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Iodine-Catalyzed Selective Synthesis of 2-Sulfanylphenols *via* Oxidative Aromatization of Cyclohexanones and Disulfides

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Abstract: Iodine-catalyzed intermolecular dehydrogenative aromatizations of six-membered cyclohexanones for the selective synthesis of 2-sulfanylphenols have been developed. Both aryl and alkyl disulfides can be used as sulfanylation reagents to give the desired products in good yields under the optimized reaction conditions. The catalytic reaction uses dimethyl sulfoxide or oxygen as the terminal oxidant and avoids the use of transition metal catalysts. In addition, α-sulfanyl enones could also be obtained *via* an iodine-catalyzed oxidative system from simple cyclic ketones using dimethyl sulfoxide as the oxidant.

Keywords: cyclic ketones; dehydrogenation; iodine; phenols; sulfanylation

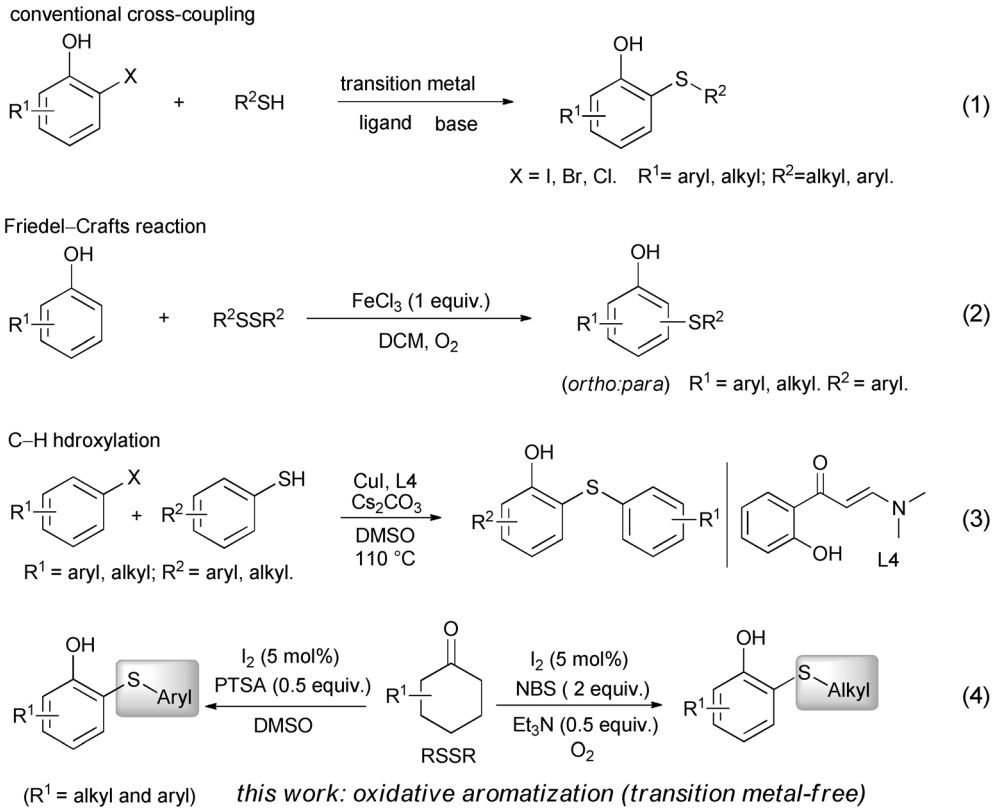
Introduction

Aromatic thioethers exists in a variety of natural products and synthetic drugs. Among thioether derivatives, 2-sulfanylphenols play a significant role in biologically and pharmaceutically active molecules and drugs.[1] Within these molecules, the thioether functionality confers particular properties to the phenol ring. Phenols are also key intermediates of attractive reactive substances in organic synthesis.

Over the past decades, a large number of methods has been developed for the synthesis of aromatic thioethers from a wide range of aromatic moieties and sulfur-containing reagents.[2] Nevertheless, procedures for the formation of a C–S bond at the *ortho* position of phenols are still rare,[3] among which the most direct and applicable procedures are the transition metal-catalyzed cross-coupling reactions [Eq. (1), Scheme 1].[4] An alternative method was reported by Takaki and co-workers, who found that 2-sulfanylphenols could be synthesized by sulfanylation of phenols using a stoichiometric amount of $FeCl_3$ under an oxygen atmosphere [Eq. (2), Scheme 1].[5] Mixtures of *ortho*- and *para*-substituted thioethers of phenols can be obtained under these Friedel–Crafts conditions. A third interesting approach involves an Ullmann-type C–S bond cross-coupling step between aryl halides and aryl thiols and selective hydroxylation of aryl thioethers to form 2-sulfanylphenols [Eq. (3), Scheme 1].[6] All these approaches require aromatic substrates in the presence of metal catalysts.

