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Oxidative dearomatization of phenols and polycyclic aromatics with hydrogen peroxide triggered by heterogeneous sulfonic acids

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Abstract: We report herein a method for the oxidative dearomatization of phenols and bare polycyclic arenes into the corresponding quinoid derivatives using hydrogen peroxide. The reaction is catalyzed by sulfonic acids and best results were achieved using heterogenized species. The best results using phenols were achieved through the use of a hybrid material, namely a perfluorinated polymer functionalized with sulfonic acid groups supported on silica. The dearomatization of polycyclic aromatic hydrocarbons performed better using the polymeric acid catalyst. These methods operate under mild conditions, using mild and benign oxidants and thus minimizing the formation of wastes.

Introduction

The quinone motif is found in a myriad of functional molecules, both of synthetic, technological and societal interest.[1-6] For this reason, several methods for the preparation of these derivatives have been developed. Among these, the oxidative dearomatization of bare aromatics represents the most appalling route,[1, 7-8] and that of phenols and naphthols an easier yet sensible target.[9-10] These approaches are nonetheless sometimes hindered by the intrinsic chemical challenge connected with the removal of the aromaticity of these rings. This, in turn, often demands for forcing experimental conditions and/or complex catalytic systems.

In particular, nature offers as usual bright examples of active and selective routes to dearomatized scaffolds.[11-14] These transformations require however elaborate enzymes to be performed. Artificial catalyst could be apparently simpler, although often involve costly transition metals or tailor-made organocatalysts.[15-21] Oxidations of activated aromatics, such has heterocycles,[22] phenols and naphthols is by far more studied than that of unfunctionalized arenes, for which a few reports are available. Most of the reported methods use relatively strong and expensive oxidants, including hypervalent iodine reagents,[23] NBS[24] and organic peroxides.[25] On the contrary, reports with hydrogen peroxide,[26] which is a cheaper and more benign chemical, are at present limited to the use of transition-metal based catalysts.[27,28] Notable exceptions are represented by the use of diphenyldiselenide as precursor of the mediator for the homogeneous oxidation of 1-naphthols[28] and a recent report that uses 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).[29] Moreover, to the best of our knowledge a practical method for the dearomatization of simple arenes with this oxidant has not been reported yet.
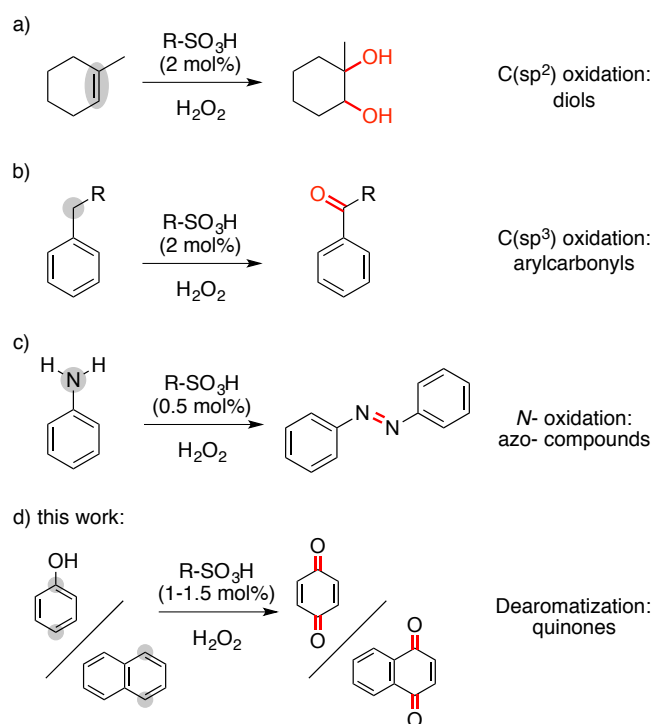
Scheme 1. Metal-free oxidations catalyzed by heterogeneous sulfonic acids.

Our group reported in the last few years several applications of sulfonic acid derivatives in oxidation reactions. Although these materials are best known for their strong Brosted-acid properties, we showed that sulfonic acid groups tethered on silica can efficiently catalyse the oxidation of trisubstituted alkenes into the corresponding diols under mild conditions (Scheme 1, a).[30] More recently, we turned our attention on perfluorinated sulfonic acids, which rather unexpectedly proved

to be valuable metal-free oxidation catalysts. They can be used for instance to convert a variety of (aryl)methylene groups into the corresponding carbonyl derivatives (Scheme 1, b).[31] This direct, double C-H functionalization is usually limited to a few transition-metal based complexes. An analogous approach enabled the development of a method for the synthesis of arylazo derivatives from the corresponding anilines (Scheme 1, c).[32] Overall, these approaches showed the potential for the development of simple synthetic methods that are capable to trigger elaborate oxidations under mild conditions. Moreover, these reactions always employ hydrogen peroxide as oxidant. This is a cheap, sustainable and benign chemical for oxidation reactions and this, together with the typical features of heterogeneous catalysts, ensure that these methods allow the minimization of chemical wastes.

