf, which would subsequently lead, via H-elimination from XV, to the formation of the desired allylic fluorinated product.

7. Lewis base catalyzed chloroamidation of olefins

Yeung and co-workers achieved a Lewis base catalyzed chloroamidation of olefinic substrates using diphenyl selenide as the catalyst.²⁴ The reaction was carried out in the presence of olefins, 20 mol% selenium catalyst, NCS and an acetonitrile-water mixture at room temperature. A wide range of substrate scope was studied, including those that were acid labile, with 40-90% yield (Scheme 11).

A plausible mechanism for the reaction is described in Scheme 12. The first step is the activation of the chlorine atom

$$R^{1}$$
 R^{2}
 R^{2}
 R^{1}
 R^{2}
 R^{2}
 R^{2}
 R^{2}
 R^{3}
 R^{2}
 R^{2}
 R^{3}
 R^{2}
 R^{3}
 R^{2}
 R^{3}
 R^{2}
 R^{3}
 R^{2}
 R^{3}
 R^{4}
 R^{3}
 R^{4}
 R^{3}
 R^{4}
 R^{5}
 R^{5

Scheme 11 Chlorination of olefins.

by NCS via the Lewis basic diphenyl selenide to form intermediate XVI. The electrophilic Cl transfers to an olefin to form the haliranium ion intermediate XVIII. At this point, acetonitrile attacks the intermediate XVIII, which is subsequently quenched by a molecule of water to form the desired chloroamide product.

8. Selenium catalyzed bromoesterification, bromolactonization and oxidation of alcohols

Our group has developed a method for the bromolactonization of alkenoic acids with bromine or N-bromosuccinimide (NBS) and isoselenazolone as the catalyst in the presence of potassium carbonate. Next, the oxidation of secondary alcohols to ketones was studied using bromine as an oxidizing reagent (Scheme 13).²⁵

The proposed mechanism for bromolactonization is shown in Scheme 14. The reaction of bromine with isoselenazolone yielded isoselenazolone(IV) dibromide XX, which is in equilibrium with its ionic form XXII. Addition of an equimolar amount of pent-4-enoic acid to the isoselenazolone(v) dibromide XX produced the isoselenazolone catalyst and the bromolactone product. Traces of a side product, presumably phenylselenolactone, were observed in the reaction mixture. Transfer of Br⁺ to pent-4-enoic acid may occur by either of the two pathways: (i) reversible generation of free Br⁺ in the solution from selenium(IV) dibromide and then attack of Br⁺ on the carboncarbon double bond, or (ii) formation of the associated intermediate XXV followed by the intramolecular transfer of Br⁺ to pent-4-enoic acid.

We also compared the intermediates formed from NBS to those formed from bromine in the isoselenazolone-catalyzed bromination reaction. Addition of NBS to the isoselenazolone catalyst yielded selenium(iv) bromide succinimide XXI. The high reactivity of NBS in the isoselenazolone-catalyzed bromination reaction could be due to the electron-deficient selenium center in the selenium(IV) bromide succinimide XXI. The electrondeficient selenium atom would render a partial positive charge on the Br atom, which may facilitate faster transfer of bromine to the alkenoic acid.

The oxidation of secondary alcohols to ketones can be rationalized by considering the proposed intermediates XX/ XXII in the bromination of alkenoic acids (Scheme 15). The addition of the secondary alcohol to bromoselenonium intermediate XXII would give intermediate XXVI via the loss of HBr. Intermediate XXVI could lead to the ketone directly via the loss Perspective

Scheme 12 Proposed mechanism for the Lewis basic selenium catalyzed chloroamidation.

Scheme 13 Bromoesterification of alkenes and oxidation of alcohols catalyzed by isoselenazolone

Scheme 14 Reaction mechanism for the isoselenazolone catalyzed bromination.

of a second molecule of HBr, regenerating the isoselenazolone or via the loss of bromide to give the Swern-like oxoselenonium intermediate XXVII, which then can lose a proton to give the ketone and isoselenazolone.

