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The polyhedral nature of selenium-catalysed reactions: Se(IV) species instead of Se(VI) species make the difference in the on water selenium-mediated oxidation of arylamines†

Damiano Tanini, * Camilla Dalia and Antonella Capperucci

Selenium-catalysed oxidations are highly sought after in organic synthesis and biology. Herein, we report our studies on the on water selenium mediated oxidation of anilines. In the presence of diphenyl diselenide or benzeneseleninic acid, anilines react with hydrogen peroxide, providing direct and selective access to nitroarenes. On the other hand, the use of selenium dioxide or sodium selenite leads to azoxyarenes. Careful mechanistic analysis and ^{77}Se NMR studies revealed that only Se(IV) species, such as benzeneperoxyseleninic acid, are the active oxidants involved in the catalytic cycle operating in water and leading to nitroarenes. While other selenium-catalysed oxidations occurring in organic solvents have been recently demonstrated to proceed through Se(VI) key intermediates, the on water oxidation of anilines to nitroarenes does not. These findings shed new light on the multifaceted nature of organoselenium-catalysed transformations and open new directions to exploit selenium-based catalysis.

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Introduction

Selenium-catalysed reactions occupy a central position in organic synthesis, enabling a wide variety of valuable functional group conversions.[1] Selenium(IV) oxide, diselenides, and seleninic acids are commonly employed as catalysts in oxidation reactions often requiring hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) as oxidants.[2] A diverse range of selenium-promoted oxidative conversions, encompassing the oxidation of alkenes,[3] alcohols,[4] ketones,[5] aldehydes,[6] and alkynes,[7] as well as selenium-catalysed versions of the Baeyer–Villiger oxidation,[8] have emerged as powerful synthetic transformations. Organoselenium catalysis has been applied to α-oxyfunctionalization of alkenes[9] and ring contraction of cycloalkanones.[10] Furthermore, an array of useful selenium(IV) oxide-mediated procedures for the allylic oxidation of alkenes, cycloalkenes and alkynes, as well as the *trans*-dihydroxylation of olefins under the $SeO_2/H_2O_2/H_2O$–dioxane catalytic system, have been developed.[1b,11] For example, a SeO_2/TBHP-promoted allylic oxidation was successfully employed for the preparation of a key intermediate in the total synthesis of (−)-okilactomycin.[12] Additionally, owing to their biological relevance, selenium-catalysed thiol-disulfide interconversion reactions have been extensively investigated.[13] Because of their broad application in the synthesis of biologically valuable small molecules, oxidative reactions involving alkenes and amines are arguably among the most important functional group conversions. However, while selenium catalysed epoxidation and dihydroxylation of alkenes are well established, oxidation of amines is far less explored and only a few methodologies dealing with the synthesis of nitroso derivatives[14] or azoxyarenes[15] have been described.

Despite the large number of available procedures for the conversion of anilines into nitroarenes, most of the existing methodologies rely on the use of transition metal catalysts, require harsh reaction conditions and lead to uncontrolled oxidations and poor selectivity.[16] To the best of our knowledge, a selenium-catalysed approach for the oxidation of anilines to nitroarenes has never been described.

Herein, we report our development of an organoselenium-mediated on water oxidation of anilines to nitroarenes **1**, and detail how – contrary to what has been recently reported for the epoxidation of alkenes[17] – the reaction mechanism proceeds only through Se(IV) species. Furthermore, selenium-mediated procedures for the synthesis of benzamides **2** and azoxyarenes **3** are also described.

Results and discussion

Our initial studies focused on the reaction of aniline with hydrogen peroxide in the presence of different chalcogen-con-

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Department of Chemistry "Ugo Schiff", University of Florence, Via Della Lastruccia 3-13, Sesto Fiorentino, Firenze, Italy. E-mail: damiano.tanini@unifi.it

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Table 1 Optimisation of the reaction conditions

