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A NaI/H_2O_2-Mediated Sulfenylation and Selenylation of Unprotected Uracil and Its Derivatives

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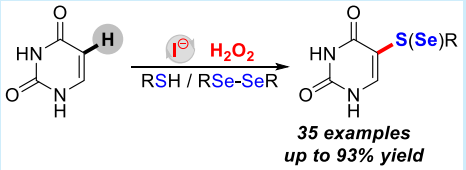
Supporting Information

ABSTRACT: An efficient iodide-catalyzed/hydrogen peroxide mediated sulfenylation and selenylation of unprotected uracil and its derivatives with simple thiols and diselenides was established. This coupling tolerates a broad variety of functional groups to provide diverse 5-sulfur/selenium-substituted uracil derivatives in good to excellent yields (up to 93%).



C-5 substituted nucleobases and nucleosides consist of an important class of compounds that are valuable nucleotide-derived tools in molecular genetics and have played very important roles in many therapeutic areas.[1] In particular, 5-sulfur/selenium-substituted uracil bases and nucleosides have a wide range of applications as part of antivirals and anticancer agents and as biological probes in phototherapy and photo-cross-linking applications (Figure 1).[2] For example, 5-phenyl-

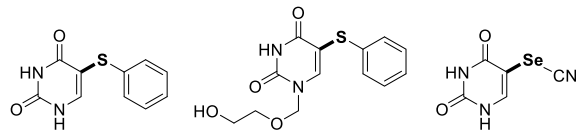
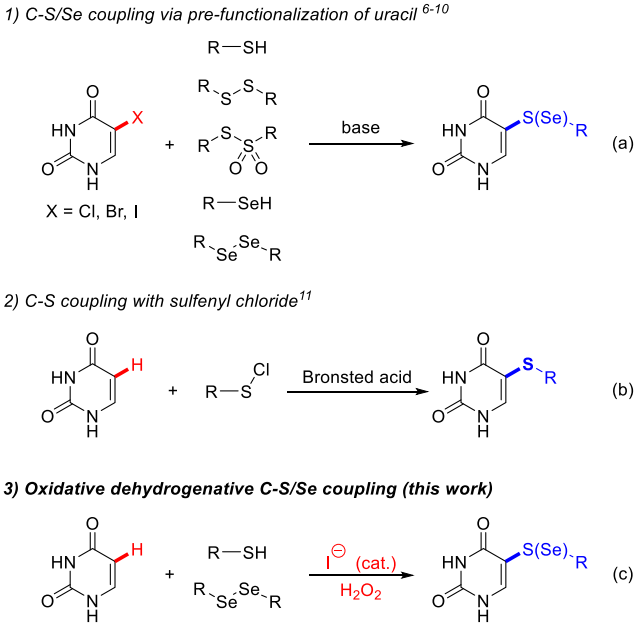


Figure 1. Selected examples of biologically active 5-sulfur/selenium-substituted uracil derivatives.

thiouracil (NSC210778) was identified as an effective inhibitor for FUDR phosphorylase, mammalian thymidine phosphorylase, DHUDase, and UrdPase,[3] while its analogue 5-(phenylthio)acyclouridine (AC1NA056) has been designed to improve oral uridine bioavailability with excellent pharmacokinetic properties for the treatment of cancer and AIDS.[4] Furthermore, selenocyanic acid with the selenide functional group at the C5-position of pyrimidine has been recognized as a potential hypoxic radiosensitizer and genomic DNA label in vitro.[5]

In the literature, a substantial number of useful C−S/Se bond formation methods have been described through base-promoted coupling reactions of thiols,[6] disulfides,[7] Bunte salts,[8] selenols,[9] or diselenides[10] with prefunctionalized uracil (eq (a), Scheme 1). Apart from this, Brönsted acid promoted cross coupling of uracil with sulfenyl chloride is another pathway for the C−S bond construction (eq (b)).[11] Although

Scheme 1. Previous Protocols for the Generation of 5-Sulfur/Selenium-Substituted Uracil Derivatives (a, b) and Our Approach (c)



these methods are useful, most of them suffer from several limitations. For example, protection groups at the *N*-1 and *N*-3 positions of uracil were required in the prefunctionalization strategy; thus, unprotected uracil targets, like 5-phenyl-thiouracil in Figure 1, were not rapidly prepared through this approach.[12] In addition, most of these methods involved toxic

