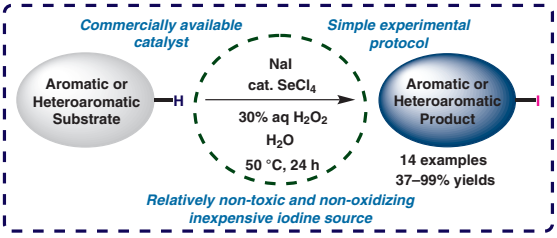
Biomimetic Iodofunctionalization of Aromatic and Heteroaromatic Compounds Catalyzed by Selenium Tetrachloride

Beatriz C. O. Rocha
Givago P. Perecim
Cristiano Raminelli*

Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Rua Prof. Artur Riedel, 275, Diadema, SP 09972-270, Brazil
raminelli@unifesp.br



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Abstract A biomimetic iodofunctionalization of aromatic and heteroaromatic compounds has been developed using NaI as a source of iodine and 30% H_2O_2 as a mild oxidant, as well as $SeCl_4$ as a commercially available catalyst in water without a co-solvent. The method affords iodinated compounds in isolated yields of 37 to 99%. The catalytic system has potential for the bromination of aromatic substrates.

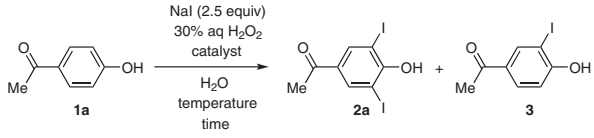
Key words biomimetic synthesis, iodofunctionalization, selenium catalysis, iodination, aqueous reaction

Iodofunctionalized molecules are versatile building blocks in preparative organic chemistry with application, for example, in cross-coupling reactions,[1] as well as in iodine–lithium[2] and iodine–magnesium[3] exchange processes. These transformations can be considered valuable methods for the formation of carbon–carbon and carbon–heteroatom bonds,[1–3] which are useful in the total syntheses of natural products[4] and in the production of polymers with varied properties.[5] Furthermore, several organic compounds containing iodine are biologically active substances[6] or have been employed in targeted molecular radiotherapy[7] and as contrast media for diagnostic imaging.[8] Therefore, a considerable number of approaches for the iodofunctionalization of organic molecules has been developed.[9–12] Among them, the one-pot diazotization–iodination of aromatic and heteroaromatic amines[10] and the electrophilic iodination of aromatic and heteroaromatic substrates[11] can be considered well-established strategies to prepare iodinated aromatic and heteroaromatic compounds. Although diazotization–iodination reactions have limitations related to the use of starting materials containing amino groups, and electrophilic iodination reactions employ relatively toxic, oxidizing, and expensive halogenating reagents, both approaches can be considered useful in organic synthesis.[10,11] To circumvent the disadvantages, Detty and co-workers have explored halogenation reactions involving halide salts as the sources of halogen and aqueous hydrogen peroxide as a mild oxidizing, and the reactions have been successfully catalyzed by chalcogen-containing compounds.[12] In these transformations the organochalcogens employed as catalysts mimic haloperoxidase enzymes[13] allowing environmentally friendly halogenations of organic substrates.[12,14] Nonetheless, to our knowledge, only one study that provides a general method for the iodination of organic substrates employing NaI and H_2O_2 catalyzed by a water-soluble organotelluride has been reported.[12d] Only low catalyst loadings were required for the iodinations described; however, the water-soluble catalyst had to be prepared in four steps from 4-*N*,*N*-bis(carboethoxymehyl)aniline.[12d] In this context, having in mind the demand for iodinated aromatic and heteroaromatic compounds in synthetic organic chemistry, along with the potential applications of iodinated compounds in medicine, we have developed a novel method for the biomimetic iodination of aromatic and heteroaromatic compounds employing NaI as iodine source, 30% H_2O_2 as oxidant, and $SeCl_4$ as catalyst, in water without a co-solvent, affording iodinated aromatic and heteroaromatic compounds in good isolated yields. Through this methodology we can avoid the limitations related to the use of starting materials containing amino groups, as well as oxidizing, and expensive halogenating reagents, with the convenience of employing $SeCl_4$ as a commercially available catalyst.