Entry	Catalyst (mol%)	Conversion	**1a** : **3a**
1	PhSeSePh (10 mol%)	43%	>98 : 2
2	PhSePh (10 mol%)	58%	24 : 76
3	^{n}BuSeSe^{n}Bu (10 mol%)	<10%	32 : 68
4	^{n}BuSe^{n}Bu (10 mol%)	17%	16 : 84
5	PhSeSePh (20 mol%)	94%[a]	>98 : 2
6	PhSe(O)OH (20 mol%)	89%[b]	>98 : 2
7	PhTeTePh (20 mol%)	71%	<2 : 98[c]
8	^{n}BuTe^{n}Bu (20 mol%)	56%	<2 : 98[c]
9	PhSSPh (20 mol%)	<10%	n.d.
10	SeO_2 (20 mol%)	96%[d]	<2 : 98
11	Na_2SeO_3 (20 mol%)	94%[d]	<2 : 98
12	K_2SeO_4 (20 mol%)	63%	<2 : 98[e]
13	Na_2SO_4 (20 mol%)	61%	<2 : 98[c]
14	None	56%	<2 : 98[e]

Conversion values and **1a** : **3a** ratios were determined by ^{1}H NMR spectroscopy of the crude material, using an internal standard. Reactions were carried out on a 1 mmol scale. [a] 92% isolated yield. [b] 86% isolated yield. [c] Traces (8–10%) of the corresponding diazo derivative (1,2-diphenyl-diazene, Ph–N=N–Ph) were detected. [d] 86% isolated yield. [e] *ca.* 40% of the corresponding diazo derivative (1,2-diphenyl-diazene, Ph–N=N–Ph) was formed.

taining catalysts, including disulfides, diselenides, ditellurides, selenides, tellurides, and inorganic selenium reagents (Table 1).

Gratifyingly, in a preliminary experiment performed using diphenyl diselenide as the catalyst, we found that the on water oxidation reaction of aniline proceeded to give nitrobenzene **1a**, although in a rather low yield (Table 1, entry 1).[18] Diphenyl selenide and alkyl-substituted organoselenium compounds, such as dibutyl diselenide and dibutyl selenide, led to the formation of the azoxyarene **3a** in a poor yield (Table 1, entries 3 and 4). On the basis of these results, we sought to increase the loading of the catalyst, and therefore, we performed the reaction in the presence of 20 mol% of diphenyl diselenide. Pleasingly, under these conditions aniline reacted smoothly with H_2O_2, providing nitrobenzene in good yield with excellent selectivity (Table 1, entry 5). Envisaging the oxidation of diphenyl diselenide as the preliminary reaction step of the catalytic cycle, benzeneseleninic acid was also examined as the catalyst (Table 1, entry 6); similar to what was observed using diphenyl diselenide, nitrobenzene **1a** was obtained in good yield with high selectivity. Notably, attempts to recover the catalyst by re-using the aqueous phase for additional oxidation cycles led to very poor yields (<10%, *vide infra*).

Intriguingly, when tellurium-containing molecules, such as diphenyl ditelluride and dibutyl telluride,[19] were employed as catalysts, aniline did not undergo oxidation to afford nitrobenzene **1a**; instead, condensation of oxidised intermediates[20] gave the azoxyarene **3a** as the main reaction product (Table 1, entries 7 and 8). On the other hand, as expected, diphenyl disulfide did not act as an effective catalyst in this transformation and only a poor conversion value was observed (Table 1, entry 9).

A series of inorganic selenium species, including selenium dioxide, sodium selenite, and potassium selenate, were also examined under the standard conditions. Notably, both selenium dioxide and sodium selenite led to the selective formation of azoxyarene **3a**, which could be isolated in excellent yield (Table 1, entries 10 and 11). On the other hand, poorer conversion and selectivity were observed when potassium selenate was used (Table 1, entry 12). Indeed, azoxyarene **3a** was formed alongside with a significant amount (*ca.* 40%) of 1,2-diphenyl-diazene and traces of nitrobenzene **1a**. Sodium sulfate led to similar results in terms of conversion and **3a** : **1a** selectivity (Table 1, entry 13). Finally, in a control experiment carried out in the absence of any catalyst, almost 50% of aniline remained unreacted and azoxyarene **3a** and 1,2-diphenyl-diazene proved to be the main reaction products (Table 1, entry 14). These results highlight the poor catalytic activity of the selenate anion, which is suggested to be scarcely involved in the catalytic cycle leading to the formation of azoxyarenes.