We report herein that suitable polymeric sulfonic acids can efficiently catalyse the oxidative dearomatization of phenols and fused polycyclic hydrocarbons into the corresponding quinones. These reactions use hydrogen peroxide as oxidant, thus forming water as coproduct of the oxidation. The method allows to operate under mild thermal conditions and can be extended to a rather ample variety of basic building blocks.

In analogy with previous oxidation methods developed by our group,[31-32] the best results in present dearomatizations were observed using heterogeneous polymeric sulfonic acids derived from Aquivion. The latter is a commercial polymer characterized by a perfluorinated backbone featuring side-chains that are decorated by sulfonic functions. These branches are more flexible compared to that of Nafion, making it a promising candidate for heterogeneous catalysis. Although the polymer could be directly employed, either in its solid form or in an aqueous dispersion, it is also convenient to anchor it on an inorganic solid support, such as silica, to more easily recover it at the end of the reaction and contribute therefore to the minimization of wastes. The resulting hybrid materials are indeed easily recyclables. Moreover, tuneable morphologies, ranging from nanoparticles to mesoporous architectures, could be easily obtained depending on the sol-gel method used for the preparation of these materials, thus offering several options for catalyst design.

Results and Discussion

In preliminary experiments, phenol (1a, 2 mmol) was mixed with a 33% aqueous solution of hydrogen peroxide (12 mmol) and acetic acid (5 mL) in the presence of an acid (1.5 mol%). The resulting mixtures were kept under stirring and heated at 80 °C for 24 hours. Table 1 shows the trend of results achieved varying the acid catalyst.

Table 1. Identification of the acid catalyst.[a]

Entry	Catalyst	Conv. of 1a (%)[b]	Yield of 2a (%)[b]	Sel. of 2a (%)[c]
1	H_2SO_4	69	28	40
2	CF_3SO_3H	70	61	87
3	Aquivion PW66S	55	29	53
4	Nafion NR50	24	23	99
5	Amberlyst IR-120	36	9	25
6	Acid alumina	37	32	86
7	Titania	23	12	52
8	Aquivion@nanoSiO$_2$	11	10	99
9	Nafion@nanoSiO$_2$	25	22	88
10	Aquivion@SiO$_2$	71	68	96
11	-	2	-	-

[a] Reaction conditions: 1a (2 mmol), 33% aqueous H_2O_2 (12 mmol), acid catalyst, acetic acid (5 mL), 60 °C for 24 hours; [b] by GC, upon calibration with an authentic sample and using dodecane as internal standard; [c] measured as yield/conversion ratio.

The use of sulfuric acid showed the feasibility of the approach (entry 1). The reaction showed a significant conversion of **1a** (69%) and the formation of the desired quinone **2a** in 28% yield, together with several unidentified byproducts that formed each in trace amounts. The use of trifluoromethanesulfonic acid (entry 2) gave a more selective reaction. The conversion of **1a** proved similar to the previous case (70%) and the yield of **2a** rose to 61%. This result suggested that fluorinated sulfonic acids might have been more selective catalyst for present transformation. This, in turn, let us to test related polymeric species. The use of Aquivion (entry 3) provided **2a** in a moderate yield (29%). A similar outcome was observed employing Nafion (entry 4, 23%), although the latter enabled to form almost exclusively **2a**. Both the conversion of **1a** and the yield of **2a** sunk when Amberlist was used (entry 5, 36% and 9%, respectively). Similarly, the use of acid inorganic materials, such as alumina and titania, provided the desired quinone in low to moderate yields (entries 6-7, 12-32%). We then tried to tune the reactivity of perfluorinated polymers with sulfonic acid functions by supporting them onto silica. In particular, two materials in which Aquivion and Nafion decorate silica nanoparticles[31-32] were tested (entries 8-9). Although the overall yield of **2a** was disappointing in both cases (10% and 22%, respectively), the desired quinone formed selectively. This suggested us that a suitably supported catalyst could have been the tool to trigger an efficient reaction. Gratifyingly, a good compromise was found using Aquivion supported on amorphous silica (entry 10). The conversion of the substrate was 71% and **2a** formed in 68% yield in this case. A control experiment without catalyst showed almost no conversion of phenol and, moreover, did not allow to detect any trace of quinone. The model reaction performed under a nitrogen atmosphere gave the same result, strongly suggesting that oxygen is not a competent oxidant for present transformation.