Initially, the reactions were carried out employing 1-(4-hydroxyphenyl)ethanone (**1a**), NaI (2.5 equiv), 30% aqueous H_2O_2 (0 to 5 equiv), the appropriate catalyst (0 to 20 mol%), and distilled water. The mixtures were stirred at room temperature or 50 °C for 24 h or 48 h (Table 1, entries 1–11; Procedure A). The use of selenium and tellurium powder was evaluated, envisioning the in situ formation of the corresponding selenium(IV) and tellurium(IV) species, which could catalyze the reaction. However, in both experiments, 1-(4-hydroxy-3-iodophenyl)ethanone (**3**) was obtained in yields lower than 5% (entries 1 and 2). When the transformation was performed in the presence of $SeCl_4$ (5 mol%) or $TeCl_4$ (5 mol%), we obtained **3** in yields of 20% and 21%, respectively (entries 3 and 4). In the absence of catalyst, compound **3** was isolated in 10% yield (entry 5). At this point, we decided to continue the experiments using $SeCl_4$ as catalyst based on the cost-benefit ratio. The use of distilled water instead of a buffer solution was reasonable because the reactions presented initial and final pH values of 6 (entries 1–5). Allowing the reaction to proceed in the absence of 30% H_2O_2, we did not observe the formation of 1-(4-hydroxy-3,5-diiodophenyl)ethanone (**2a**) or **3**. In addition, both initial and final pH values were pH 4 (entry 6). Increasing the catalyst loading to 20 mol% and the reaction time to 48 h, compounds **2a** and **3** were obtained in yields of 38% and 23%, respectively (entries 7–9). Through an increase of reaction temperature, we isolated compounds **2a** and **3** in yields of 37% and 26%, respectively (entries 10 and 11). The reactions outlined in entries 7–10 presented initial and final pH values of 6. Interestingly, when the transformation was performed at 50 °C for 48 h, the initial pH value was 6 and the final pH value was 1 (entry 11).

In an attempt to increase the yield of compound **2a**, the reactions were carried out by preparing a solution of **1a** in distilled water, which was subjected to stirring at room temperature or 50 °C. Then, a solution containing $SeCl_4$ (20 mol%) in distilled water was added. Afterwards, 2 M aqueous solutions of NaI (2.5 equiv) and of H_2O_2 (5 equiv) were added alternately to the mixture in small aliquots (every 5 min over a period of 50 min). The resulting mixture was

Table 1 Optimization of the Preparation of 4-Hydroxy-3,5-diiodoacetophenone (**2a**)[a]



Entry	Procedure	Catalyst (mol%)	30% aq H_2O_2 (equiv)	Temp (°C)	Time (h)	Isolated yield (%)		pH values[b]	
						2a	**3**	Initial (pH_i)	Final (pH_f)
1	A	Se (5)	5	r.t.	24	0	<5	6	6
2	A	Te (5)	5	r.t.	24	0	<5	6	6
3	A	$SeCl_4$ (5)	5	r.t.	24	0	20	6	6
4	A	$TeCl_4$ (5)	5	r.t.	24	0	21	6	6
5	A	–	5	r.t.	24	0	10	6	6
6	A	$SeCl_4$ (5)	–	r.t.	24	0	0	4	4
7	A	$SeCl_4$ (10)	5	r.t.	24	13	24	6	6
8	A	$SeCl_4$ (20)	5	r.t.	24	34	23	6	6
9	A	$SeCl_4$ (20)	5	r.t.	48	38	23	6	6
10	A	$SeCl_4$ (20)	5	50	24	37	26	6	6
11	A	$SeCl_4$ (20)	5	50	48	37	26	6	1
12	B	$SeCl_4$ (20)	5	r.t.	3	57	<5	6	6
13	B	$SeCl_4$ (20)	5	r.t.	24	59	27	6	6
14	B	$SeCl_4$ (20)	5	r.t.	48	62	23	6	6
15	B	$SeCl_4$ (20)	5	50	24	62	26	6	6
16	B	$SeCl_4$ (20)	5	50	48	62	26	6	6

[a] Reaction conditions: Procedure A: Compound **1a** (2 mmol), NaI (5 mmol), catalyst, H_2O (10 mL), and 30% H_2O_2 were maintained under stirring at the established temperature for the indicated time. Procedure B: To a solution of compound **1a** (2 mmol in 2.5 mL of H_2O) under stirring at the indicated temperature was added a solution of $SeCl_4$ (20 mol% in 5 mL of H_2O). Then, 2 M aqueous solutions of NaI (5 mmol) and of H_2O_2 (10 mmol) were added alternately in small aliquots (every 5 min over a period of 50 min) and the resulting mixture was maintained under stirring at the established temperature for the indicated time.
[b] pH_i: initial pH value. pH_f: final pH value.