Having established the optimal reaction conditions required to promote the oxidation of anilines to nitroarenes, we next turned our attention to evaluate the scope of this methodology. A series of variously substituted anilines were therefore treated with hydrogen peroxide in the presence of diphenyl diselenide under the standard conditions. The reaction was amenable to electron-rich and electron-poor anilines, enabling the synthesis of a diverse range of substituted nitroarenes. Oxidation of substrates bearing electron-donating groups at different positions of the aromatic ring, such as *o*- and *p*-toluidine as well as *p*-aminophenol groups, provided *o*-nitrotoluene **1b**, *p*-nitrotoluene **1c**, and *p*-nitrophenol **1d** in good yields. Similarly, a variety of nitroarenes bearing electron-withdrawing groups were smoothly obtained from the corresponding anilines. Halo-substituted anilines performed well, enabling the formation of 2-chloronitrobenzene **1e**, 4-chloronitrobenzene **1f**, and 4-fluoronitrobenzene **1g** in rather good yields. 4-Nitroaniline and *m*-trifluoromethyl aniline were also subjected to the organoseleno-mediated oxidation methodology reported here, affording 1,4-dinitrobenzene **1h** and *m*-trifluoromethyl nitrobenzene **1i**.

The methodology was also applied to pharmacologically relevant molecules, such as benzocaine and sulfanilamide. Both ester and free sulfonamide functionalities were well tolerated under the reaction conditions; selective oxidation of the amino group led efficiently to the formation of ethyl 4-nitrobenzoate **1j** and 4-nitrobenzenesulfonamide **1k**.

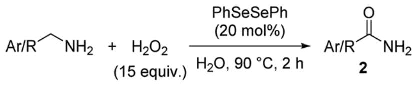
p-Aminobenzyl alcohol and *p*-aminobenzyl bromide were also successfully employed, providing access to *p*-nitrobenzyl alcohol **1l** and *p*-nitrobenzyl bromide **1m** in good yields. Notably, we observed no competing benzylic oxidation and compounds **1l** and **1m** were the sole products formed under the optimised reaction conditions. Oxidation of 4-ethynylaniline and 2-naphthylamine was also possible, leading to 4-ethynyl-nitrobenzene **1n** and 2-nitronaphthalene **1o**, respectively. Oxidation of polysubstituted anilines was also investigated. A variety of substrates bearing electron-donating or electron-withdrawing groups at different positions of the aromatic ring were employed and converted into the corresponding polysubstituted nitroarenes **1p–1t**. Remarkably, although both 2-methyl-5-nitroaniline and 4-methyl-3-nitroaniline provided the dinitroarene **1t**, higher yield was observed when the latter less hindered substrate was employed.

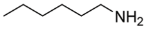
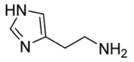
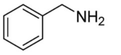
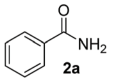
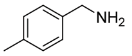
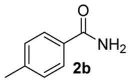
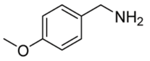
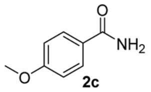
To highlight the potential utility of this methodology, we sought to apply it to the synthesis of selected nitroarenes on a gram scale. Compounds **1b**, **1c**, and **1j** were prepared in good yields through the oxidation of the corresponding anilines on a 10 mmol scale (Scheme 1).

In order to further investigate the scope and limitations of this selenium-mediated oxidation methodology, we evaluated whether it could be applied to aliphatic amines. Hexylamine and histamine proved to be unreactive and no appreciable amounts of oxidised products were observed (Table 2, entries 1 and 2). On the other hand, upon reaction with H_2O_2 in the presence of diphenyl diselenide or benzeneseleninic acid at 90 °C, benzylamines underwent oxidation at the benzylic carbon, providing the corresponding benzamides **2a–c**, although in rather low yields (Table 2, entries 3–5).