In recent years, the preparation of phenols, anilines and aryl ethers from non-aromatic substrates was described *via* dehydrogenation pathways.[7] In 2011, Stahl and co-workers reported a palladium(II)-catalyzed conversion of substituted cyclohexanones to the corresponding enones and phenols *via* successive dehydrogenation of two saturated carbon-carbon bonds of the six-membered ring with using molecular oxygen as hydrogen acceptor.[7c,d] In 2012, a copper-catalyzed methodology for the synthesis of aromatic ethers through oxidative condensation of alcohols and 2-cyclohexenones was reported by Li and co-workers.[7e] With the development of green chemistry, molecular iodine has played a valuable role in modern organic synthesis especially for sp^3 C–H bond functionalization.[8]

The development of efficient and convenient synthetic approaches toward known molecules is highly desirable. In our continuous work on the C–S, C–N, and C–O bond forming reactions,[9] an iodine-catalyzed aerobic dehydrogenative aromatization was developed for the synthesis of 2-sulfanylphenols with non-aromatic ketones and disulfides [Eq. (4),



Scheme 1. Strategies for the synthesis of 2-sulfanylphenols.

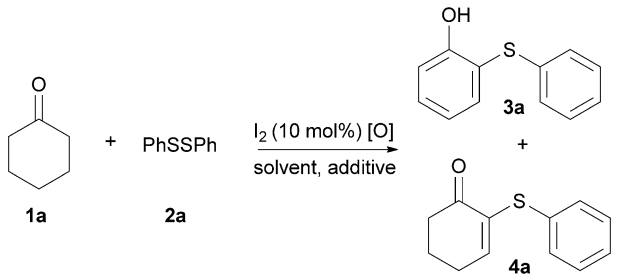
Scheme 1]. Aryl disulfides can be easily transformed to 2-arylthiophenols with the additive of 0.5 equiv. of PTSA using DMSO as oxidant. 2-Alkylthiophenols can be obtained in the presence of 2 equiv. of NBS and the reaction may proceed *via* the formation of an activated sulfur-containing intermediate, *N*-sulfanylsuccinimide, followed by α-sulfanylation of cyclic ketones and oxidative aromatization.

Results and Discussion

At first, we started our studies by reacting cyclohexanone with diphenyl disulfide in the presence of 10 mol% of iodine and 0.5 equiv. of PTSA in the solvent CH_3CN at 80 °C under air or oxygen atmosphere. However, the product 2-(phenylthio)phenol (**3a**) was detected only in 16% yield under oxygen atmosphere after 12 h reaction (Table 1, entries 1 and 2). Several kinds of solvents were tested and it was found that the yield of the product could not be improved under catalysisby iodine with O_2 as oxidant (Table 1, entries 3–7). When 5 equiv. of DMSO were added as oxidant, we were delighted to find that product **3a** was obtained in 64% yield after column chromatography (Table 1, entry 8). Subsequently, several oxidants such as H_2O_2, TBHP and Oxone were tested for the reaction and it was found that the reaction could only proceed well using DMSO as oxidant (Table 1, entries 9–11). DMSO was further tested as both solvent and oxidant to optimize the reaction conditions, which gave a slightly higher yield in **3a** of 76% (Table 1, entry 12). Reducing the dosage of iodine catalyst to 5 mol% could improve the yield of **3a** to 89% while reducing the amount of PTSA could improve the yield of **4a** to 25% (Table 1, entries 13 and 14). To our delight, the by-product **4a** could be obtained in 86% without using PTSA as the additive (Table 1, entry 15). Based on this result, other additives such as HCl, NH_4Cl and TfOH, were screened for the reaction (Table 1, entries 16–18). However, they showed slightly lower activity compared to PTSA.