maintained under stirring at room temperature or 50 °C for 3 h, 24 h or 48 h (Table 1, entries 12–16; Procedure B). By employing Procedure B, at room temperature for 3 h, **2a** and **3** were isolated in yields of 57% and <5%, respectively (entry 12). On increasing the reaction time to 24 h, and then to 48 h, compounds **2a** and **3** were obtained in yields of 59–62% and 23–27%, respectively (entries 13 and 14). When the transformation was carried out at 50 °C for 24 h or 48 h, the products **2a** and **3** were isolated in similar yields of 62% and 26%, respectively (entries 15 and 16). All reactions performed using Procedure B presented initial and final pH values of 6 (entries 12–16).

By employing the optimal conditions, i.e., the conditions that promoted the highest incorporation of iodine into **1a** (Table 1, entry 15), we examined the scope of the transformation using phenols, anilines, and pyrazoles (**1a–o**) with electron-donating and electron-withdrawing groups (Table 2).[15] By performing the reaction with phenolic compounds containing electron-withdrawing groups (**1a–c**), we obtained the diiodinated products **2a–c** in yields from 54% to 90% (entries 1–3). The relatively low yield achieved for compound **2b** (entry 2) was tentatively attributed to hydrolysis of the cyano group under the reaction conditions. However, no experimental evidence was obtained to support such a proposal. When 4-methylphenol (**1d**) was subjected to the diiodination reaction, 2,6-diiodo-4-methylphenol (**2d**) was isolated in 30% yield (entry 4). The optimized reaction conditions did not work as expected for phenolic compounds containing electron-donating groups. By reducing the amounts of NaI and H_2O_2 to 1.25 equiv and 2.5 equiv, respectively, di- and monohalogenated phenols (**1e–g**) provided monoiodinated products (**2e–g**) in yields from 57% to 76% (entries 5–7). Likewise, the anilines **1h–j** led to the formation of monoiodinated anilines (**2h–j**) in isolated yields from 71% to 92% (entries 8–10). When pyrazole (**1k**) was treated with NaI (1.25 equiv) and H_2O_2 (2.5 equiv) in the presence of $SeCl_4$ (20 mol%) using distilled water as solvent at 50 °C for 24 h, 4-iodopyrazole (**2k**) was obtained in 25% yield (entry 11). In this reaction the starting material **1k** was partially recovered and unidentified by-products were produced according to GC/MS analysis. By increasing the amounts of NaI (2.5 equiv), H_2O_2 (5 equiv), and $SeCl_4$ (40 mol%), we isolated 4-iodopyrazole (**2k**) in 37% yield (entry 11). Treatment of 3,5-dimethylpyrazole (**1l**) with NaI (1.25 equiv), H_2O_2 (2.5 equiv), and $SeCl_4$ (20 mol%) gave 4-iodo-3,5-dimethylpyrazole (**2l**) in 99% yield (entry 12). Similarly, when 1-phenylpyrazole (**1m**) was subjected to the monoiodination reaction, 4-iodo-1-phenylpyrazole (**2m**) was isolated in 65% yield (entry 13). The iodination reaction of 3-amino-1,5-dimethylpyrazole (**1n**) provided the monoiodinated product **2n** in 75% yield (entry 14). Conversely, when 1,5-dimethyl-1*H*-pyrazole-3-carboxylic acid (**1o**) was subjected to the iodination reaction, 4-iodo-1,5-dimethyl-1*H*-pyrazole-3-carboxylic acid (**2o**) was not obtained, the starting material **1o** was partially recovered, and unidentified substances were produced according to GC/MS analysis (entry 15).

Table 2 Iodofunctionalization of Aromatic and Heteroaromatic Compounds **1**[a]