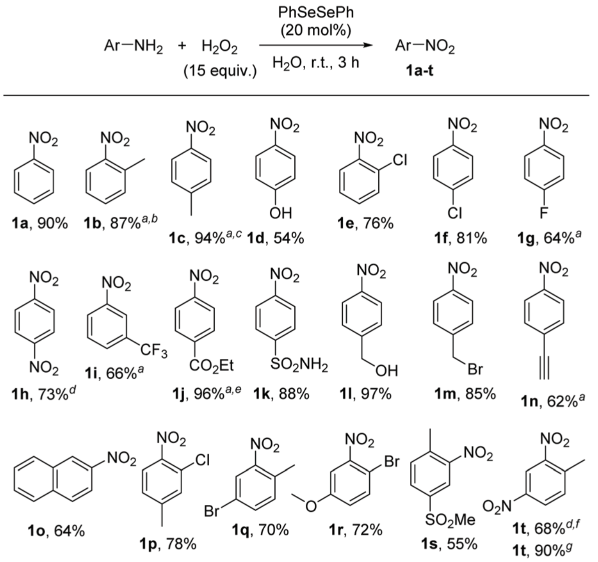
On the basis of the results obtained during the investigation of different selenium-based catalysts (Table 1, entries 10 and 11), we also envisaged the possibility of developing an alternative on water procedure for the synthesis of azoxyarenes **3**. Indeed, although the reaction of anilines with SeO_2/H_2O_2 in different solvents has been previously reported,[15] to the best of our knowledge, the on water SeO_2-catalysed oxidation of anilines remained unexplored. To investigate the reaction, a variety of anilines were therefore treated with H_2O_2 in the presence of a catalytic amount of SeO_2. The reaction scope was found to be broad, encompassing both electron-poor and electron-rich substrates. A series of azoxyarenes bearing methyl **3b** and **3c**, chloride **3d** and **3e**, bromide **3f**, and fluoride **3g** groups at the *ortho-* and *para*-positions of the aromatic ring were efficiently obtained. 3-(Trifluoromethyl)aniline was also converted into the corresponding azoxy derivative **3h**. Furthermore, benzocaine, anthranilic acid, and 4-ethynylaniline worked well in this on water reaction, enabling the synthesis of azoxyarenes **3i–3k** bearing ester, carboxylic acid, and alkyne functionalities, respectively (Scheme 2).

Table 2 On water selenium-mediated oxidation of aliphatic amines



Entry	Amine	Product	Yield (%)
1		n.r.	—
2		n.r.	—
3		 **2a**	46[a]
4		 **2b**	32
5		 **2c**	37[a]

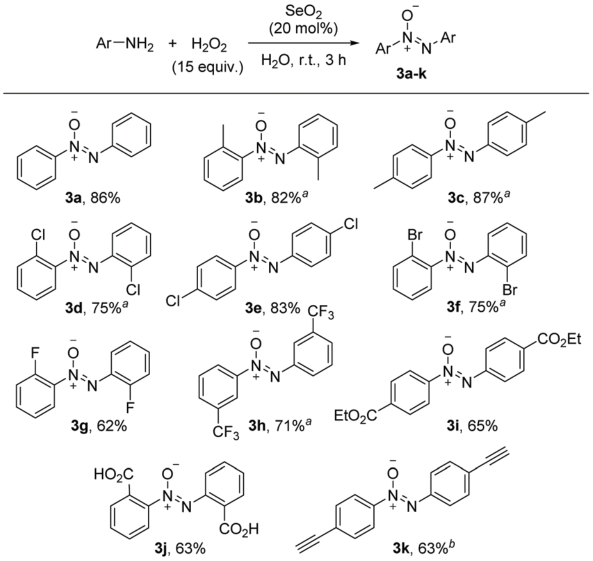
[a] Comparable yields were achieved when benzeneseleninic acid was used instead of diphenyl diselenide.



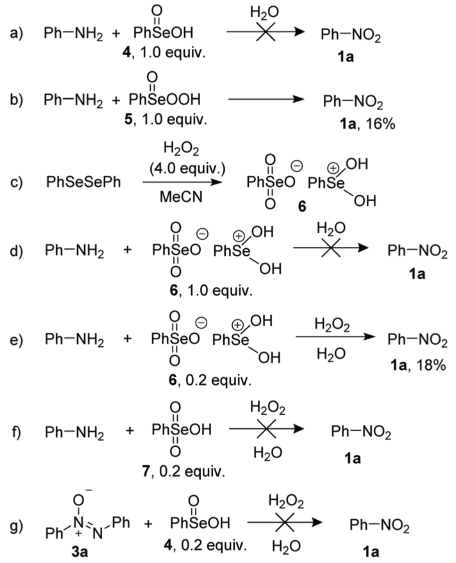
Scheme 1 The scope of the on water selenium-mediated oxidation of anilines with hydrogen peroxide to give nitroarenes. Isolated yields are reported. [a]Comparable yields were achieved when benzeneseleninic acid was used instead of diphenyl diselenide. [b]**1b** was obtained in 81% yield on a gram scale by the oxidation of *o*-toluidine (10 mmol; reaction time: 5 h). [c]**1c** was obtained in 88% yield on a gram scale by the oxidation of *p*-toluidine (10 mmol; reaction time: 5 h). [d]The reaction was performed at 60 °C. [e]**1j** was obtained in 89% yield on a gram scale by the oxidation of ethyl 4-aminobenzoate (10 mmol; reaction time: 5 h). [f]Obtained from 2-methyl-5-nitroaniline. [g]Obtained from 4-methyl-3-nitroaniline.