With the most promising catalyst in hand, we next switched to vary other reaction parameters for the oxidative dearomatization of **1a** (Table 2).

The screening of an organic solvent of the reaction revealed that a polar, water-soluble species is required to form the quinone in good yields. Indeed, the conversion of the substrate is hampered in hexane (entry 1) and it increases linearly with the polarity of the solvent (entries 2-3). These results suggest that a better mixing of the organic substrate with the oxidant is crucial for the reaction. We next tested the effect of the temperature (entries 4-5). The reaction performed at 80 °C showed a very high conversion of phenol (95%), which was however coupled with a deep erosion of the selectivity (**2a**, 14%). On the contrary, reducing the temperature to 40 °C did not reduce significantly the yield of **2a** (65%). Similarly, the use of a lower excess of oxidant (entry 6, 8 mmol) seemed feasible (**2a**, 58%).
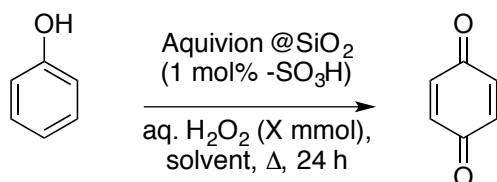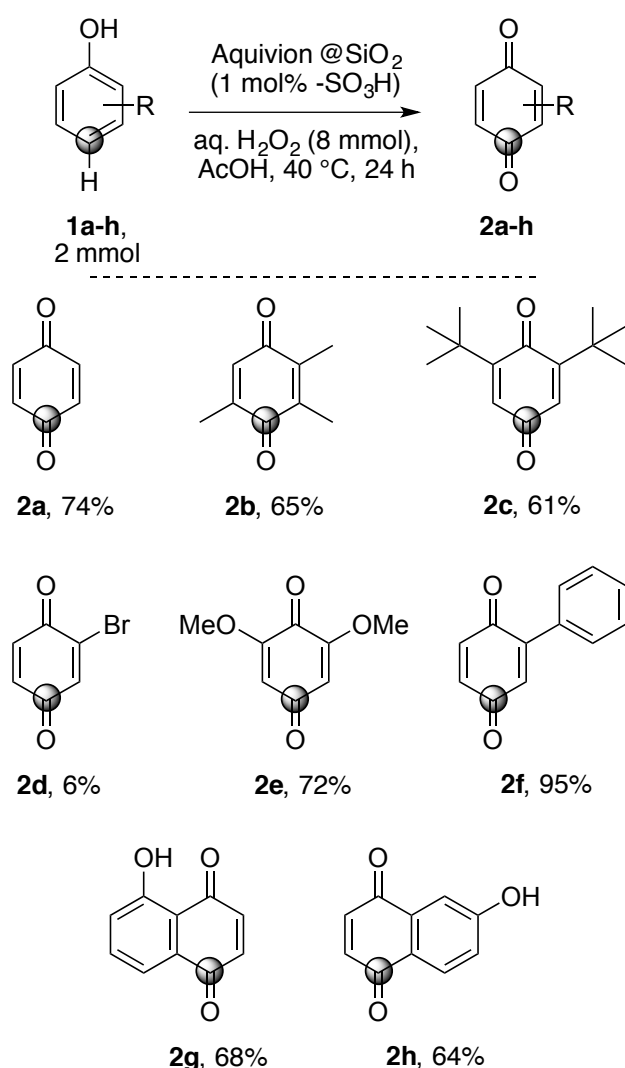
Table 2. Optimization of reaction conditions.[a]

Entry	Catalyst (mol% H^+)	Solvent	T (°C)	Conv. of **1a** (%)[b]	Yield of **2a** (%)[b]	Sel. of **2a** (%)[c]
1	1.5	hexane	60	-	-	-
2	1.5	MeCN	60	41	29	71
3	1.5	DMSO	60	62	46	74
4	1.5	AcOH	80	95	14	15
5	1.5	AcOH	40	75	65	87
6[d]	1.5	AcOH	40	81	58	72
7[d]	3	AcOH	40	86	12	14
8[d]	1	AcOH	40	80	74	92
9[e]	1	AcOH	60	58	54	92
10[f]	1	AcOH	60	98	-	-

[a] Reaction conditions: **1a** (2 mmol), 33% aqueous H_2O_2 (12 mmol), acid catalyst, 5 mL of solvent, for 24 hours; [b] by GC, upon calibration with an authentic sample and using dodecane as internal standard; [c] measured as yield/conversion ratio; [d] with 8 mmol of H_2O_2; [e] with 4 mmol of H_2O_2; [f] with 20 mmol of H_2O_2.