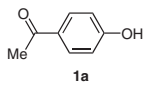
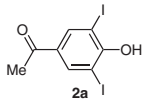
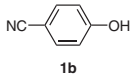
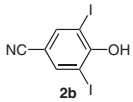
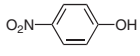
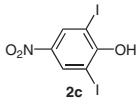
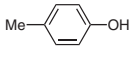
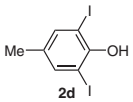
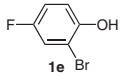
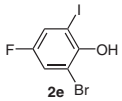
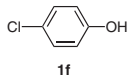
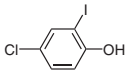
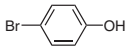
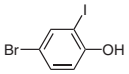
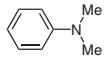
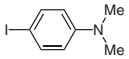
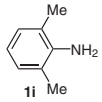
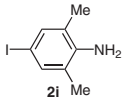
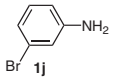
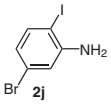
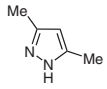
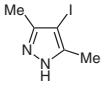
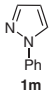
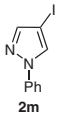
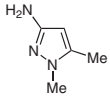
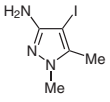
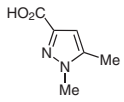
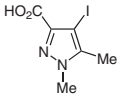
Entry	Aromatic compound **1**	Iodinated aromatic compound **2**	Isolated yield (%)
1	 **1a**	 **2a**	62 (44)[b]
2	 **1b**	 **2b**	54
3	 **1c**	 **2c**	90
4	 **1d**	 **2d**	30
5	 **1e**	 **2e**	76[c]

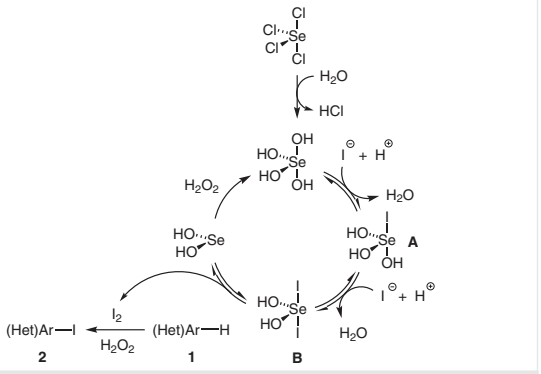
Table 2 (continued)

Entry	Aromatic compound **1**	Iodinated aromatic compound **2**	Isolated yield (%)
6	 **1f**	 **2f**	57[c]
7	 **1g**	 **2g**	61[c]
8	 **1h**	 **2h**	92[c]
9	 **1i**	 **2i**	86[c]
10	 **1j**	 **2j**	71[c]
11	 **1k**	 **2k**	25[c] (37)[d]
12	 **1l**	 **2l**	99[c]
13	 **1m**	 **2m**	65[c]
14	 **1n**	 **2n**	75[c]
15	 **1o**	 **2o**	0[c]

[a] Reaction conditions: To a solution of compound **1** (2 mmol in 2.5 mL of H_2O) under stirring at 50 °C was added a solution of $SeCl_4$ (20 mol% in 5 mL of H_2O). Then, 2 M aqueous solutions of NaI (5 mmol) and of H_2O_2 (10 mmol) were added alternately in small aliquots (every 5 min over a period of 50 min) and the mixture was maintained under stirring at 50 °C for 24 h.
[b] Obtained using 20 mol% of SeO_2.
[c] Obtained using 2.5 mmol of NaI and 5 mmol of H_2O_2.
[d] Obtained using 40 mol% of $SeCl_4$, 5 mmol of NaI, and 10 mmol of H_2O_2.

A reasonable catalytic cycle to provide iodinated compounds **2** commences with hydrolysis of $SeCl_4$ leading to $Se(OH)_4$. After that, intermediates **A** and **B** are produced through ligand exchange reactions. Then, intermediate **B** undergoes reductive elimination, affording molecular iodine and $Se(OH)_2$, which, in the presence of hydrogen

peroxide, regenerates $Se(OH)_4$.[12] The incorporation of iodine into aromatic and heteroaromatic compounds **1** takes place via electrophilic iodination (Scheme 1).[11e–g]



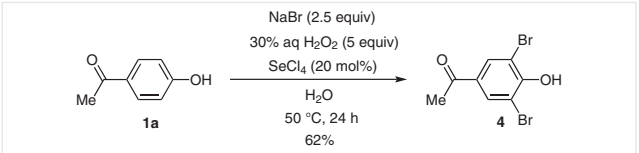
Scheme 1 Catalytic cycle proposed for the iodination reaction of compounds **1**

We carried out the treatment of **1a** with NaI (2.5 equiv) and H_2O_2 (5 equiv) using $SeCl_4$ (20 mol%) in water at 50 °C for 24 h (Table 1, entry 15) to conduct analyses of the reaction medium by electrospray ionization mass spectrometry (ESI-MS), employing positive (ESI+) and negative (ESI–) modes, aiming to identify transient species related to the catalytic cycle of Scheme 1, as well as to follow the transformation progress at 1, 3, 6, 12, and 24 hours. However, no transient species related to the catalytic cycle of Scheme 1 were detected.