Using the optimized reaction conditions mentioned above, a variety of cyclic ketones and aryl disulfides was tested to determine the scope and limitations of the method. The results listed in Table 2 demonstrated that most of the aryl disulfides **2** tested underwent smooth transformation to afford the corresponding 2-sulfanylphenols **3** in good to excellent yields (Table 2, **3a–c)**. To our surprise, cyclic ketones bearing a phenyl group gave 2-sulfanylphenols in high yield due to the fact that the phenyl group could increase the electron density of the cyclic ketone (Table 2, **3d–f**), wherein, cyclic ketones bearing alkyl groups may give moderate yields under optimized reaction conditions

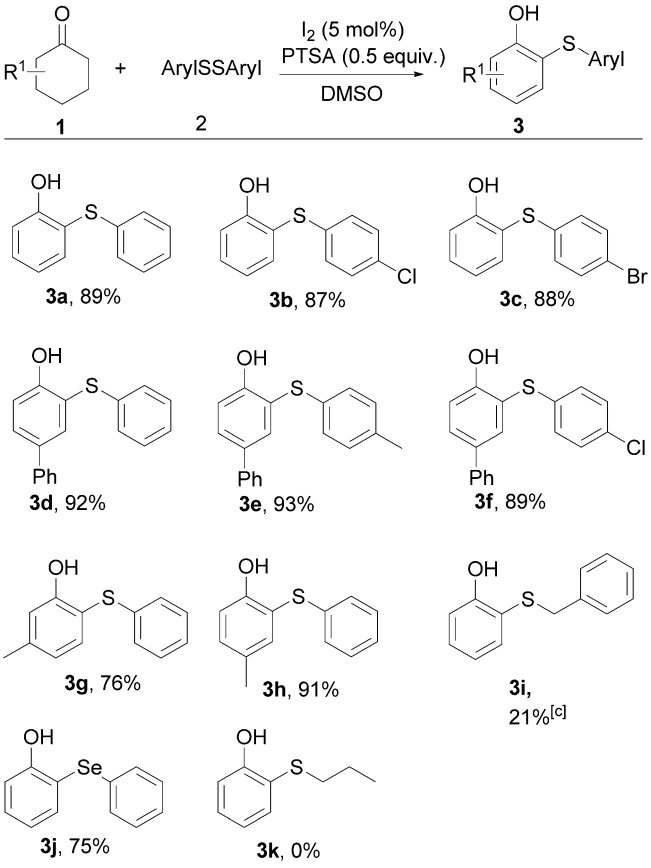
Table 1. Optimization of reaction conditions for the sulfanylation of enones.[a]



Entry	Solvent	[O] (equiv.)	Additive	Yield [%][b] 3a	4a
1	CH_3CN	air	PTSA	<5	<5
2	CH_3CN	O_2	PTSA	16	0
3	DMC	O_2	PTSA	<5	0
4	DCE	O_2	PTSA	<5	0
5	*i*-PrOH	O_2	PTSA	11	0
6	toluene	O_2	PTSA	<5	<5
7	EtOAc	O_2	PTSA	9	0
8	CH_3CN	DMSO (5)	PTSA	64	<5
9	CH_3CN	H_2O_2 (3)	PTSA	12	0
10	CH_3CN	TBHP (3)	PTSA	15	0
11	CH_3CN	Oxone (3)	–	23	0
12	DMSO	–	PTSA	76	15
13[d]	DMSO	–	PTSA	89 (88[c])	trace
14[d,e]	DMSO	–	PTSA	61	25
15[d]	DMSO	–	–	<5	86
16[d]	DMSO	–	HCl	63	0
17[d]	DMSO	–	NH_4Cl	32	45
18[d]	DMSO	–	TfOH	69	0

[a] *Reaction conditions:* **1a** (1.2 mmol), **2a** (0.5 mmol), catalyst (10 mol%), additive (0.5 mmol), solvent (2 mL), 12 h, 80 °C, in a 25-mL sealed tube.
[b] Yield of isolated product after column chromatography.
[c] Under an N_2 atmosphere.
[d] 0.05 mmol iodine were used.
[e] 0.2 mmol PTSA were used.

Table 2. Sulfanylation of phenols with aryl disulfides.[a,b]



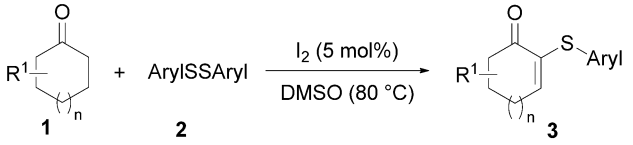
[a] *Reaction conditions:* **1** (1.2 mmol), **2** (0.5 mmol), catalyst (0.05 mmol, 5 mol%), PTSA (0.5 mmol), DMSO (2 mL), 80 °C, 12 h, in a 25-mL sealed tube.
[b] Yield of isolated product after column chromatography.
[c] 0.1 mmol (10 mol%) iodine was used.