We then tested the optimal amount of catalyst (entries 7-8). While an increased loading of sulfonic acid sites proved detrimental (**2a**, 12%), the use of 1 mol% of catalyst gave the best result (entry 8, 74%). Further modification of the amount of oxidant (entries 9-10) did not improve the yield of **2a**.

With best conditions in hands, we next tested the scope of the reaction (Scheme 2).

Phenol could be decorated with alkyl groups, including bulky ones, without a significant erosion of the yield. Indeed, both 2,3,5-trimethylphenol and 2,6-ditertbutylphenol provided the corresponding quinones **2b** and **2c** with a yield similar to that of **2a** (65%, 61% and 74%, respectively). These results suggest that steric hindrance at the *ortho-* position of both the hydroxyl group and its *para-* C-H one could be tolerated by the reaction. On the contrary, electron-withdrawing groups on the aryl ring are not tolerated, as witnessed by the meagre 6% of **2d** that features a bromide substituent. The method tolerates the presence of alkoxy groups, such as in phenol **1e** that provided the corresponding quinone **2e** in 72% yield. Gratifyingly, 2-phenylphenol provided quinone **2f** in almost quantitative yield (95%). The reaction could be extended to polycyclic phenols. In particular, 1,8-dinaphthol provided quinone **2g** in 68% yield. Its 1,7- peer gave **2h** in a comparable yield (64%).

Scheme 2. Scope of the dearomatization of phenols and naphthols, isolated yields.

The low yield observed with halophenols let us attempt to perform an additional reoptimization on these substrates. Further modification of reaction conditions (active species, amount of oxidant, temperature) did not allowed however to achieve a meaningful increase in the isolated yield of **2**, which topped at 10% for **2d** (see SI for details). Similarly, phenols with strongly electron withdrawing groups, such as 2- or 3-nitrophenol, were unsuitable to undergo present oxidation. These observations indicate that electron-rich arenes are required by the dearomatization method. Preliminary tests using

thiophenol showed its complete consumption when reacted under conditions optimized for **1a**. However, no dearomatization took place and benzesulfonic acid was the main product isolated (17%), suggesting that significant decomposition of the electron-rich starting material occurred. The use of benzeneselenol or diphenyldiselenide, which might have led to relevant Se- decorated quinones,[33] followed suit.

In all cases, quinones **2** are formed almost exclusively and mass balance is accounted for by unreacted starting material. The residual peroxide content upon warming for 24 hours is always negligible. This suggests that partial thermal decomposition of the oxidant takes place throughout the reaction and likely explain the requirement of a slight molar excess of the latter to push the conversion of the substrate. We supported this hypothesis by monitoring the conversion of the substrate through time by GC. The reaction showed a negligible initial induction time, followed by a linear period prior to the final plateau, in which the concentration of the oxidant in solution has likely already faded (see Supporting Info for details). At this stage, addition of a further batch of oxidant could further push the conversion of substrates **1** but did not improve the yield of products **2**. Similarly, efforts to replace hydrogen peroxide with oxygen (up to 20 bar) proved fruitless at present.

We proved that the sulfonic acid acts as a heterogeneous catalyst through the Sheldon test.[34] In particular, the reactivity did not evolve further into the clean homogeneous solution upon filtration, in agreement with the control experiment (Table 1, entry 10).

In typical experiments, the solid catalyst can be recovered upon the reaction by filtration. Upon washing with water and ethanol (3 x 10 mL), the material can be efficiently recycled and preserved its activity for three consecutive reactions. The reduced activity results accompanied by a concomitant decrease in the acidity of the material. This correlates with analogous observations made during the study of related benzylic oxidations.[31] Upon depletion of its Bronsted acid sites, the material can be however reactivated by treatment with a sulfuric acid solution in order to restore its original loading of -SO₃H groups. This approach allows to reuse the material for further experiments.