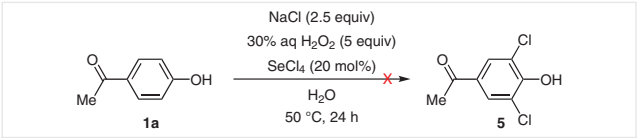
In an attempt to provide some experimental support for the catalytic cycle shown in Scheme 1, we performed qualitative tests aiming to confirm the formation of molecular iodine in the reaction medium.[16] Accordingly, we prepared aqueous solutions of $SeCl_4$ (0.08 M) and of NaI (2 M). Then, by addition of 2.5 mL of NaI (2 M) to 5 mL of $SeCl_4$ (0.08 M), both colorless solutions produced a brownish mixture, indicating a possible formation of molecular iodine; this conclusion was supported by addition of a solution of starch (1%; 5 mL), which produced a black mixture. In addition, another test was performed, in which we prepared the brownish solution (as described above) and added a saturated solution of $Na_2S_2O_3$ (5 mL) leading to a colorless aqueous solution presumably by reduction of molecular iodine back to iodide.

Aiming to expand the scope of the developed transformation (Table 2), we considered the use of NaBr and NaCl for the introduction of Br and Cl atoms, respectively, in aromatic and heteroaromatic compounds **1**. Thus, we treated **1a** with NaBr (2.5 equiv) and H_2O_2 (5 equiv) using $SeCl_4$ (20 mol%) in water at 50 °C for 24 h and obtained 1-(3,5-dibromo-4-hydroxyphenyl)ethanone (**4**) in 62% yield (Scheme 2).

Allowing **1a** to react with NaCl (2.5 equiv) and H_2O_2 (5 equiv) employing $SeCl_4$ (20 mol%) in water at 50 °C for 24 h, 1-(3,5-dichloro-4-hydroxyphenyl)ethanone (**5**) was not obtained. Instead, the starting material **1a** was partially recovered, and unidentified substances were produced according to GC/MS analysis. It is worth mentioning that, in the case of the reaction using NaCl, the pH remained between 0 and 1 throughout the reaction (Scheme 3).



Scheme 2 Dibromination reaction of compound **1a**



Scheme 3 Dichlorination reaction of compound **1a**

The structures proposed for compounds **2a–n**, **3**, and **4** are supported by their ^1H and ^{13}C NMR, IR, and mass spectra (see the Supporting Information).

In summary, a biomimetic iodofunctionalization of aromatic and heteroaromatic compounds has been developed that employs NaI as an inexpensive iodine source, 30% H_2O_2 as a mild oxidizing agent, and $SeCl_4$ as a commercially available catalyst, in water without a co-solvent, affording iodinated aromatic and heteroaromatic compounds in good isolated yields. The method can be considered an attractive alternative approach to prepare iodinated compounds, with potential applications in organic synthesis, medicinal chemistry, and medicine. In addition, the catalytic system developed presents potential for the bromination of aromatic and heteroaromatic compounds. In this sense, we intend to explore the bromination of aromatic and heteroaromatic substances and the results will be disclosed in due course.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690337.

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(15) **Preparation of Iodinated Compounds 2a–n and 3; General Procedure:** To a solution of compound **1a–o** (2 mmol in 2.5 mL of H_2O) under stirring at 50 °C was added a solution of $SeCl_4$ (20 mol% in 5 mL of H_2O). Then, 2 M aqueous solutions of NaI (5 or 2.5 mmol) and of H_2O_2 (10 or 5 mmol) were added alternately in small aliquots (every 5 min over a period of 50 min) and the mixture was maintained under stirring at 50 °C for 24 h. A saturated aqueous solution of $Na_2S_2O_3$ (10 mL) was then added to the reaction, the mixture was extracted with ethyl acetate (3 × 20 mL) and the organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using an appropriate eluent, to afford the desired product **2a–n** and **3**.

1-(4-Hydroxy-3,5-diiodophenyl)ethenone (2a): Yield: 483 mg (62%); off-white solid; R_f = 0.55 (CH_2Cl_2); mp 173 °C [lit.17 173 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.26 (s, 2 H), 3.38 (s, 1 H), 2.51 (s, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 194.7, 159.8, 139.7, 132.8, 86.4, 26.6. IR (KBr): 3173, 1665, 1460, 1393, 1233 cm^{-1}. MS (EI): m/z (%) = 387.7 (71.7), 372.7 (100.0), 217.8 (18.2), 91.0 (25.6), 43.0 (59.3).

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