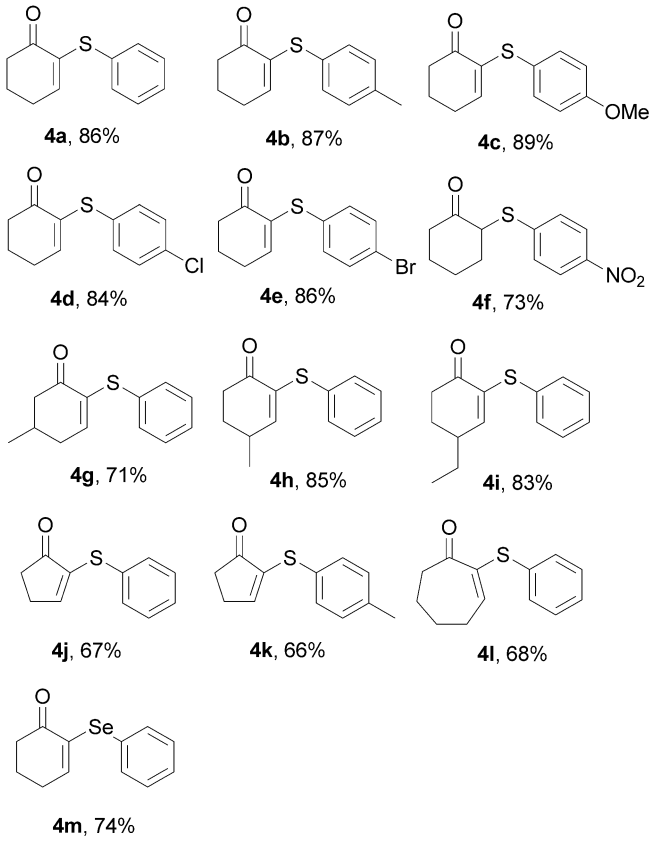
(Table 2, **3g–h**). Dibenzyl disulfide was converted to 2-(benzylthio)phenol in low yield while no product was detected from the reaction between dialkyl disulfides and cyclic ketones (Table 2, **3i**, **3k**). Under the optimized conditions, diphenyl diselenide was well tolerated and the product 2-(phenylselanyl)phenol was obtained in 75% yield (Table 2, **3j**).

In order to gain further understanding of our present work and research how the possible product can be formed under the optimized conditions, a number of cyclic ketone substrates was screened to test the yield of α-sulfanyl enones.[10] The results are listed in Table 3 and α-sulfanyl enones **4** could be obtained in good yields from most of the aryl disulfides (Table 3, entries **4a–e)**. However, 2-(4-nitrophenylsulfanyl)-cyclohexanone (**4f**) was obtained in relatively low yield when 4-nitrophenyl disulfide (**2f**) was used as sulfanylation reagent under normal conditions. Further dehydrogenation of **4f** cannot proceed under the present reaction conditions because the deactivated sulfur is not sufficiently reactive to react with iodine (Table 3, **4f**). The reactions of cyclic ketones with a variety of aryl disulfides coupling partners proceeded in high yields (Table 3, **4g–l**). To our delight, a diselenide can also be converted to the desired product **4m** under normal conditions in high yield (Table 3, **4m**). Based on these results, we proposed that an electrophilic species RS^+ may be formed. An electron-withdrawing group attached to R would be unfavorable for the formation of these species.

Under the optimized reaction conditions mentioned above, dialkyl disulfides could not be transformed to 2-sulfanylphenols *via* this iodine-catalyzed oxidative system with DMSO as oxidant and PTSA as additive due to the fact that an electrophilic species $AlkylS^+$ could not be formed with the aid of iodine catalyst. Thus, a further exploration was performed using *N*-sulfanylsuccinimide reagent formed *in situ* as sulfur-containing reagent.

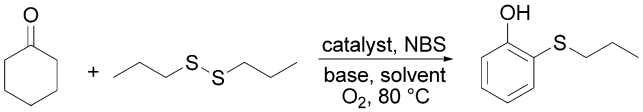
Table 3. Sulfanylation of enones with aryl disulfides.[a]





[a] *Reaction conditions:* **1** (1.2 mmol), **2** (0.5 mmol), catalyst (5 mol%), DMSO (2 mL), 12 h, in a 25 mL sealed tube.
[b] Yield of isolated product after column chromatography.