We then wondered whether a more challenging oxidative dearomatization of bare arenes could have been possible using present catalytic system. A few experiments using benzene as model utterly failed, suggesting that the energetic stabilization due to aromaticity was a too steep cliff to overcome in this case. Reasoning that this energetic toll would move inversely to the conjugation of an aromatic π-system, we tested naphthalene. Gratifyingly, the reaction of **3a** adopting previously optimized conditions showed the formation of traces of naphthoquinone **4a**. A significant improvement was observed performing the reaction at a higher temperature, namely 80 °C, which enabled the formation of **4a** in 47% yield. We noticed however that together with 31% of unreacted starting material, partial decomposition occurred in this case. We thus tried to evaluate again which heterogeneous acid moiety proved better (Table 3).
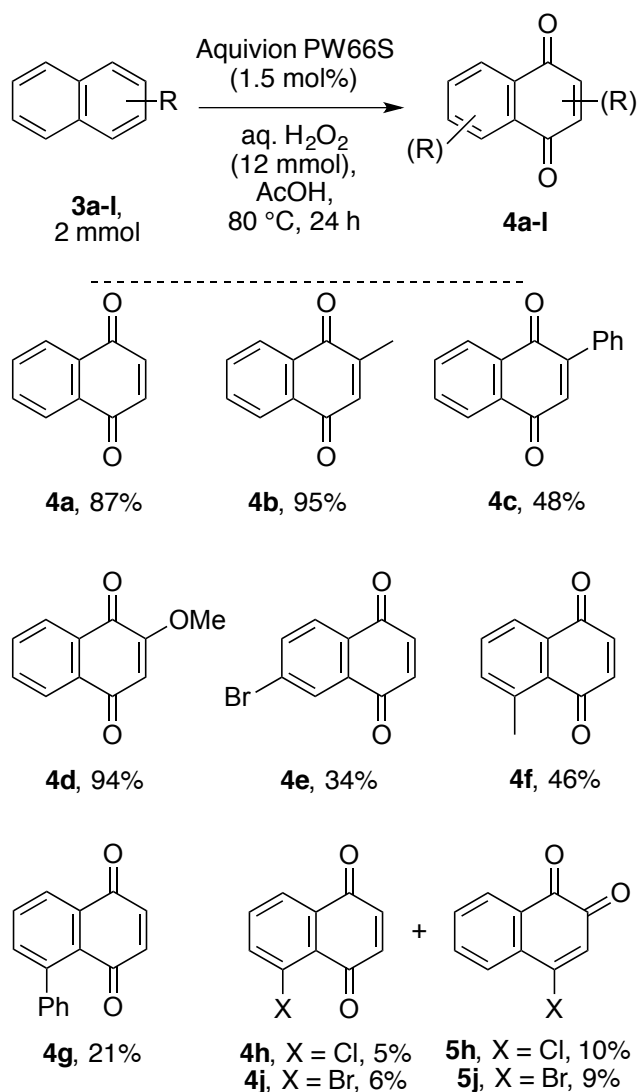
Table 3. Oxidative dearomatization of naphthalene.[a]

| Entry	Catalyst (mol% H⁺)	Temp. (°C)	Conv. of **3a** (%)[b]	Yield of **4a** (%)[b]	Sel. of **4a** (%)[c]
1	Aquivion @SiO₂ (1.5)	80	69	47	68
2	-(CH₂)₃-SO₃H @SiO₂ (1.5)	80	61	33	54
3	SiO₂	80	10	1	10
4	Aquivion PW66S (1.5)	80	47	44	94
5	Aquivion PW66S (7)	80	51	50	98
6	Aquivion PW66S (13)	80	83	58	70
7	Aquivion PW66S (1.5)	100	83	52	63
8[d]	Aquivion PW66S (1.5)	80	99	45	44
9[e]	Aquivion PW66S (1.5)	80	91	88	97

The use of silica decorated with propylsulfonic groups confirmed the feasibility of the approach, delivering quinone **4a** in 33% yield (entry 2). On the contrary, the inorganic support is not competent for the reaction (entry 3). Surprisingly, the formation of byproducts was almost inhibited using the unsupported perfluorinated sulfonic acid (entry 4), which gave the desired product in 44% yield together with the unreacted starting material (53%). The yield can be further pushed by increasing the loading of the acid catalyst (entries 5-6), although at expense of selectivity. Similarly, increasing the temperature to 100 °C proved to be a dead end (entry 7). The use of 18 mmol of oxidant followed suite (entry 8). On the contrary, the use of 12 mmol of hydrogen peroxide proved decisive (entry 9), affording **4a** in 88% yield. The scope of the reaction was then studied (Scheme 3).