While selenium oxide- or selenite-promoted oxidations are widely accepted to proceed through peroxyselenous acid,[21,22] the mechanism of reactions catalysed by diselenides or seleninic acids is still debated. Although peroxyseleninic acid has been regarded for a long time as the only plausible key intermediate, new evidence demonstrating the involvement of Se(VI) species has recently emerged.[17]

In order to elucidate the reaction mechanism, a series of control experiments were carried out (Scheme 3). Firstly, we investigated the reaction of aniline with a stoichiometric amount of benzeneseleninic acid **4** in the absence of hydrogen peroxide (Scheme 3, reaction (a)). No reaction occurred under these conditions, thus demonstrating that benzeneseleninic acid does not act as an oxidant in this process. On the other hand, when reacted with a stoichiometric amount of peroxyseleninic acid **5**,[23] aniline underwent oxidation rapidly to afford nitrobenzene **1a**, although in a low yield (Scheme 3, reaction (b)). Next, we turned our attention to evaluating whether Se(VI)

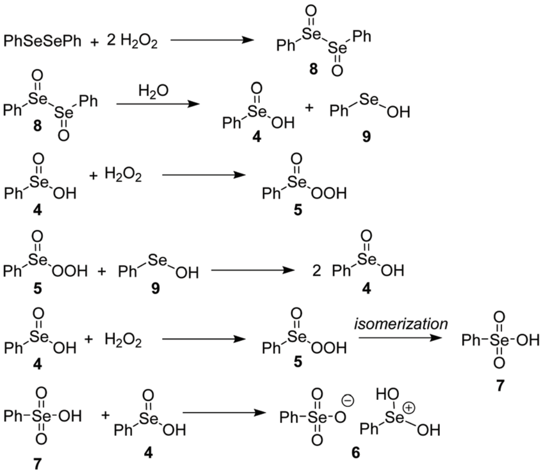


Scheme 2 The scope of the on water selenium-mediated oxidation of anilines with hydrogen peroxide to give azoxyarenes. Isolated yields are reported. [a]Comparable yields were achieved when sodium selenite was used instead of selenium dioxide. [b]Reaction time: 1.5 h.



Scheme 3 Control experiments.

species could be involved in the catalytic cycle leading to nitroarenes. Indeed, in a very recent inspiring paper, Back and coworkers reported that Se(VI) species play a central role in the mechanism of the selenium-mediated epoxidation of alkenes with hydrogen peroxide.[17] Particularly, the selenonium selenonate **6** was demonstrated to be the key catalytic intermediate. The reaction of such a salt with hydrogen peroxide affords benzeneselenonic acid **7**, which is further oxidised to the corresponding peroxyselenonic acid. The latter is believed to be an active oxidant involved in the epoxidation of alkenes.[17]



Scheme 4 Steps involved in the conversion of diphenyl diselenide into selenonium salt **6**.

Diphenyl diselenide was therefore treated with an excess (4.0 equiv.) of hydrogen peroxide providing the corresponding selenonium selenonate **6** (Scheme 3, reaction (c)). The stoichiometry of the oxidation reaction can be easily rationalised considering the reactions presented in Scheme 4.[24] The formation of the doubly oxidised species **8** requires 2.0 equivalents of H_2O_2. Hydrolysis of **8** affords benzeneselenenic acid **9** and benzeneseleninic acid **4**; the latter reacts with H_2O_2 to provide the peroxyseleninic acid **5**, which – as reported by Back *et al.* – oxidises **9** to generate two equivalents of benzeneseleninic acid **4**. Finally, **4** undergoes oxidation and isomerization to yield benzeneselenonic acid **7**, which leads to the formation of the selenonium selenonate salt **6** by protonating seleninic acid **4**. The exclusive formation of the salt was confirmed by obtaining the ^{77}Se NMR spectrum of the product, which – in line with the literature-reported data[17] – revealed two signals (a sharp peak at 1026 ppm and a broad peak at 1218 ppm, spectrum **I** in Fig. 1).