Table 4. Optimization of reaction conditions for transition-metal-free sulfanylation of phenols.[a]



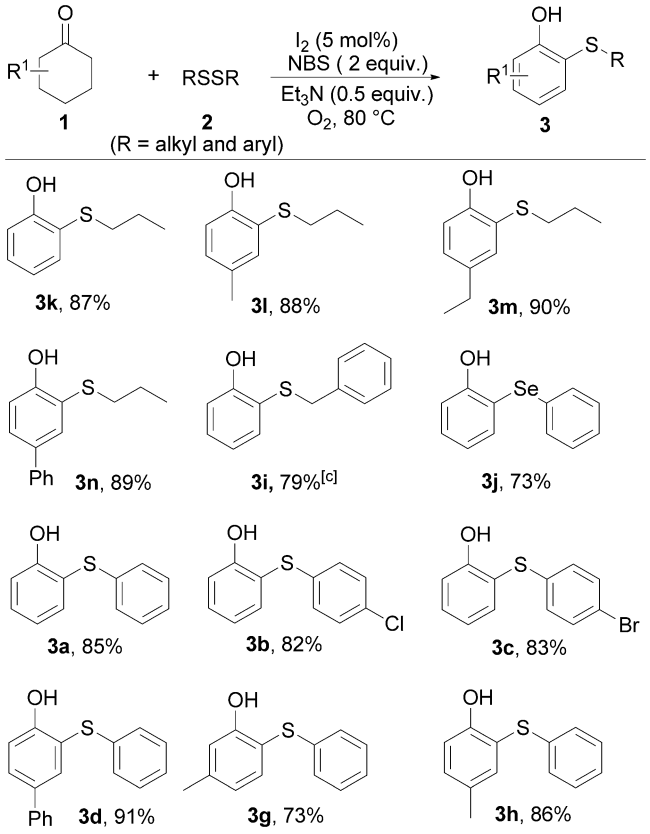
Entry	Catalyst	Base	Solvent	Yield [%][b]
1	–	–	CH_3CN	15
2	–	Et_3N (0.5)	CH_3CN	37
3	iodine (0.1)	Et_3N (0.5)	CH_3CN	61
4	iodine (0.1)	Et_3N (0.5)	DMC	21
5	iodine (0.1)	Et_3N (0.5)	DCE	33
6	iodine (0.1)	Et_3N (0.5)	toluene	<5
7	iodine (0.1)	Et_3N (0.5)	DMF	79
8[d]	iodine (0.1)	Et_3N (0.5)	DMF	53
9	iodine (0.1)	Et_3N (1)	DMF	59
10	iodine (0.05)	Et_3N (0.5)	DMF	87 (23[c])
11	iodine (0.05)	K_2CO_3 (0.5)	DMF	41
12	iodine (0.05)	KF (0.5)	DMF	35
13	iodine (0.05)	pyridine (0.5)	DMF	17
14[e]	iodine (0.05)	Et_3N (0.5)	DMF	0
15[f]	iodine (0.05)	Et_3N (0.5)	DMF	0
16	I_2O_5 (0.1)	Et_3N (0.5)	DMF	0
17	TBAI (0.1)	Et_3N (0.5)	DMF	0
18	NaI (0.1)	Et_3N (0.5)	DMF	0

[a] *Reaction conditions:* **1a** (1.2 mmol), **2h** (0.5 mmol), catalyst (0.05 mmol, 5 mol%), NBS (2 mmol), solvent (2 mL), 80 °C, 12 h, in a 25-mL sealed tube under O_2 atmosphere.
[b] Yield of isolated product after column chromatography.
[c] Under an N_2 atmosphere.
[d] 3 mmol NBS were used.
[e] 2 mmol NIS were used instead of NBS.
[f] 2 mmol NCS were used instead of NBS.

To begin our study, the reaction of cyclohexanone and dipropyl disulfide in the presence of 2 equiv. of NBS was explored in the CH_3CN at 80 °C under an oxygen atmosphere. We were delighted to find that the product, 2-(propylthio)phenol (**3k**), was obtained in 15% yield after column chromatography. Encouraged by this result, the reaction was optimized and the results are summarized in Table 4. The yield of **3k** could be increased to 37% by addition of 0.5 equiv. of Et_3N (Table 4, entries 1 and 2).The yield of **3k** was further increased to 61% in the presence of 0.1 equiv. of I_2. Based on these results, several kinds of solvents were then tested and the highest yield of 79% was obtained when the reaction was carried out in DMF (Table 4, entry 7). Increasing the dosage of NBS to 3 equiv. or of Et_3N to 1 equiv. led to decreases of the yield of **3k** to 53% or 59%, respectively (Table 4, entries 8 and 9). Reducing the dosage of iodine to 5 mol% led to an increase of the yield of **3k** to 87% (Table 4, entry 10). Under an N_2 atmosphere only 23% of **3a** was isolated (Table 4, entry 10). Bases such as K_2CO_3, KF and pyridine were screened to optimize the reaction conditions, which showed that Et_3N was the more efficient (Table 4, entries 11–13). When using other reagents, for instance, NIS or NCS, instead of NBS, or other iodine-containing non-metal catalysts, such as I_2O_5, TBAI or NaI, instead of I_2, no product **3k** was detected (Table 4, entries 14–18).