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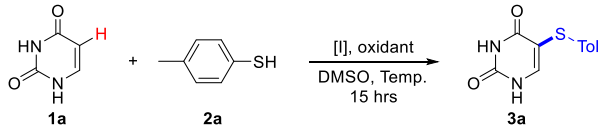
basic/acidic reagents and harsh reaction or inert atmosphere conditions. We were determined to improve current protocols by delivering a C−S/Se bond construction transformation for the facile preparation of 5-sulfur/selenium-substituted uracil derivatives with environmentally benign starting materials and reagents. Herein, we report our progress in the development of an efficient oxidative dehydrogenative C−S/Se coupling with uracil. It is worth noting that environmentally benign hydrogen peroxide was used as the oxidant. Both thiols and diselenides were effectively coupled with unprotected uracil and its derivatives to afford the desired products in good to excellent yields (eq (c)).

Inspired by our previous work on iodide-catalyzed C−C/C−N bond formation and chemical modulation of nucleic acids,[13] we initiated an investigation with the coupling between uracil **1a** with 4-methylphenylthiol **2a** (Table 1). To our delight, the initial attempt with 3 equiv of NaI and TBHP as the oxidant afforded the desired product 5-*p*-tolylthiouracil **3a** in an isolation yield of 81% (entry 1), indicating that this iodide-catalyzed C−S bond formation was indeed applicable. Switching the iodide source or oxidant led to inferior results (entries 2−5). However, when hydrogen peroxide was used as the oxidant, the coupling product **3a** was obtained in a good yield (75%) (entry 6). Contrary to other commonly employed chemical oxidants, hydrogen peroxide does not produce residues or gases and is an ideal oxidant for large-scale production. Thus, we became determined to improve this process, and further optimization led to the isolation of **3a** in 80% yield upon performing the reaction with 50% of NaI (entry 10). However, further decreasing the loading of NaI impeded the coupling (entry 11). By comparison, the identical reaction without iodide source or hydrogen peroxide resulted in trace product (entries 12 and 13), indicating that both were essential for this coupling reaction.

Table 1. Optimization of the C−S Coupling Reaction Conditions[a]