Similarly, the oxidation of benzyl alcohol into the corresponding benzoic acid was achieved by Arends and co-workers in 2009 by using tert-butyl hydroperoxide (TBHP) as an oxidant in the presence of a diphenyl diselenide catalyst.²⁶

Further, we have reported the symmetrical bis(p-anisyl)selenide catalyzed bromo/iodo lactonization of linear alkenoic acids with N-bromo succinimide by using 4-dimethylaminopyridine (DMAP) as a co-catalyst and NaHCO₃ as an additive (Scheme 16). A series of medium-sized bromo/iodo lactones possessing high transannular strain were synthesized regioselectively. 77Se NMR spectroscopy, HRMS, and theoretical studies revealed that the reaction proceeds via a selenium-DMAP active catalyst. 27

The reaction between catalyst A, co-catalyst B and NBS provided intermediate XXVIII (Scheme 17). The alkene and terminal acid of alkenoic acid would bind with intermediate XXVIII and provide XXIX. The selenium-nitrogen coordination

Scheme 15 Mechanism for the oxidation of secondary alcohols to ketones with bromine.

Scheme 16 Regioselective synthesis of medium-sized halolactones and bromooxepanes.

elongates the Se-Br bond and thus facilitates the generation of Br⁺. The formation of the bromiranium ion and the interaction of the carboxylate ion with the ammonium ion in the same species would favour the cyclization that leads to medium-sized bromolactones and concomitant regeneration of selenium catalyst A and co-catalyst B.

Similarly, a Lewis base diphenyl selenide catalyzed method for the bromolactonization of cyclopropylmethyl diesters was demonstrated by Yeung and co-workers.²⁸ This protocol provided multifunctional syn γ -lactones.

NBS XXIX XXVIII NaHCO₃

Scheme 17 Proposed catalytic cycle for bromolactonization.

9. Lewis base selenium catalyzed carbosulfenylation of alkenylboronates

Denmark and co-workers developed a Lewis base catalyzed enantio- and diasteroselective approach for the carbosulfenylation of di- and trisubstituted alkenylboronic esters (Scheme 18).29 The reaction was initiated via a 1,2-migration of a zwitterionic thiiranium-boronate that would lead to the formation of anti carbosulfenylation products containing two vicinal stereogenic centers. The reaction shows good enantioselectivity (up to 99:1 e.r.).

10. Oxacyclization of alkenoic acids and alkenols

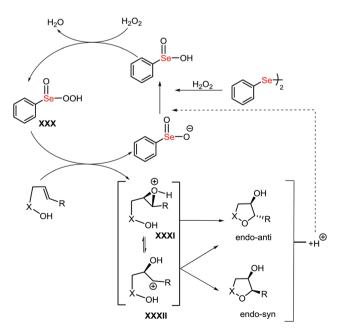
A simple organocatalytic method for the synthesis of lactones or cyclic ethers has been developed by Santi and co-workers (Scheme 19).³⁰ The reaction involves the cyclofunctionalization of γ , δ -unsaturated acids and alcohols by using H_2O_2 as an oxidant, providing the desired products in good yields with high stereoselectivities.

In the presence of the H₂O₂ oxidant, the diphenyl diselenide catalyst forms benzeneselenonic acid XXX (Scheme 20). The unsaturated acids or alcohols in the presence of XXX furnish epoxide intermediates XXXI. The epoxide intermediates afforded the stereospecific trans-disubstituted lactones via the formation of carbocations XXXII.

With the double bond having a substituent capable of stabilizing the nearby carbocation XXXII, the formation of the anti-isomer seemed like the major product rather than the syn isomer.

Scheme 18 Carbosulfenylation of alkenylboronates.

Scheme 19 Selenium catalyzed oxidative cyclization of alkenoic acids and alkenols



Scheme 20 Proposed mechanism for oxacyclization.