Having optimized the reaction conditions, a variety of non-aromatic ketones and disulfides was tested to determine the scope and limitations of the method. The results listed in Table 5 demonstrated that the alkyl and benzyl disulfides **2** tested underwent smooth transformation to afford the corresponding 2-sulfanylphenols **3** in high yields (Table 5, **3i**, **3k–m**). Cyclohexanones bearing aryl groups were easily transformed to the desired products under optimized conditions (Table 5, **3n**). To our delight, diaryl disulfides also reacted well under the optimized reaction conditions

Table 5. Iodine-catalyzed aerobic oxidative synthesis of 2-sulfanylphenols under the optimum conditions.[a,b]



[a] *Reaction conditions:* **1** (1.2 mmol), **2** (0.5 mmol), catalyst (0.05 mmol, 5 mol%), NBS (2 mmol), solvent (2 mL), 80 °C, 12 h, in a 25-mL sealed tube under an O_2 atmosphere.

[b] Yield of isolated product after column chromatography.

[c] 0.1 mmol (10 mol%) iodine was used.

(Table 5, **3a–d**, **g**, **h**). Diphenyl diselenide reacted well under the optimized conditions and the product 2-(phenylselanyl)phenol was obtained in 73% yield (Table 5, **3n**).

To explore the catalytic mechanism, some blank and parallel experiments were carried out and the results are listed in Scheme 2. No product was detected when cyclohex-2-enone was used as the ketone partner under normal conditions [Eq. (5), Scheme 2]. α-(Phenylthio)cyclohex-2-enone cannot be converted to 2-(phenylthio)phenol in the presence of PTSA alone [Eq. (6), Scheme 2] while α-(phenylthio)cyclohexanone can be easily transformed to 2-(phenylthio)phenol in 88% yield catalyzed by iodine with PTSA as additive [Eq. (7), Scheme 2]. These results illustrated that the sulfanylation of cyclic ketones occurred as the first step in this reaction followed by dehydrogenation to the final product. With the aid of NBS in DMF, dipropyl disulfide could be easily transformed to intermediate 1-(propylthio)pyrrolidine-2,5-dione (**5a**) in high yield [Eq. (8), Scheme 2]. The dehydrogenative product could be obtained in good yield from non-aromatic ketones *via* one-pot two-step procedure [Eq. (9), Scheme 2].