The reaction of **3b**, which has a 2-methyl substituent, afforded almost quantitatively Vitamin K-3 (**4a**, 95%). It is worth noting the dearomatization occurred chemoselectively on the most electron rich ring of the substrate in this case. This effect was confirmed using reagent **3c**, for which a single isomer of the product was observed. Product **4c** was retrieved in 48% yield, together with 43% of unreacted substrate. The steric hindrance of the 2-phenyl substituent likely reduced the reactivity of this substrate. The selective dearomatization was observed using 2-methoxynaphthalene, which afforded the corresponding quinone **4d** in 94% yield. The presence of an electron withdrawing group shifts course, leading to the functionalization of the least substituted ring (**4e**, 34%). In analogy to the reaction of phenols, a reduced electronic density has however a negative impact on yields. The presence of a methyl or a phenyl group at position 1- on the substrate lead to the functionalization of the least hindered ring, too (products **4f-g**, 46% and 21%, respectively). The reaction of 1-halonaphthalenes gave two products, both in low yields. Together with **4h-j**, in which the most electron rich ring underwent the oxidation, we isolated the 1,2-quinones **5h** and **5j** (10% and 9%, respectively).

4a, 87%   **4b**, 95%   **4c**, 48%

4d, 94%   **4e**, 34%   **4f**, 46%

4g, 21%   **4h**, X = Cl, 5%   **5h**, X = Cl, 10%
4j, X = Br, 6%   **5j**, X = Br, 9%

Scheme 3. Scope of the dearomatization of naphthalenes, isolated yields.

The method has been tested on heavier fused polycyclic arenes. In particular, the reaction of anthracene led to the formation of anthraquinone (**4k**) in 89% yield (Scheme 4). On the contrary, the use of phenanthrene gave just traces of the expected 1,2-quinone. The substrate was almost completely consumed in this case and diphenyl-2,2'-dicarboxylic acid was isolated in 45% yield. This result suggested that two contiguous carbonyl groups could be oxidatively cleaved under present conditions. We tested this hypothesis using pyrene. The reaction provided once again traces of 1,2-quinone, together with phenanthrene-4,5-dicarboxylic acid (50%) as major product.
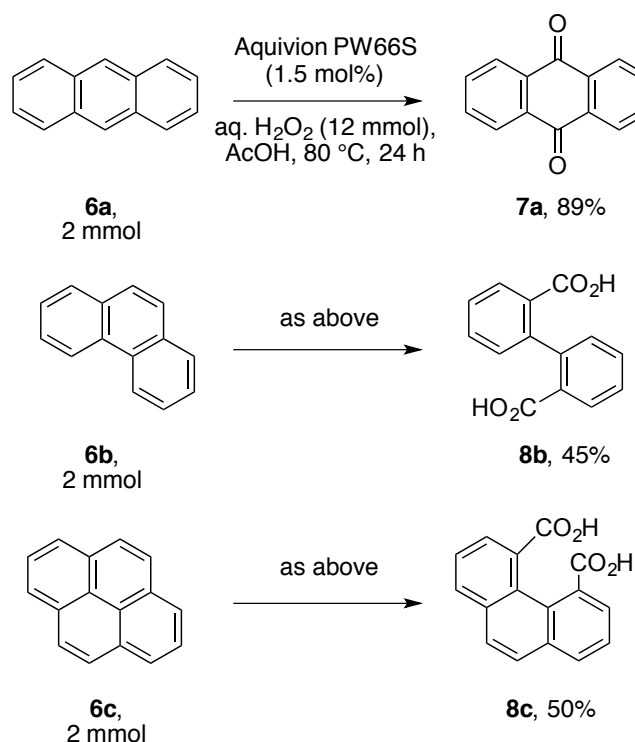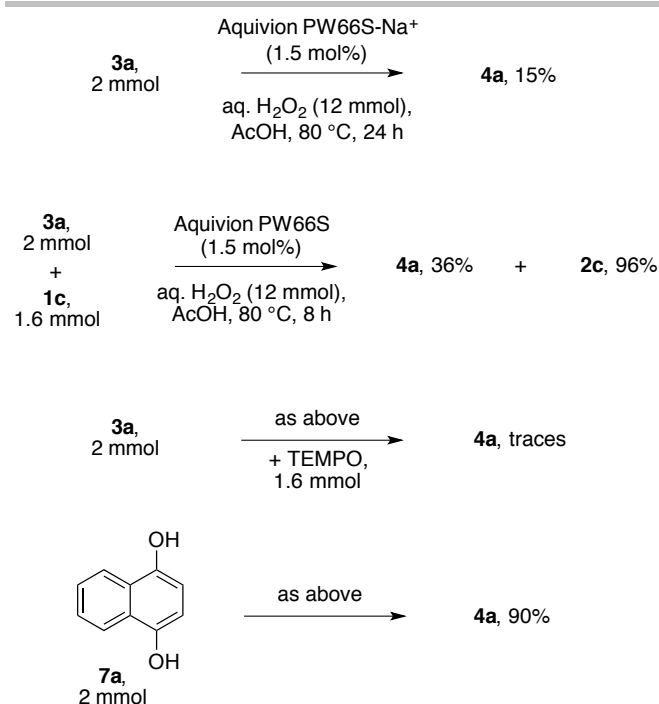