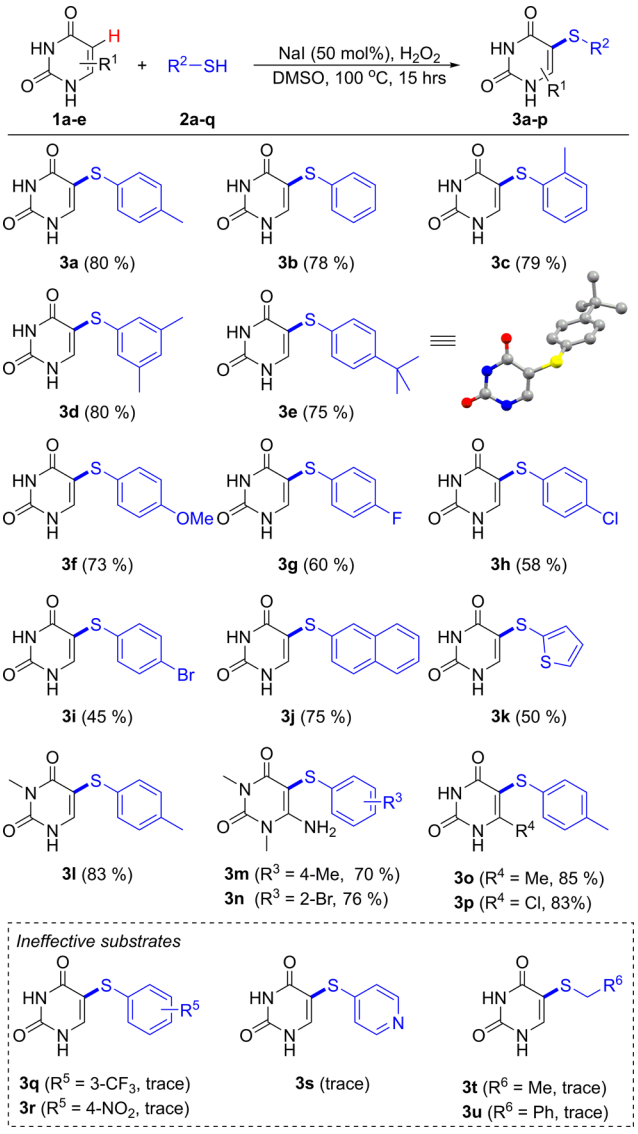
1a + **2a** → **3a**

entry	[I] (equiv)	oxidant (equiv)	temp (°C)	yield (%)
1	NaI (3)	TBHP (3)	100	81
2	KI (3)	TBHP (3)	100	51
3	TBAI (3)	TBHP (3)	100	66
4	NaI (3)	DTBP (3)	100	32
5	NaI (3)	O_2 (1 atm)	100	NR[b]
6	NaI (3)	H_2O_2 (3)	100	75
7	NaI (3)	H_2O_2 (6)	50	83
8	NaI (3)	H_2O_2 (9)	100	92
9	NaI (1)	H_2O_2 (9)	100	89
10	**NaI (0.5)**	**H_2O_2 (9)**	**100**	**80**
11	NaI (0.1)	H_2O_2 (9)	100	21
12	NaI (0.5)		100	trace
13		H_2O_2 (9)	100	trace

[a]Reaction conditions: uracil **1a** (0.2 mmol, 22.4 mg, 1 equiv), 4-methylphenylthiol **2a** (0.3 mmol, 37.5 mg, 1.5 equiv), iodide source, oxidant in DMSO (3 mL) at the designated temperature under open air for 15 h. Isolated yields of **3a** are given. [b]NR: no reaction.

After the establishment of the C−S coupling reaction conditions, the substrate scope and functional group tolerance of this procedure were explored (Scheme 2). A variety of substituted arylthiols **2a−i**, fused aryl thiol **2j**, and hetero-

Scheme 2. Substrate Scope of Thiols and Uracil Derivatives in the Sulfenylation



arylthiol **2k** were treated with simple uracil **1a**. The desired 5-sulfururacils **3a−k** were efficiently obtained through this coupling reaction in good to excellent yields, although electron-withdrawing groups (F/Cl/Br, **3g−i**) did result in moderate yields. X-ray crystal structure of the product **3e** confirmed the C−S construction (see the Supporting Information for details). Notably, the 6-substituted products were not detected in all cases. Additionally, this protocol was applicable not only to natural uracil but also to its substituted derivatives. For example, good yields of the 5-sulfur-substituted products **3l−p** were obtained with the N1/3- and/or C6-substituted uracil. However, when 4-nitro- or trifluoromethyl-substituted phenylthiols **2q−r** or pyridinyl thiol **2s** were used, trace products were observed. Alkyl thiols **2t−u** were also not applicable for this transformation.

With this useful sulfenylation protocol of uracil in hand, we further investigated the possibility of C−Se bond formation with diselenides. It turned out that the NaI/H_2O_2 system could