11. Lewis acid selenium catalyzed bromination of arenes

Yeung and co-workers developed a mild method for the electrophilic halogenation of arenes using selenonium salts as Lewis acids and *N*-bromo succinimide as the halogenating source (Scheme 21).³¹

Selenium catalyzed dichlorination of olefins

Denmark and co-workers have achieved a diphenyl diselenide catalyzed syn dichlorination of alkene substrates with good stereospecificity.³² The reaction was carried out in the presence of benzyltriethylammonium chloride (BnEt3NCl) as the chlorine source, N-fluoropyridinium salt 1 as the oxidant and 2,6-lutidine N-oxide 2 as an additive. A wide range of acyclic alkenes was studied with primary allylic alcohols (Scheme 22).

This approach was further utilized in the synthesis of chlorosulfolipid polychlorinated natural products.

The proposed mechanism was initiated via the generation of an active form of catalyst PhSeCl₃ (Scheme 23). Addition of an olefin to XXXIII provided the seleniranium ion intermediate XXXIV.

$$F_{3}C \longrightarrow CF_{3}$$

$$Me \quad (5 \text{ mol } \%)$$

$$R \longrightarrow H \qquad NBS \quad (1.2 \text{ equiv})$$

$$(CH_{2}CI)_{2}, 23 \text{ °C}, 24 \text{ h}$$

$$R = Me, OMe$$

$$Ar = \text{phenyl, naphthyl, anthranyl}$$

Scheme 21 Chalcogenium salt catalyzed electrophilic bromination of

Scheme 22 Selenium-catalysed syn-dichlorination of alkenes.

The nucleophilic ring opening of **XXXIV** occured by the chloride ion and the resulting intermediate **XXXV** underwent the anti-elimination of selenium with Cl^- *via* intermediate **XXXVI** to provide the *syn* dichlorinated product.

13. Selenium catalyzed carbon-nitrile bond formation

A novel organoselenium catalyzed method has been accomplished by Lautens and co-workers for the synthesis of organonitriles from

Scheme 24 Organoselenium catalyzed dehydration of aldoximes.

aldoximes in the presence of H_2O_2 as the oxidant under air atmosphere (Scheme 24).³³

The mechanism was initiated by the oxidation of the selenium catalyst with H_2O_2 to give ArSeOH **XXXVII** that was the active form of the catalyst (Scheme 25). Aryl selenenic acid **XXXVII**, after the removal of water, provided anhydride **XXXVIII**. The reaction of the aldoxime with **XXXVIII** formed the intermediate **XXXIX**. Relocation of **XXXIX** produced the selenoxide intermediate **XXXX**, which underwent elimination and lead to the formation of the desired nitrile products. Aryl selenenic acid was regenerated in the reaction.

Selenium catalyzed oxidation of benzylpyridine

Law and co-workers have demonstrated the chemoselective oxidation of the sp³ C-H bond of benzylpyridines by using O₂

Scheme 23 Proposed catalytic cycle for the dichlorination of alkenes.

Scheme 25 Possible catalytic cycle for the synthesis of organonitriles from aldoximes

Scheme 26 Oxidation of benzylpyridines with molecular oxygen to benzoylpyridines.

as the oxidant and phenyl selenyl bromide as the catalyst to afford benzoylpyridines (Scheme 26).34 A wide range of ketones was obtained with good yields in aqueous DMSO medium, where acetic acid acted as a promoter to initiate the reaction.

A mechanism was proposed for the oxidation of benzyl pyridine (Scheme 27). The reaction proceeds by the interaction of benzylpyridine with acetic acid to produce salt XXXXI. The phenyl selenyl bromide catalyst undergoes homolytic cleavage to form a phenyl selenyl radical, which interacts with XXXXI and generates intermediate XXXXII. Then, oxidation of XXXXII by molecular oxygen would afford peroxy radical intermediate XXXXIII, which upon protonation would generate hydroperoxidate intermediate XXXXIV. In the end, the removal of AcOH and water molecules provides the desired ketone product.