Scheme 4. Scope of the dearomatization of polycyclic aromatic hydrocarbons, isolated yields.

Reactions performed with unsupported polymeric sulfonic acids did not allow however to easily recover the catalyst, which was used in tiny amounts and remained mostly dispersed in the aqueous phase. This limit is nonetheless smoothed by the low loading (1 mol%) used in present method.

In order to gain insights on the mechanism of present dearomatization of aromatic polycycles, we performed additional experiments on naphthalene derivatives (Scheme 5).

Firstly, we further proved the role played by the acid catalyst. To this end, the perfluorinated sulfonic acid was treated with a molar excess of soda, dried and subjected to titration in order to confirm the absence of protic acid sites on the resulting material. The latter was then used to perform our model reaction on **3a**. Low conversion was observed upon 24 hours under heating, and **4a** was isolated in 15% yield. This result shows the relevance of the acidity of the material for the dearomatization.

In order to ascertain whether the process occurs through a radical or ionic mechanism, we then tested the model reaction of **3a** in the presence of 2,6-diterbutylphenol (**1c**), which is a well-known radical inhibitor. The reaction gave quinone **2c** in almost quantitative yield while the conversion of naphthalene remained moderate, and **4a** was recovered in a meagre 36% yield. The model reaction was tested in the presence of TEMPO, which inhibited almost completely the dearomatization of the substrate, leading to the formation of the desired product in traces. Taken together, these results strongly suggest that the dearomatization process occur through a radical mechanism, in analogy with related oxidations triggered by heterogeneous sulfonic acid previously developed by our group.[30-32]

3a,
2 mmol

Aquivion PW66S-Na+
(1.5 mol%)
———————————————→
aq. H_2O_2 (12 mmol),
AcOH, 80 °C, 24 h

4a, 15%

3a,
2 mmol
+
1c,
1.6 mmol

Aquivion PW66S
(1.5 mol%)
———————————————→
aq. H_2O_2 (12 mmol),
AcOH, 80 °C, 8 h

4a, 36%   +   **2c**, 96%

3a,
2 mmol

as above
———————————————→
+ TEMPO,
1.6 mmol

4a, traces

OH

OH

7a,
2 mmol

as above
———————————————→

4a, 90%

Scheme 5. Mechanistic probes.

Finally, we attempted the oxidation of 1,4-naphthalene diol (**7a**) under our optimized conditions. The starting material was completely consumed in 4 hours, affording **4a** in 90% yield. The efficiency of this dearomatization could suggest that dihydroxylated arenes might be intermediates of the overall reaction.

Conclusion

We reported a synthetic method for the oxidative dearomatization of phenols and polycyclic aromatic hydrocarbons catalyzed by a perfluorinated polymeric sulfonic acid. Reactions can be performed under mild conditions, with low catalyst loadings and using a benign oxidant. Taken together, these features minimize the formation of wastes. The method allows to access functionalized scaffolds from basic building blocks in a concise fashion. We hope these findings will contribute to future developments of oxidation methods using sulfonic acid catalysts.