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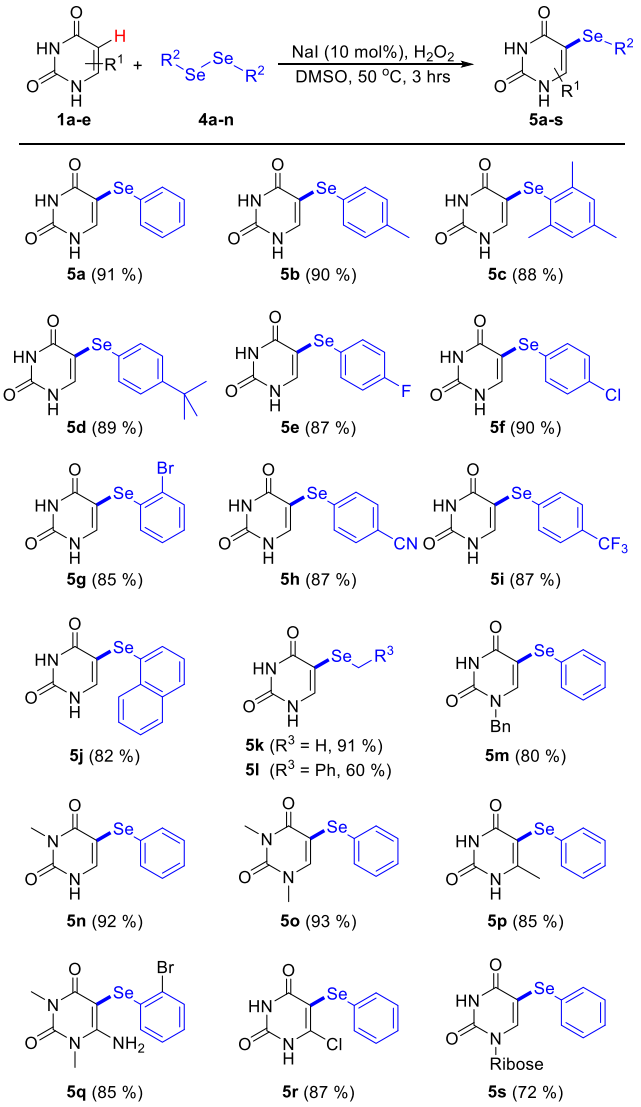
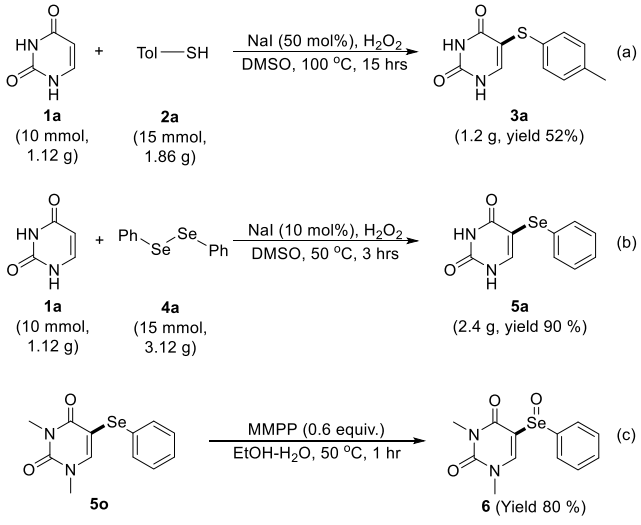
also successfully install selenium groups at the C5 position (Scheme 3). With a catalytic loading of NaI (10%), aryl (**4a**–**j**), fused aryl (**4k**), and alkyl (**4l**–**m**) diselenides were efficiently coupled with natural uracil **1a** and diverse substituted uracil derivatives **1b**–**e**, generating the corresponding products **5a**–**s** in excellent yields. Notably, the electronic effects of the functional groups on the phenyl ring did not have a significant impact to the yields. Gratifyingly, C6-substituted uracils **1e**–**g** upon reacting with diphenyl diselenide **4a** furnished the corresponding selenide derivatives **5q**–**r** in excellent yields. Significantly, this selective functionalization could also be applied to sugar-substituted uracil, from which the selenylation product **5s** was obtained in an isolated yield of 72%.

Scheme 3. Substrate Scope of Diselenides and Uracil Derivatives in the Selenylation