In 2017, Yu and co-workers developed an organoseleniumcatalyzed green method for the deoximation of aldoximes to furnish ketones and aldehydes by using H2O2/air as a green oxidant (Scheme 28).35

Similarly, very recently in 2019, Se/Fe co-catalyzed aerobic oxidative deoximation of an aldoxime to the corresponding ketone was achieved by Xu and co-workers using peroxide as the oxidant.36

Scheme 27 Proposed mechanism for the oxidation of benzoylpyridines

Scheme 28 Deoximation of aldoximes with H_2O_2 to aldehydes or ketones

Next, Yu and co-workers demonstrated an organoseleniumcatalyzed mild oxidative sp² C-C bond cleavage of alkenes.³⁷ The reaction was carried out in the presence of ethanol with hydrogen peroxide as the oxidant, which resulted in carbonyl compounds.

15. Catalytic oxidation of organothiols to organo disulfides

In 2018, we developed the aerial oxidation of organothiols to the respective disulfides in the presence of the bis(2,1-phenylene)bis(azanediyl)bis(methylene)diphenol diselenide catalyst, which mimics sulfhydryl oxidase and glutathione peroxidase (GPx) enzymes for the oxidation of thiols by oxygen and hydrogen peroxide, respectively, into disulfides (Scheme 29).38 The aerial oxidation of organothiols has been achieved in the presence of

RSH + Air
$$\frac{(1 \text{ mol } \%)}{\text{CH}_3\text{CN, rt}}$$
 RSSR
R = alkyl, aryl, heteroaryl

Scheme 29 Aerial oxidation of organothiols to organo disulfides.

Scheme 30 Mechanism for the selenium catalyzed oxidation of thiols by air and hydrogen peroxide

one mol% of a synthesized diselenide sulfhydryl oxidase mimic without using any external oxidant, metal, base, or photosensitizeddye at room temperature. The use of the organoselenium catalyst, which has a two electron redox property, is crucial for the transformation.

A tentative mechanism is illustrated in Scheme 30. The diselenide reacts with the thiol to produce selenol XXXXV and selenenyl sulfide XXXXVI. Selenenyl sulfide XXXXVI may further react with an additional molecule of thiol to produce selenol XXXXV, expectedly. The oxidation of XXXXV by O2 would afford selone XXXXVII and hydrogen peroxide by an electron transfer followed by a proton transfer from N-H and Se-H bonds unprecedentedly (cycle I). Selenenyl sulfide XXXXVI could also react with oxygen leading to selone, HO2. and PhS[•] radicals and the latter would dimerize to RSSR. The nucleophilic addition of sulfur from RSH to the selenium of selone XXXXVII followed by a proton transfer would provide selenenyl sulfide XXXXVI and thus complete the catalytic cycle. Selenol XXXXV and selenenyl sulfide XXXXVI also catalyze the oxidation of the thiol by the hydrogen peroxide oxidant by following the GPx-enzymatic triads XXXXV, XXXXVI and XXXXVIII (cycle II). The selenol reacts with peroxide to form selenenic acid XXXXVIII, which is reduced by another molecule of RSH to afford water and selenenyl sulfide.

16. Conclusion

In recent times, organoselenium catalysis has become a hot topic in synthetic chemistry and attracted much attention of chemists because of its virtues in organic synthesis. Organoselenium catalyzed reactions are cost-effective as compared to metal, and show good functional group tolerance under simple and mild reaction conditions. In this review, innumerable features of organoselenium compounds are summarised and major achievements from the last decade are emphasized.

Mainly, diorgano diselenides were used as catalysts in various kinds of oxidation reactions. Also, it seems that organoselenium catalyzed reactions largely involved strong oxidizing agents such as peroxides or halogenating reagents. Furthermore, the oxidation of olefins has been mainly accomplished by organoselenium catalysis. The oxidation of difficult organic substrates and the utilization of environment-friendly oxidants such as aerial oxygen and water in organoselenium catalysis are vet to be explored and could be a promising research area for organoselenium catalysis in the future.

Conflicts of interest

There are no conflicts to declare.

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