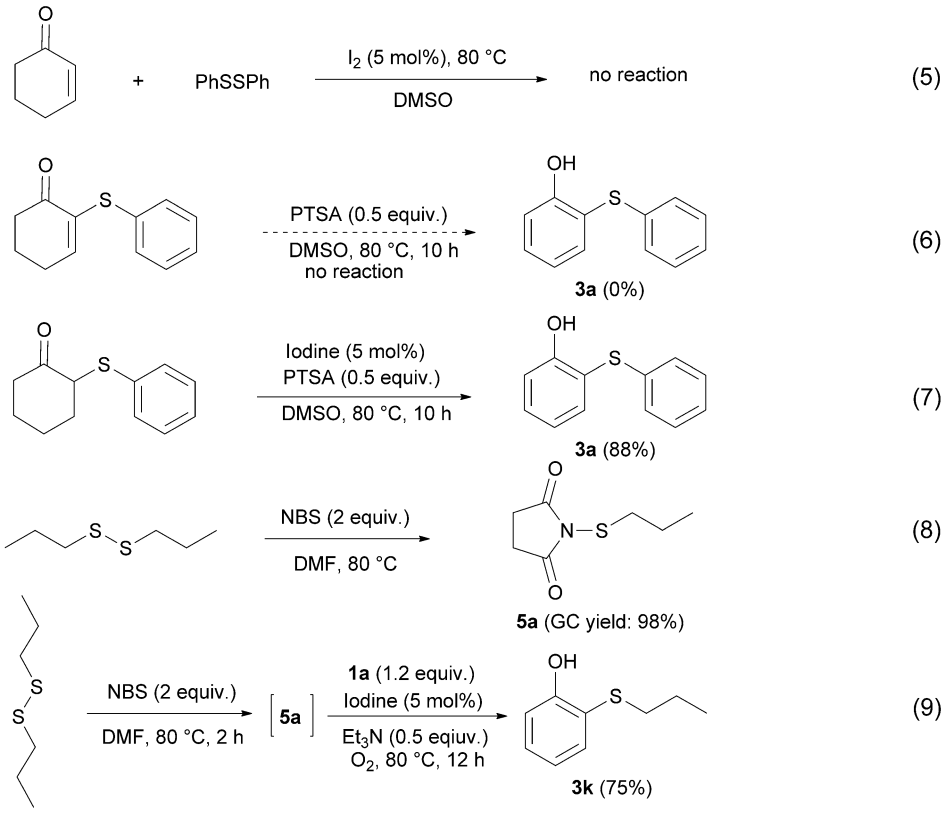
Based on the results obtained above, an iodine-catalyzed oxidative system was proposed to explain the reaction mechanism (Scheme 3). Aryl disulfide reacts with I_2 to form an electrophlic species ArylSI (**M2**).[11] which reacts with intermediate **M1** obtained from protonation of cyclohexanone to give an intermediate α-sulfanyl ketone *via* an S_N2 process [Eq. (10), Scheme 3]. Oxidation of α-sulfanyl ketone with iodine gives an intermediate **M3**. Deprotonation of **M3** gives the intermediate **M4**. The by product α-sulfanyl enone is obtained *via* deprotonation of intermediate **M4**. Continuous oxidation of α-sulfanyl enone with iodine gives the intermediate **M5**. The final product is formed then by deprotonation of the intermediate **M6**. In the oxidative system, iodine can be regenerated from the oxidation of HI by DMSO conveniently and the acidic conditions provided by PTSA were favorable for the regeneration of iodine catalyst[7i,8g] [Eq. (2), Scheme 3]. Alkyl disulfide reacts with NBS to form an electrophlic species 1-(alkylthio)pyrrolidine-2,5-dione (**N2**), which reacts intermediate **N1** obtained from activation of cyclic ketone by Et_3N to give an intermediate α-sulfenyl ketone. In these reaction conditions, iodine can be regenerated from the oxidation of HI by O_2 conveniently [Eq. (11), Scheme 3]. And the final product is formed by the same reaction mechanism [Eq. (12), Scheme 3].

Conclusions

A transition metal-free iodine-catalyzed oxidative aromatization based on sequential processes in one-pot has been developed for the selective synthesis of 2-sulfanylphenols from non-aromatic ketones. 2-Arylthiophenols were synthesized with DMSO as oxidant and 0.5 equiv. of PTSA as additive. 2-Alkylthiophenols were obtained from NBS-promoted intermolecular aerobic dehydrogenative aromatization. In addition, α-sulfanyl enones could also be formed *via* an iodine-catalyzed oxidative system from simple cyclic ketones through a dehydrogenation strategy using DMSO as oxidant. A detailed reaction mechanism was proposed for this reaction and the regeneration of iodine catalyst.

Experimental Section

All chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. The progress of the reactions was monitored by TLC



Scheme 2. Parallel and blank experiments tested to explore the reaction mechanism.

(silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on Silicycle silica gel (200–300 mesh). Melting points were obtained using a Yamato melting point apparatus Model MP-21 and are uncorrected. IR spectra were recorded on a Shimadzu spectrophotometer using KBr discs. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard. All the products were identified by comparison of their physical and spectral data with those reported in the literature.

General Procedure for Iodine-Catalyzed Synthesis of 2-Arylthiophenols with Aryl Disulfides