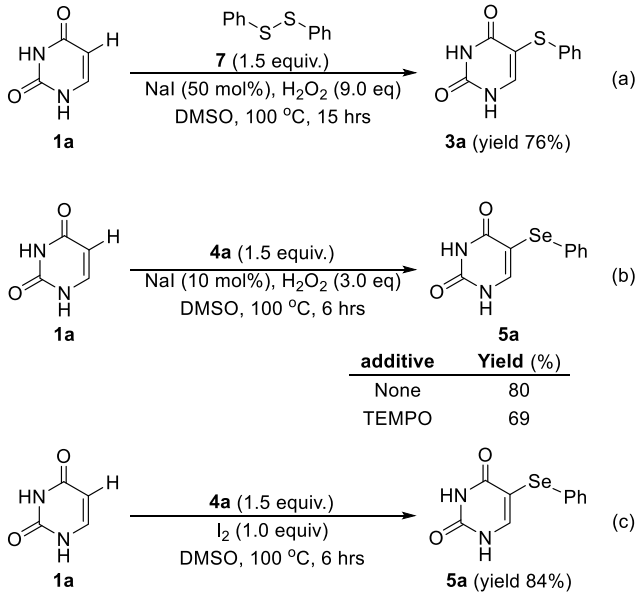
The scale-up experiments were later conducted. To our delight, the reaction afforded the products **3a** and **5a** in moderate to good yield (Scheme 4, eqs (a, b)). Furthermore, treatment of the compound **5o** with magnesium monoperoxyphthalate (MMPP) gave the selenone product **6** in high yield (eq (c)).[14]

Scheme 4. Scale-up Experiments and Post-Functionalization of Sulfenyl and Selenyl Uracil Products



For the elucidation of the reaction mechanism, some preliminary controlled experiments were performed (Scheme 5). When the sulfenylation was proceeded with 1,2-diphenyldisulfane **7** under standard conditions, a comparable yield of **3a** was obtained (eq (a)), which implied that the sulfenylation and selenylation may undergo a similar mechanism. A slight decrease of **5a** was isolated in the presence of TEMPO (eq (b)), indicating that a nonradical pathway might be involved in the reaction. We also conducted the standard selenylation in the presence of iodine and the product **5a** was isolated in a comparable yield, which suggested that the generation of iodine may be involved in this transformation (eq (c)).

Scheme 5. Control Experiments



additive	Yield (%)
None	80
TEMPO	69

While the exact mechanism awaits further elucidation, on the basis of previous research and preceding experiments, a plausible mechanism using diselenide as example is outlined in Scheme 6. It is considered that the iodide was first oxidized by H_2O_2 to iodine, which then activated the thiol or diselenide to

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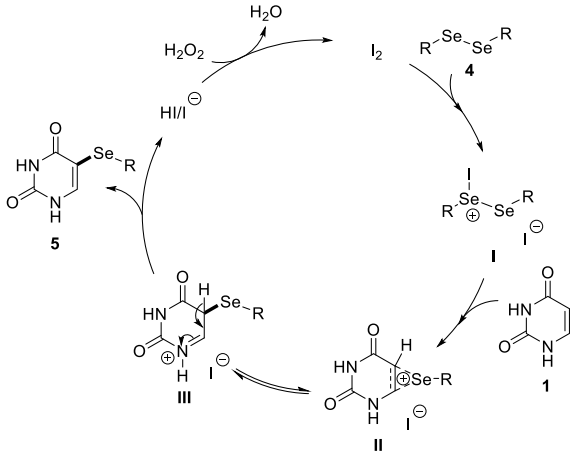
Scheme 6. Proposed Reaction Mechanism



afford the highly electrophilic sulfonium or selenium cation intermediate **I**.[15] An electrophilic addition of uracil to these cationoid reagents resulted in relatively unstable seleranium cation **II** and/or iminium ion intermediate **III**,[16] followed by elimination of hydrogen iodide HI to afford the C-5-substituted uridine products. It is reasonable to expect that C-5 would be more nucleophilic than C-6 so that the substitution afforded the C-5-substituted product exclusively.[17]

In conclusion, we have established a direct iodide/hydrogen peroxide mediated sulfenylation/selenylation of natural uracil and its derivatives. This operationally simple and scalable approach showed excellent substrate scope and tolerance of a diverse of functional groups and produced the corresponding 5-sulfur/selenium-substituted uracil derivatives in good to excellent yields. Mechanistic studies have suggested that an electrophilic substitution pathway may be involved in this process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02183.

Complete experimental details, characterization data for the prepared compounds (PDF)

Accession Codes

CCDC 1934844 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare the following competing financial interest(s): Institute of Chemistry, Chinese Academy of Sciences (ICCAS) has filed a patent on the discovery and development of this method that are described in the paper presented on January 29, 2019, at the National Intellectual Property Administration (Chinese provisional patent application no. 2019100843077).

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