Experimental Section

General remarks

Chemicals were purchased from commercial sources and were used as received without further purification. All reactions were carried out in glass tailed test tubes and analyzed by TLC (Thin Layer Chromatography) on silica gel 60 F254. Flash column chromatography was performed on silica gel 60 (70–230 mesh). GC analyses were performed with an Agilent Tenchnologies 7820A equipped with a FID detector and a 30 m capillary column. Low resolution GC-MS analyses (EI) were performed with an Agilent Technologies 7820A gas chromatograph coupled to an 5977B mass selective detector (Agilent Technologies) working at 70 eV ionizing voltage. High resolution MS analyses (ESI) were recorded on a LTQ ORBITRAP XL Thermo Mass Spectrometer. Reactions that required heating were performed with the use of non-flammable high-vacuum grade silicon oil. NMR spectra were recorded on Bruker AVANCE 300 and 400 spectrometers in deuterated chloroform, using the solvent residual signals as internal reference (7.26 and 77.00 ppm, respectively for 1H and 13C). The terms m, s, d, t, q and quint represent multiplet, singlet, doublet, triplet, quadruplet and quintuplet, respectively, and the term br means a broad signal.

Preparation of Aquivion@SiO₂ (Table 1)

The catalyst was prepared adapting a literature procedure.[35] Typically, in a two-necked flask, Aquivion D98-20BS–water dispersion (11.0 g) was added to a solution of tetraethoxysilane (TEOS, 15.0 g). The solution has been stirred for 2 hours at room temperature and then

heated at 100 °C for 18 hours. The final solid was centrifuged and washed with deionized water until the supernatant fluid has a neutral pH (150 ml). The solid was finally dried in an oven heated at 120 °C for 15 hours. Surface acidity of the resulting material was measured by titration method and was found to be 0.47 mmol H^+/g.

General procedure for the catalytic dearomatization of phenols

In a glass tailed test tube equipped with a septum, acetic acid (5 ml), an aqueous H_2O_2 solution (35%, 0.73 ml, 8.0 mmol) and Aquivion supported on amorphous silica were added (0.02 mmol, 1 mol% -SO_3H). The resulting mixture was stirred in a pre-heated oil bath at 40 °C for 1 hour and the phenolic substrate (2.0 mmol) is then added. The obtained mixture was stirred at 40 °C for further 24 hours. The catalyst was filtered and the reaction mixture was diluted with ethyl acetate (20 ml) and washed with abundant water (3 x 30 ml). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was then analysed by GC or GC-MS and finally purified by flash column chromatography on silica gel using a 8:2 mixture of hexane-ethyl acetate as eluent.

General procedure for the catalytic dearomatization of polycyclic aromatics

In a glass tailed test tube equipped with a septum, the substrate (2.0 mmol) was dissolved in acetic acid heated at 80 °C under stirring. Upon complete solubilization, Aquivion PW66S (0.03 mmol, 1.5 mol% -SO_3H) and an acqueous H_2O_2 solution, (35%, 1.11 ml, 12.0 mmol) are sequentially added to the tube. The latter was transferred dropwise using a syringe. The mixture was kept to 80 °C for 24 hours. The catalyst was filtered and the reaction mixture was diluted with ethyl acetate (20 ml) and washed with abundant water (3 x 30 ml). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was then analyzed by GC or GC-MS and finally purified by flash column chromatography on silica gel using a 8:2 mixture of hexane-ethyl acetate as eluent.

4-chloronaphthalene-1,2-dione 5h: the general procedure was followed using the correspondent naphtalene (324 mg, 2 mmol). Purification by chromatography on silica gel yielded **5h** (38 mg, 10%) as a yellow solid. ^{1}H-NMR (300 Mhz, CDCl$_3$): δ 8.17-8.06 (m, 2H), 7.80-7.76 (m, 2H), 7.20 (d, J = 4.49 Hz, 1H); ^{13}C-NMR (101 Mhz, CDCl$_3$): δ 182.6, 177.9, 146.3, 138.0, 135.9, 134.5, 134.1, 133.7, 127.5, 126.7; ESI-HRMS calcd. for $C_{10}H_6ClKO_2$ [M+K$^+$], 229.9531, found, 229.9524; M.P.: 186-187 °C.

6-bromonaphthalene-1,4-dione 4e: The general procedure was followed using the correspondent naphtalene (410 mg, 2 mmol). Purification by chromatography on silica gel yielded **4e** (353 mg, 34%) as an orange solid. ^{1}H-NMR (300 Mhz, CDCl$_3$): δ 8.21 (d, J = 1.8 Hz, 1H), 7.91 (dt, J = 5.1, 8.3 Hz, 2H), 6.99 (s, 2H); ^{13}C-NMR (101 Mhz, CDCl$_3$): δ 184.2, 183.8, 138.8, 138.4, 137.0, 132.9, 129.5, 128.2; ESI-HRMS calcd. for $C_{10}H_6{}^{79}BrO_2Na$ [M+Na$^+$], 258.9365, found 258.9376. M.P.: 117-119 °C.

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