Having compound **6** in hand, we next investigated whether it could be involved in the mechanism leading to the formation of nitroarenes. No reaction was observed when aniline was treated with a stoichiometric amount of selenonium selenonate **6** in the absence of hydrogen peroxide (Scheme 3, reaction (d)). However, nitrobenzene **1a** was formed, although in a poor yield, upon reaction of aniline with hydrogen peroxide in the presence of **6** in water (Scheme 3, reaction (e)). Remarkably, when dichloromethane was used as the solvent instead of H_2O, no traces of nitrobenzene **1a** were detected and a complex mixture of products was formed. We reasoned that the reconversion of the selenonium salt **6** into the corresponding seleninic acid **4** would reasonably explain the observed catalytic properties of **6** in water. To demonstrate this hypothesis, **6** was solubilised in H_2O and the ^{77}Se NMR spectrum was recorded (Fig. 1, spectrum II). Conversion of the selenonium cation into benzeneseleninic acid quickly occurred. Indeed, the disappearance of the signal at 1218 ppm

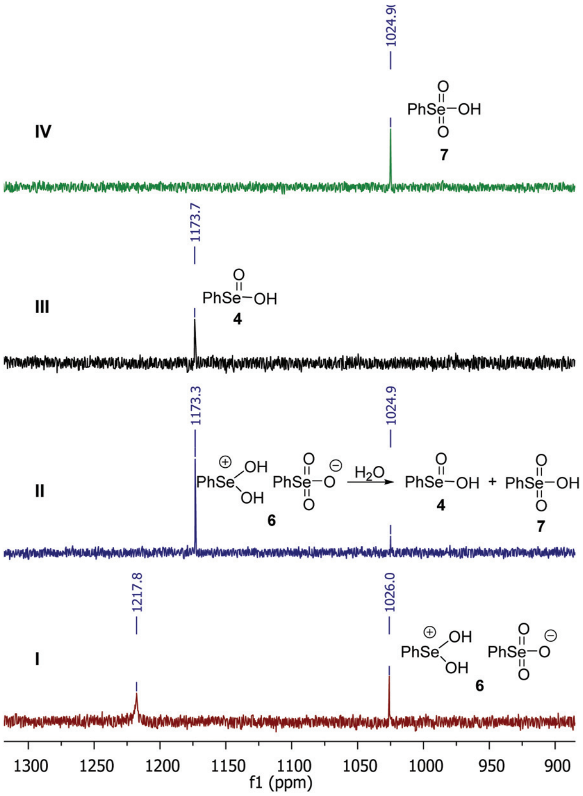
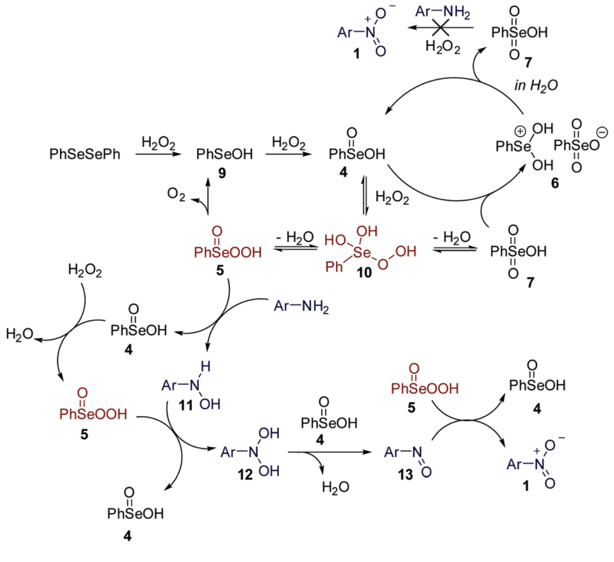


Fig. 1 ^{77}Se NMR spectra of species involved in the oxidation of anilines. I (red spectrum): ^{77}Se NMR spectrum of selenonium selenonate **6** ($CDCl_3$, δ = 1026.0, 1217.8 ppm). II (blue spectrum): generation of seleninic acid **4** and benzeneselenonic acid **7** upon solubilisation of **6** in H_2O/D_2O (NMR coaxial tube, δ = 1173.3 and 1024.9 ppm). III (black spectrum): ^{77}Se NMR spectrum of an authentic sample of **4** (D_2O, δ = 1173.7 ppm). IV (green spectrum): ^{77}Se NMR spectrum of the aqueous phase recovered after the oxidation of aniline under standard conditions (D_2O, δ = 1024.9; the chemical shift matched that obtained for an authentic sample of benzeneselenonic acid **7**).

accompanied by the appearance of a shielded sharp peak at 1173 ppm clearly revealed the formation of **4**, along with **7** (Fig. 1, spectra II and III).