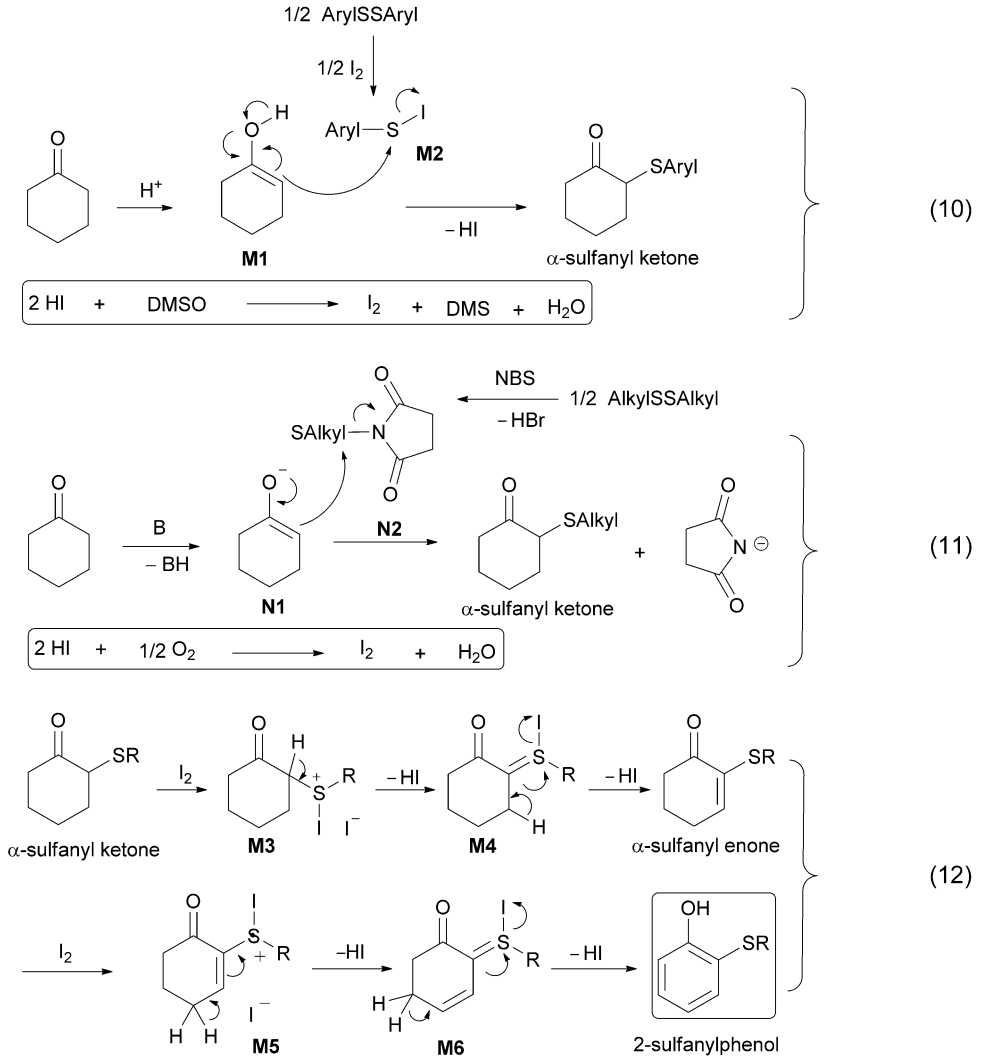
A mixture of cyclic ketone (1.2 mmol), aryl disulfide (0.5 mmol) and PTSA (0.5 mmol) was dissolved in DMSO (2 mL) at 80 °C in a flask, then iodine (0.05 mmol, 5 mol%) was added. The reaction proceeded under an air atmosphere for the indicated time until complete consumption of starting material as monitored by TLC. The solution was diluted with EtOAc (10 mL), washed with H_2O (3×10 mL), and then the organic layer was separated and concentrated under vacuum and the crude product was purified by column chromatography (PE:EtOAc, 20:1) to provide the analytically pure product **3**.

General Procedure for Iodine-Catalyzed α-Sulfanylation of Enones with Aryl Disulfides

A mixture of cyclic ketone (1.2 mmol) and aryl disulfide (0.5 mmol) was dissolved in DMSO (2 mL) at 80 °C in a flask, then iodine (0.05 mmol, 5 mol%) was added. The reaction proceeded under an air atmosphere for the indicated time until complete consumption of starting material as monitored by TLC. The solution was diluted with EtOAc (10 mL), washed with H_2O (3×10 mL), and then the organic layer was separated and concentrated under vacuum and the crude product was purified by column chromatography (PE:EtOAc, 20:1) to provide the analytically pure product **4**.

General Procedure for Iodine-Catalyzed 2-Sulfanylation of Phenols with Alkyl Disulfides

A mixture of cyclic ketone (1.2 mmol), disulfide (0.5 mmol) and Et_3N (0.5 mmol) was added in DMF (2 mL) at 80 °C in a sealed tube, then NBS (2 mmol) and iodine (0.05 mmol, 5 mol%) were added. The reaction proceeded under an O_2 atmosphere for the indicated time until complete consumption of starting material as monitored by TLC. The solution was diluted with EtOAc (10 mL), washed with H_2O (3× 10 mL), and then the organic layer was separated and concentrated under vacuum and the crude product was purified by column chromatography (PE:EtOAc, 30:1) to provide the analytically pure product **3**.



Scheme 3. Proposed mechanism for the formation of 2-sulfanylphenols and α-sulfanyl enones.

Acknowledgements

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