These results suggest that the epoxidation of alkenes and the oxidation of anilines involve two different selenium-containing active oxidants. Thus, although the epoxidation of alkenes[17] involves Se(VI) key catalytic intermediates as active oxidants, the conversion of anilines into the corresponding nitroarenes reasonably proceeds only through Se(IV) species. To further rule out a catalytic pathway involving Se(VI) species, we subjected aniline to a reaction with H_2O_2/H_2O in the presence of the selenonic acid **7**, and observed no evidence of nitrobenzene **1a** (Scheme 3, reaction (f)). Finally, no reaction occurred when azoxyarene **3a** was treated with hydrogen peroxide in the presence of catalytic amounts of benzeneseleninic acid (Scheme 3, reaction (g)). In order to ascertain the fate of the used selenium-containing species, the aqueous phase recovered after the oxidation of aniline (extraction of the product with ethyl acetate)[25] was investigated by ^{77}Se NMR spectroscopy. The NMR spectrum displayed a sharp peak at 1025 ppm, clearly revealing the presence of selenonic acid **7** (Fig. 1, spectrum IV) and demonstrating that under the above described reaction conditions, the selenium-containing catalyst was overoxidised to afford Se(VI) derivatives. These data provide an explanation for the poor yield observed upon direct recycling of the aqueous phase (*vide supra*). However, **7** can be recovered and reduced back to benzeneseleninic acid or diphenyl diselenide upon treatment with hydrochloric acid or zinc and hydrochloric acid, respectively. To illustrate the recycling performance of the system, the aqueous phase recovered after the oxidation of *p*-toluidine was concentrated and treated with HCl in order to convert benzeneselenonic acid **7** into benzeneseleninic acid **4**.[26] The formation of benzeneseleninic acid, which was easily precipitated from water, was confirmed by ^{77}Se NMR spectroscopy.[27] The so regenerated catalyst was employed in the oxidation of *p*-toluidine, enabling the synthesis of *p*-nitrotoluene in comparable yield with respect to the first cycle (91% yield on a 2 mmol scale reaction).

On the basis of control experiments and literature-reported data,[28] a plausible reaction mechanism is proposed in Scheme 5. As stated above, both diphenyl diselenide and benzeneseleninic acid can be employed in the oxidation of anilines to nitroarenes with hydrogen peroxide. Diphenyl diselenide acts as a precatalyst and the first step of the reaction mechanism proceeds through its sequential oxidation to benzeneselenenic acid **9** and, finally, to benzeneseleninic acid **4**, which is the active catalytic species involved in the oxidation of aniline. The reaction of **4** with hydrogen peroxide in water reasonably provides the peroxyselenurane **10**, whose dehydration could lead to peroxyseleninic acid **5** or selenonic acid **7**. On the other hand, the reaction of selenonic acid **7** with seleninic acid **4** might provide the selenonium salt **6**, which, in water, is readily reconverted into parent acids **4** and **7**.



Scheme 5 Proposed reaction mechanism for the formation of nitroarenes **1**.

Therefore, although **6** has been demonstrated to play a key role in reactions performed in organic solvents, it is only marginally involved when H_2O is used. In the proposed mechanism, both **10** and **5** are believed to be the active oxidant species. The reaction of aniline with **5** or **10** affords the hydroxylamine **11**, which is further oxidised to dihydroxylamine **12** upon reaction with a second equivalent of oxidant **5** or **10**. In both these steps, benzeneseleninic acid **4** is regenerated. The dihydroxylamine **12** reasonably undergoes water elimination to afford nitrosoarene **13** through a benzeneseleninic acid-mediated proton transfer process. In the final step of the cycle, nitrosoarene **13** reacts with **5** to provide nitroarene **1** and benzeneseleninic acid **4**.

Conclusions

In conclusion, we have reported an unprecedented selenium-catalysed methodology for the oxidation of anilines under mild on water conditions. Mechanistically, the formation of nitroarenes involves only Se(IV) active oxidant species. Evidence suggestive of the exclusion of Se(VI) derivatives from the catalytic cycle was provided by ^{77}Se NMR studies and mechanistic analyses.

Conflicts of interest

There are no conflicts to declare.

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